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Etude des aspects fondamentaux liés à l'élaboration d'un TPV du type PP/EPDM

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« Les sciences ont deux extrémités qui se touchent. La première est la pure ignorance naturelle où se trouvent tous les hommes en naissant. L'autre extrémité est celle où arrivent les grandes âmes qui, ayant parcouru tout ce que les hommes peuvent savoir, trouvent qu'ils ne savent rien, et se rencontrent en cette ignorance d'où ils étaient partis ; mais c'est une ignorance savante qui se connaît. Ceux d'entre deux, qui sont sortis de l'ignorance naturelle, et n'ont pu arriver à l'autre, ont quelque teinture de cette science suffisante, et font les entendus. Ceux-là troublent le monde, et jugent mal de tout. »

B. PASCAL - Oeuvres complètes II, Ed. Le Guern

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Introduction générale

Introduction générale

A une époque où la société exige des matériaux aux propriétés de plus en plus spécifiques, les mélanges de polymères ont su trouver leur place en se révélant tout à fait appropriés à de nombreuses applications industrielles, en particulier dans le domaine de l'automobile. Leur étude a été particulièrement stimulée ces dernières années de par l'intérêt qu'ils suscitent aussi bien d'un point de vue universitaire qu'industriel.

Les thermoplastiques, d'une façon générale, présentent une facilité de mise en œuvre particulièrement intéressante par rapport aux élastomères réticulés classiques. Les élastomères, quant à eux, sont les seules à pouvoir répondre à des applications nécessitant un comportement de type caoutchoutique. De là est née l'idée de mélanger un thermoplastique et un élastomère en vue d'obtenir une synergie des caractéristiques techniques de l'élastomère couplées à la facilité de mise en œuvre du thermoplastique. L'intérêt économique d'un tel mélange est évident. La vulcanisation de la phase élastomère permet, de surcroît, d'améliorer significativement les propriétés de ces mélanges et conduit à la formation des dits thermoplastiques vulcanisés (TPV). Cette classe de matériaux peut ainsi offrir des performances techniques parfois aussi bonnes que certains vulcanisats classiques tout en présentant les propriétés de mise en œuvre de tout thermoplastique Ceci confère aux industries la possibilité de développer des matériaux élastomères recyclables aux propriétés spécifiques et adaptables aux besoins du marché. La diversité des domaines concernés et des applications potentielles a induit le développement d'une très large gamme de TPV. La possibilité de recycler ces systèmes polymères est un atout majeur sur les élastomères traditionnels. Enfin, leurs propriétés spécifiques, alliées à leur faible coût de production, leur assurent une position de premier plan sur le marché des polymères.

Ces TPV constituent ainsi une classe de matériaux polymères de plus en plus demandée, cependant leur élaboration est particulièrement complexe. Ils constituent un système d'étude très large car leur élaboration implique de considérer plusieurs aspects fondamentaux comme le mélange de polymères, la chimie de la réticulation, la diffusion du plastifiant, la mise en œuvre, etc. Le but principal de ces travaux de recherche est donc d'étudier certains de ces aspects dans l'optique de mieux cerner les mécanismes fondamentaux impliqués lors de l'élaboration des matériaux, en vue d'optimiser et de mieux contrôler leurs propriétés finales. La morphologie de ce type de matériaux polymères est la clé de leurs propriétés spécifiques, ainsi est-il primordial de la maîtriser tout au long du processus d'élaboration afin de pouvoir ajuster autant que possible les caractéristiques du produit fini. Nos travaux ont donc principalement porté sur l'étude morphologique et rhéologique de mélanges modèles de type polyoléfine / élastomère en fonction des conditions de mélange et de l'état d'avancement de la réaction de réticulation de la phase élastomère.

Ce mémoire de thèse a ainsi pour but de présenter les travaux de recherche que nous avons menés pour tenter de corréler la morphologie et les propriétés mécaniques finales de ce type de mélanges. La méthodologie a consisté tout d'abord à s'immerger dans la problématique liée à l'élaboration d'un tel mélange et de considérer chaque mécanisme impliqué afin d'obtenir une image globale de la complexité du procédé d'élaboration. Du point de vue industriel, dans la majorité des cas, la fusion du thermoplastique, la dispersion de l'élastomère, la diffusion du plastifiant ainsi que la réticulation de la phase élastomère et l'inversion de phase se déroulent simultanément en moins d'une minute à des températures comprises entre 200 et 300°C, ce qui rend l'étude des mécanismes individuels impossible. D'où la nécessité d'analyser chacun des mécanismes et l'influence de chaque paramètre sur la morphologie finale du TPV de façon aussi indépendante que possible. Afin de nous affranchir des interactions entre les processus impliqués, il nous a donc semblé judicieux de tenter d'individualiser chaque contribution et de décomposer ces processus en étudiant des systèmes modèles simplifiés.

Ce manuscrit est organisé comme suit. L'étude bibliographique, présentera l'état de l'art dans ce domaine, et sera donc développée en premier lieu. Après un rapide second chapitre résumant les matériaux et techniques utilisés, les résultats de nos recherches seront présentés sous forme de publications. Nous aborderons, dans le troisième chapitre, l'étude des propriétés élastiques de réseaux d'élastomères plastifiés couplée à une modélisation phénoménologique de ces réseaux. L'objectif est de corréler leur structure à leurs propriétés de relaxation et de recouvrance. Nous nous intéresserons ensuite, dans le quatrième chapitre, à la caractérisation morphologique de mélanges PP/EPDM non réticulés en accordant une attention toute particulière à la morphologie co-continue, source de propriétés très intéressantes d'un point de vue de la recouvrance élastique. Enfin, le cinquième et dernier chapitre de cette thèse portera sur l'étude des mécanismes de dispersion de réseaux d'élastomères plastifiés en présence d'une phase thermoplastique. Ces résultats nous permettront de conclure pragmatiquement sur de nombreux aspects essentiels à la synergie des propriétés de tels mélanges de polymères.

Chapitre I

Bibliographie

Chapitre I - Bibliographie

I. Qu'est-ce qu'un Thermoplastique Vulcanisé ?

Les thermoplastiques vulcanisés représentent une famille de mélanges de polymères présentant une gamme de propriétés morphologiques, physiques, mécaniques et de transformation originales et variées.

Une formulation TPV se compose :

- d'une phase élastomère,
- d'une phase thermoplastique,
- d'un agent réticulant,
- de charges,
- de plastifiant,
- d'agents de protection et de compatibilisation, etc.

Figure 1 - Exemple d'application du Vegaprene®

Les TPV les plus développés à l'heure actuelle sont ceux à base de polypropylène et d'EPDM, mais il existe quelques exemples de tels matériaux dans lesquels la phase élastomère est constituée d'un autre élastomère (poly (butadiène-acrylonitrile, polyisoprène, isoprène bromé, etc.).

L'élaboration de telles formulations requiert notamment une culture scientifique importante ainsi que beaucoup d'expérience et de savoir-faire afin de maîtriser au mieux l'ajustement de certaines propriétés, parfois antagonistes, que réclament certaines applications industrielles.

Dans le cadre de nos travaux, nous nous sommes intéressés en particulier aux mélanges PP/EPDM plastifiés, similaire aux formulations du type Végaprène®, produit commercialisé par Hutchinson pour des applications en particulier dans le domaine automobile (Figure 1). Dans ce cas, la phase thermoplastique est constituée de polypropylène, l'élastomère est un EPDM (terpolymère d'éthylène-propylène-diène), et une quantité souvent importante de plastifiant est incorporée à ces phases. Le polypropylène assure ainsi la facilité de mise en œuvre typique des thermoplastiques, tandis que l'EPDM réticulé assure, entre autres, l'élasticité et la résistance aux chocs et à la déchirure du mélange. Le PP présente quant à lui un point de fusion élevé et une forte cristallinité ce qui lui confère une bonne résistance à la température et des propriétés de mise en œuvre très intéressantes. Cependant sa principale faiblesse est sa mauvaise résistance aux chocs qui peut être améliorée par la présence de l'élastomère réticulé, d'où l'utilité d combiner ces deux polymères. L'EPDM est un terpolymère d'éthylène, de propylène et d'un diène (dans notre cas l'éthylidène-norbornène) avec une chaîne principale saturée, ce qui explique son excellente stabilité thermique et sa résistance aux agents oxydants (ozone, oxygène) lorsqu'il est réticulé. De par leur nature, le PP et l'EPDM sont immiscibles et leur mélange requiert donc la connaissance et la maitrise de nombreux mécanismes afin d'obtenir une synergie intéressante de leurs propriétés respectives.

Le caractère unique et propre aux TPV est qu'ils subissent une étape de réticulation sous cisaillement au cours du procédé d'élaboration. Celle-ci conduit à des modifications morphologiques importantes en particulier une inversion de phase (cf. paragraphe V.4.) due à l'augmentation rapide et importante de la viscosité de l'élastomère. La formation d'un réseau chimique tridimensionnel au sein de cette phase élastomère dispersée dans une matrice thermoplastique permet au matériau de présenter des propriétés originales. Au final, les propriétés mécaniques du TPV sont proches de celles d'un élastomère réticulé tout en conservant un caractère de mise en œuvre propre aux thermoplastiques[1].

Etant donné la corrélation procédé (mélange - chimie) – morphologie – propriétés mécaniques typique de tout TPV, il est nécessaire de contrôler parfaitement la morphologie finale de ces mélanges[2, 3]. Celle-ci dépend entre autres de la proportion et de la nature de chacun des constituants, de l'interface entre les polymères, de la cristallinité du PP, de la cinétique de réticulation, de la présence d'un agent compatibilisant, etc. Afin de la maîtriser tout au long du processus d'élaboration, il faut considérer plusieurs aspects :

- la chimie de réticulation de la phase élastomère,
- la compatibilisation du mélange en prenant en compte les aspects de tension interfaciale et la rhéologie,
- la dispersion de composés de faibles viscosités (réactifs, charges, plastifiants),
- le procédé de fabrication (malaxage en discontinu et extrusion en continu).

La mise en œuvre des TPV implique donc des mécanismes d'élaboration complexes du point de vue de la chimie de réticulation, des aspects rhéologiques, de l'inversion de phase, de la diffusion et du rôle du plastifiant, de la tension interfaciale entre les phases élastomère et thermoplastique, et des problèmes liés à la mise en œuvre de matières plastiques de hautes viscosités. Nous allons ainsi aborder chacun des aspects liés à l'élaboration du Végaprène® afin d'évaluer la complexité et les zones d'ombre d'une telle voie d'élaboration[4].

II. Chimies de réticulation

La réticulation d'un élastomère consiste à créer un réseau macromoléculaire, c'est à dire de réaliser le pontage des chaînes de l'élastomère par le biais de liaisons covalentes, permettant ainsi de lui conférer des propriétés de haute élasticité caoutchoutique (Figure 2).

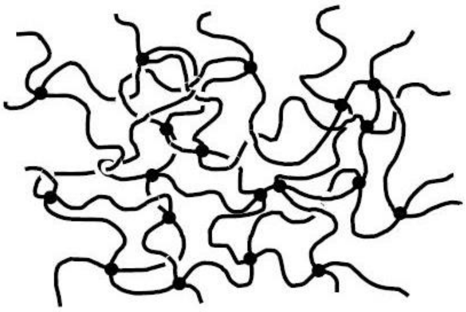


Figure 2 - Représentation schématique d'un réseau d'élastomère réticulé[5]

De plus, la densité de réticulation de l'élastomère induit des différences significatives de propriétés viscoélastiques (Figure 3).

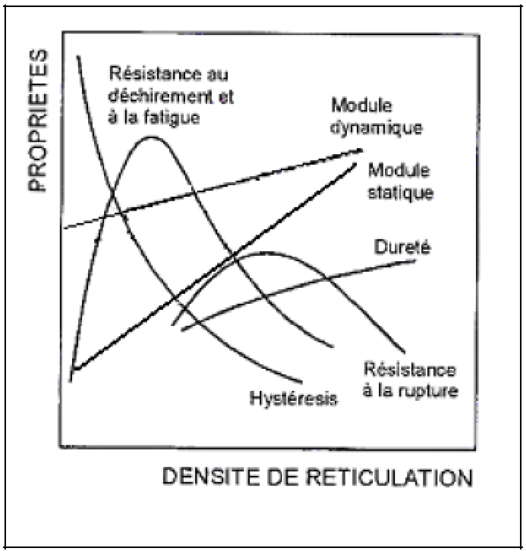


Figure 3 - Influence de la densité de réticulation sur les propriétés mécaniques des élastomères[6].

Dans le cas des TPV l'élastomère est réticulé en présence de la phase thermoplastique sous cisaillement, on parle de réticulation dynamique. Cette étape se déroule lors du mélange en voie fondue : l'élastomère est ainsi réticulé *in situ* au cours du procédé en présence du thermoplastique[7].

Les recherches à ce sujet ont été initiées par Gessler et al.[8]. Plus tard, Fischer[9, 10] a élaboré des mélanges PP / EPDM avec des proportions importantes d'EPDM. En jouant sur la quantité de catalyseur il est possible d'élaborer des mélanges par réticulation partielle de l'élastomère avant ou pendant le mélange avec la phase thermoplastique. Coran et Patel[11] ont ensuite réussi à réticuler entièrement la phase élastomère et ont mis en avant la corrélation morphologie - propriétés finales de ce genre de matériaux. Selon eux, pour que le mélange reste thermoplastique la phase élastomère devait être dispersée sous forme de micro-gels de 1 à 2 µm pendant l'étape de mélange[12].

Ce processus permet ainsi de mélanger intimement le thermoplastique et l'élastomère, et de réticuler l'élastomère en améliorant ainsi très nettement certaines propriétés du matériau en particulier par rapport à des mélanges PP/EPDM non réticulés[13-15]. L'homogénéité, la densité et la nature chimique des nœuds de réticulation ainsi que leur taille ont des conséquences directes sur la morphologie[16] ainsi que le comportement viscoélastique[5] et mécanique[17, 18] des mélanges vulcanisés. Cette chimie de réticulation peut toutefois détériorer certaines propriétés mécaniques ou conduire à une dégradation de la phase thermoplastique (coupure de chaînes, réticulation)[4]. Il faut donc veiller à trouver le bon compromis afin d'obtenir la structure, la morphologie et donc les propriétés souhaitées.

Cette réticulation peut s'effectuer à l'aide de divers composés chimiques, or le choix de l'agent réticulant induit des différences radicales de propriétés. Industriellement, étant donné les spécificités qu'ils induisent, les peroxydes, le soufre et les résines phénoliques sont les plus communément utilisées. Une vulcanisation forme des ponts soufrés entre les chaînes mais l'action de peroxydes ou de résines phénoliques, que l'on assimile par abus de langage à une vulcanisation, permet aussi de réticuler les chaînes élastomères. Ces différents agents réticulants conduisent à des réseaux, donc des propriétés, foncièrement différentes. Ces différents types de réaction chimique de réticulation sont décrites ci-après.

Tout d'abord, le soufre est un agent de réticulation largement utilisé qui conduit à la formation de ponts sulfures plus ou moins longs (Figure 4), de structure S_x avec x = 1 à 8.

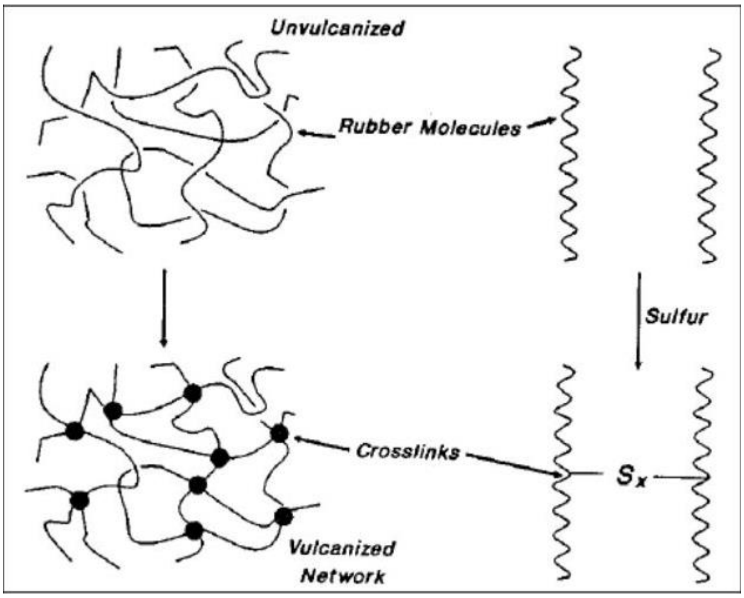


Figure 4 - Schématisation de la formation d'un réseau élastomère par des ponts sulfures de longueurs variables S_x[6].

La réticulation des élastomères par le souffre s'effectue généralement en présence d'activateurs du type ZnO, acide stéarique, disulfure de dibenzothiazole ou de tétraméthyle thiurame[6, 19]. Cet agent de réticulation est principalement utilisé dans l'optique d'un renforcement des élastomères et des TPV[20]. Cependant, bien que très bon marché, ce n'est pas forcément le meilleur agent de réticulation car il induit une faible processabilité du TPV due à l'augmentation de la taille des particules d'élastomères dispersées dans la phase thermoplastique. Les ponts sulfures générés pendant la vulcanisation subissent une réaction d'échange avec les sulfures, qui dans certains cas peut conduire à une coalescence significative des particules d'élastomères.

Les peroxydes sont eux aussi largement utilisés pour la réticulation des TPV, les principaux étant les peroxydes de dibenzoyle, de dialkyle, d'alkyle-aralkyle, de diaralkyle, les peroxy-kétales et les peroxy-esters. Ce type de réticulation permet de créer des liaisons covalentes C-C intermoléculaires par un processus radicalaire au niveau des liaisons C=C des chaînes élastomères. Malgré leur avantage de conduire à la formation de nœuds de réticulation particulièrement stables[21], les peroxydes présentent l'inconvénient majeur de dégrader les chaînes polymères thermoplastiques (scissions, branchements) et réduire de ce fait les propriétés et la cohésion globales de l'ensemble. D'une façon générale, un élastomère réticulé par un peroxyde aura une meilleure tenue au vieillissement qu'un élastomère vulcanisé par du soufre mais ce dernier aura de meilleures propriétés dynamiques.

Les deux types d'agents de réticulation précédents, bien que largement utilisés, ne seront pas considérés dans la suite de ce mémoire : nous nous intéresserons principalement aux résines phénoliques telles que celles employées dans les formulations du type Végaprène®. En présence d'un activateur acide, comme le dichlorure d'étain $SnCl_2$, ces résines phénoliques, dénommées également 'résol', réagissent avec les insaturations de l'EPDM portées par les motifs diéniques du terpolymère. Les étapes de réticulation des chaînes élastomères d'EPDM par les résols sont résumées dans la Figure 5.

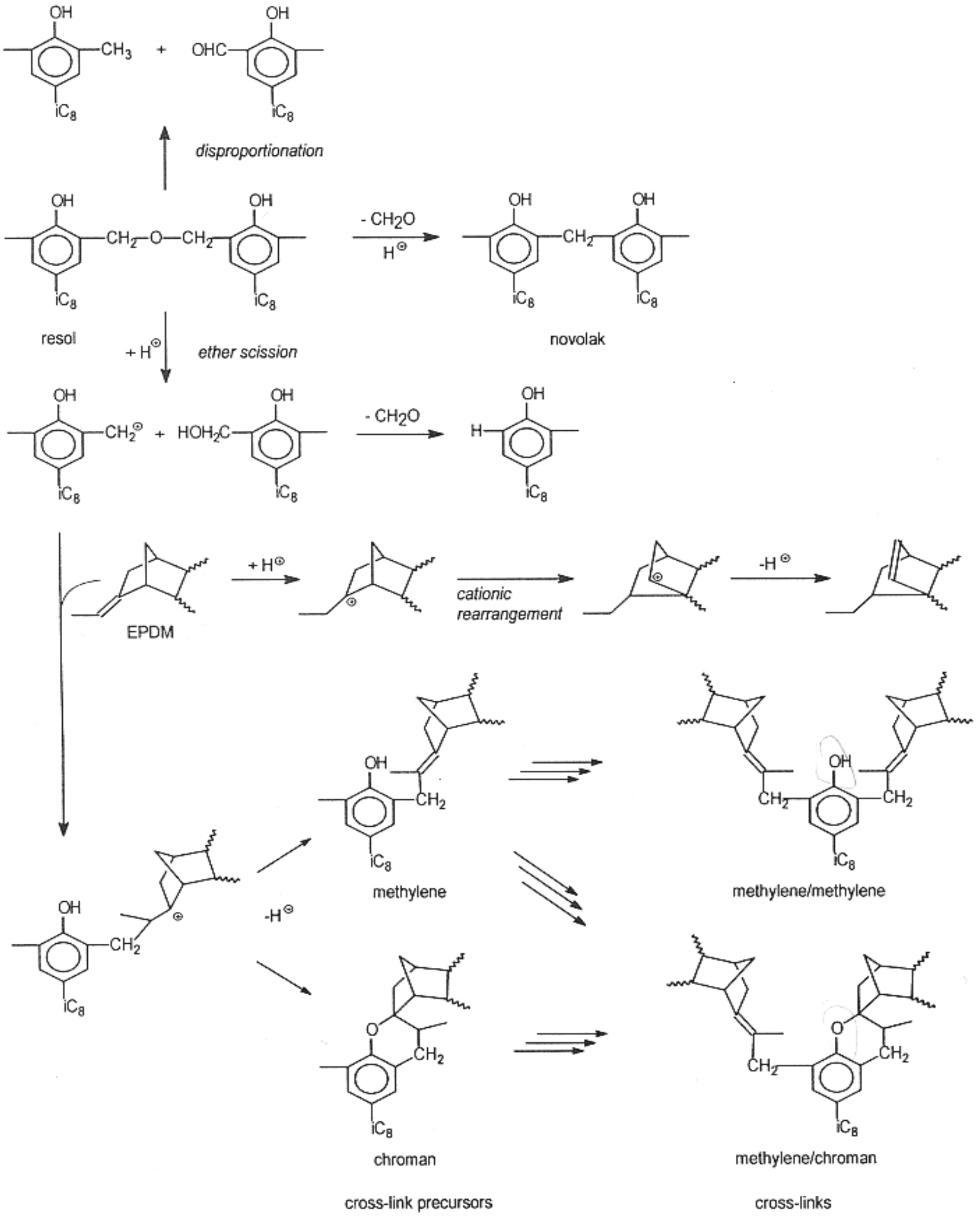


Figure 5 - Produits et mécanismes réactionnels de la réticulation de l'EPDM par une résine phénolique[22]

Ces résines phénoliques sont très efficaces pour la réticulation des élastomères du type terpolymère contenant des diènes non-conjugués comme l'EPDM. La réticulation de l'EPDM conduit à un mélange de précurseurs de réticulation, de ponts de réticulation et de produits secondaires tels que des structures pontées par le méthylène, insaturées ou des cycles saturés. Cela conduit à la formation de deux types de ponts méthylène-méthylène et méthylène-chroman (Figure 5).

Un TPV dont la phase élastomère a été réticulée par une résine phénolique présente de façon générale de meilleures propriétés que ceux réticulés par le soufre ou les peroxydes. La réticulation est plus efficace et sélective. Le matériau montre alors une résistance aux huiles accrue et une bien meilleure élasticité due à l'homogénéité de la structure des réseaux formés. Ces résines dégradent moins la phase thermoplastique contrairement aux peroxydes et au soufre ce qui permet de conserver pleinement les propriétés de mise en œuvre du PP.

Il faut toutefois noter que la dissipation visqueuse de l'EPDM est telle qu'elle induit un échauffement très rapide de la matière fondue. La réticulation des chaînes est de façon générale extrêmement rapide et peut parfois s'initier sans même ajouter d'agent réticulant par simple oxydation (i.e. béta scission puis recombinaison) des chaînes élastomères. Cependant elle conduira dans ce cas à des réseaux très 'imparfaits'. Il est intéressant de noter que la température de réticulation du mélange, en influant sur la cinétique de réticulation et la réactivité de l'agent réticulant, conduira à des réseaux plus ou moins denses et homogènes. La densité de réticulation des réseaux formés dépendra donc en partie de la teneur en fonctions diène de l'élastomère et de la réactivité de la résine. Comme nous le verrons dans le chapitre III, les mécanismes de relaxation et de recouvrance élastique de ce type d'élastomère sont fortement influencés par la densité de réticulation et la nature du réseau (en particulier, la présence de 'défauts' tels que les chaînes pendantes).

III. Influence de l'incorporation de charges

Les interactions polymères – charges conduisent elles aussi à d'importantes conséquences du point de vue mécaniques et rhéologiques[23]. L'introduction de charges est destinée à apporter un renforcement aux élastomères[24], aux thermoplastiques[25] et, de façon plus spécifiques, aux TPV[26].

Lorsque leur dispersion est bonne, leur présence permet d'augmenter les modules et de compenser, en même temps, la faiblesse éventuelle d'autres propriétés (résistance aux chocs, au déchirement, à l'abrasion des vulcanisats)[27].

Outre l'intérêt économique lié à l'incorporation de charges, celles-ci peuvent modifier drastiquement les propriétés finales des TPV. L'adsorption des chaines polymères (Figure 6), couplé à la présence d'un réseau chimique au sein de l'élastomère, peut induire une nette amélioration de la résistance physique et de l'élasticité de l'élastomère, donc du mélange.

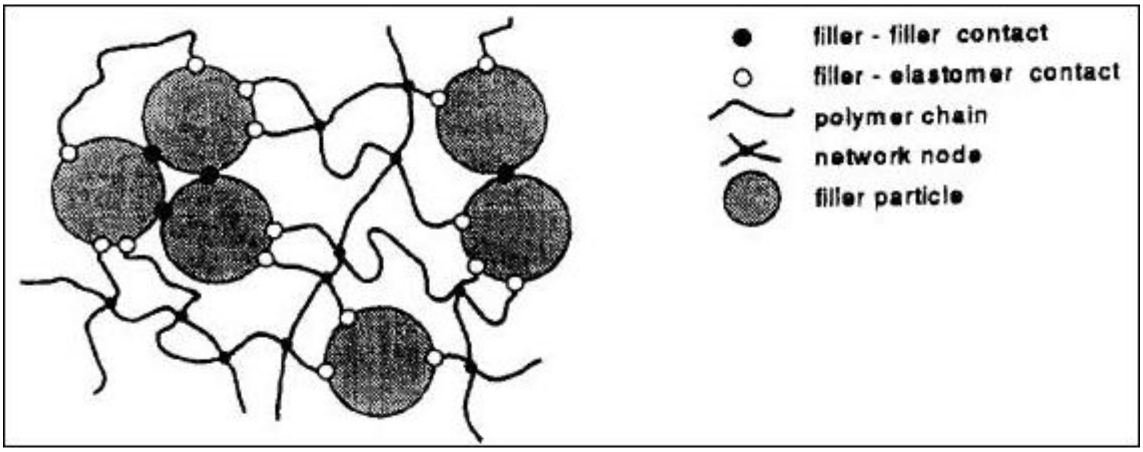


Figure 6 – Microstructure schématique d'un réseau d'élastomère chargé[6].

Les interactions charges – matrice, et le renforcement de manière générale, dépendent de trois facteurs principaux :

- la surface spécifique des charges conditionnée par la taille et leur facteur de forme.
- l'activité chimique des groupements de surface (hydroxyles pour la silice, carboxyles pour le noir de carbone).
- le facteur de forme et la nanostructuration des charges.

L'ensemble des types de structures que l'on peut rencontrer au sein d'un élastomère chargé se trouve représenté dans la Figure 7.

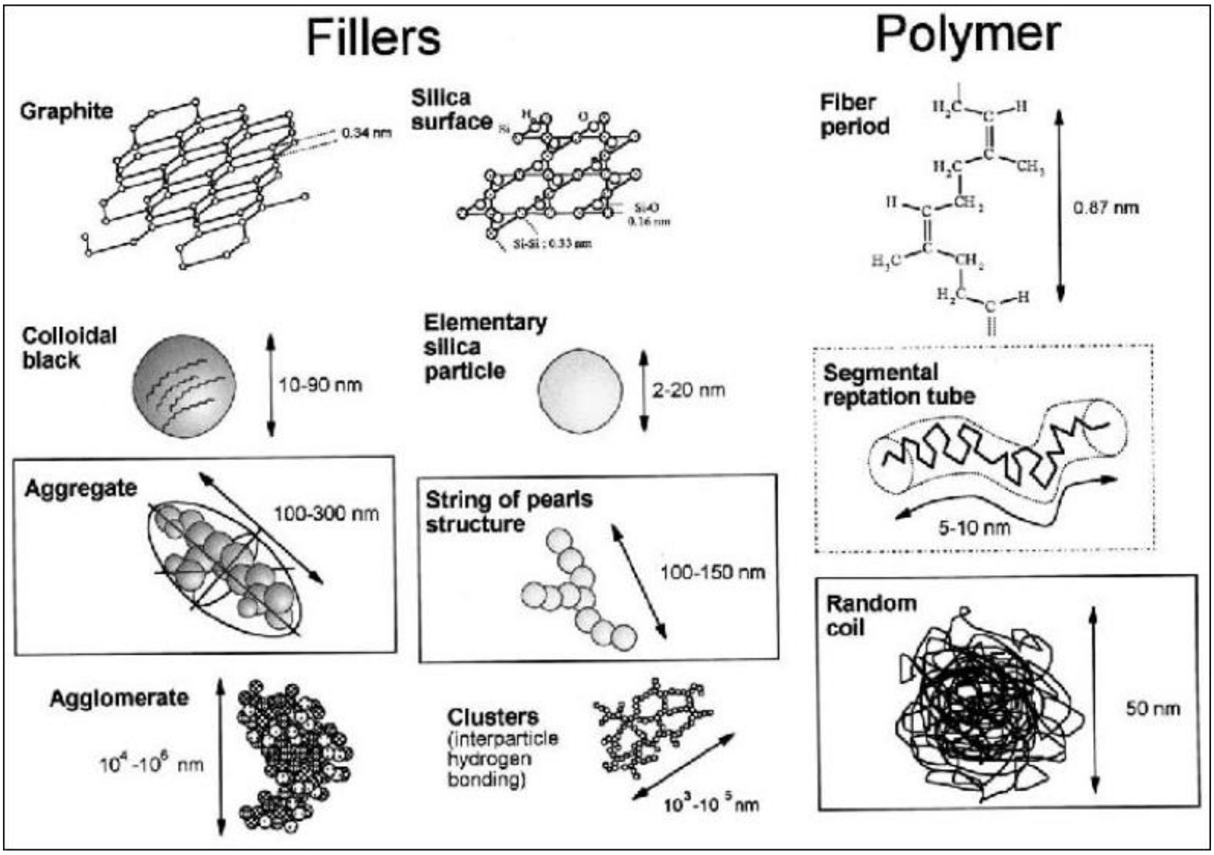


Figure 7 – Structures primaires et secondaires de particules dans les élastomères[28].

En résumé, les différentes composantes de l'action d'une charge vis-à-vis d'un élastomère donné s'additionnent comme l'a indiqué Payne[29].

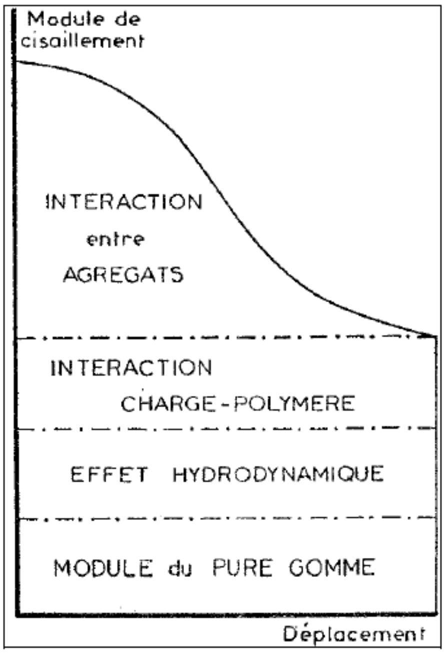


Figure 8 – Influence des effets d'une charge sur le module de cisaillement d'un vulcanisat[6].

La figure 8 montre en effet que le module initial d'un vulcanisat chargé résulte non seulement de l'effet hydrodynamique de l'addition de la charge à un mélange pure gomme et des liaisons charge-élastomère mais également des interactions entre les agrégats primaires (pour donner les agglomérats). Ce facteur, particulièrement important pour les très faibles déformations (environ 1%) disparaît complètement pour des déformations plus importantes par suite de la destruction des agglomérats.

Le renforcement étant nécessaire dans la plupart des applications courantes, outre la montmorillonite et la carbonate de calcium qui sont relativement peu utilisés, deux types de charges sont particulièrement bien adaptées aux TPV : la silice[30, 31] et le noir de carbone[32]. Le noir de carbone est l'agent renforçant prépondérant, cependant les nanocharges de silice, en particulier hydrophobes, sont de plus en plus utilisées de par leur affinité avec les phases élastomères de façon générale et l'amélioration significative de la résistance des mélanges qu'elles induisent[33-35].

La qualité de dispersion de ces charges (rupture des agglomérats, distribution homogène des agrégats) est l'élément clé de ce renforcement. En effet, l'agrégat est la structure indivisible à l'origine du renforcement via les interactions élastomère-particule. A l'inverse les agglomérats, aisément fractionnables par travail mécanique, sont souvent à l'origine de défauts amorçant l'endommagement.

Un autre effet de ces charges a été observé par Elias et al.[33, 34] dans le cas de systèmes non réactifs : la présence de charges peut induire une compatibilisation des phases se traduisant par la réduction de taille des gouttelettes de la phase élastomère dispersée. Les charges peuvent migrer de la phase la moins favorable vers la plus favorable thermodynamiquement. De plus, le caractère hydrophile ou hydrophobe de ces charges a un impact net sur leur migration. Les charges hydrophobes ont tendance à empêcher la coalescence des gouttelettes, tandis que la silice hydrophile abaisse la tension interfaciale du mélange thermoplastique / élastomère. Le chapitre V traitera entre autre de l'influence de nanocharges de silice hydrophiles et hydrophobes sur les morphologies de mélanges PP/EPDM.

IV. Rôle du plastifiant

La souplesse des TPV est majoritairement gouvernée par leur teneur en plastifiant, composé qui joue un rôle essentiel dans les mécanismes de relaxation et de stabilisation de la morphologie[36]. La présence d'une grande quantité d'huile et sa distribution au sein des phases polymères en question affecte directement la morphologie et les propriétés du matériau[37].

Dans les TPV du type PP/EPDM, le plastifiant a tendance à se concentrer dans l'EPDM et dans la phase amorphe de PP avec un coefficient de distribution PP/EPDM d'environ 0.8[38]. La réticulation entraîne toutefois un relargage de l'huile dans le PP, ce qui peut donner un effet de surface huileux au mélange[4].

Les travaux de Sengers et al.[39] ont porté sur l'étude de mélanges binaires polymère/plastifiant et ont conduit à la modélisation de la distribution de l'huile dans les TPV du type PP/EPDM. Cette étude a montré que la concentration en huile est d'autant plus importante dans la phase élastomère que la teneur en PP du TPV est grande. Cela a été confirmé par les travaux de Jayaraman et al.[37], qui ont également caractérisé cette distribution du plastifiant par microscopie électronique à transmission (MET)..

Les mécanismes de diffusion de l'huile dans un polymère de plus haute viscosité sont très peu décrits dans la littérature, hormis dans les travaux de Cassagnau et al.[38, 40]. Leurs recherches ont conclu que le coefficient de diffusion du plastifiant est similaire pour l'EPDM et le PP. Il semblerait toutefois que la diffusion du plastifiant dans l'EPDM soit du type élastique : l'huile diffuse et gonfle la matrice sans provoquer de désenchevêtrements, alors que dans le cas du PP il semble y avoir un désenchevêtrement et une diffusion mutuelle de l'huile et du PP.

Les travaux de Litvinov[41] ont démontré que, dans le cas de mélanges PP/EPDM réticulés sous cisaillement, la mobilité des molécules de plastifiant diminuait avec l'augmentation de la densité de réticulation. Le plastifiant assure aussi une compatibilisation des deux phases en présence par le biais de jonctions physiques à l'interface.

Enfin, il faut préciser que lors de la cristallisation de la phase PP, une partie du plastifiant va être rejetée dans la phase EPDM. Au final, à température ambiante, la phase EPDM sera donc forcément plus riche en plastifiant.

V. Morphologie et Développement des Structures

La morphologie des mélanges PP/EPDM réticulé dynamiquement gouverne leurs propriétés mécaniques et rhéologiques[42-45]. Diverses morphologies peuvent être observées : la phase dispersée peut être fibrillaire, nodulaire. Dans le cas de mélanges de polymères immiscibles comme le PP et l'EPDM, la morphologie du mélange dépendra de nombreux paramètres, dont principalement :

- la composition du mélange (présence d'agent compatibilisant, de stabilisant, de plastifiant)[46, 47],
- la proportion de chacun des constituants[48],
- le rapport de viscosité des phases[42],
- la tension interfaciale entre les polymères[49],
- les conditions de réticulation sous cisaillement[50, 51] et du procédé, en particulier le cisaillement et la température[52-55].

Parmi ces paramètres, la tension interfaciale a une influence prépondérante sur la morphologie et les propriétés mécaniques du mélange. En effet, ce paramètre est représentatif de l'affinité, donc de l'adhésion des phases en présence. Plus l'adhésion entre ces phases est bonne, plus la contrainte appliquée au matériau sera transmise dans le volume même du matériau. En résumé, plus la tension interfaciale sera faible, meilleure sera l'adhésion des phases, et plus la phase minoritaire sera dispersée finement. Outre la nature des polymères en présence, il est possible d'abaisser la tension interfaciale de mélanges de polymères par compatibilisation des phases via l'ajout de charges[34], de copolymères à blocs[56], de polymères fonctionnalisés, d'agent de couplage, etc. Dans notre cas, les mélanges PP/EPDM présentent une tension interfaciale relativement basse d'environ 0,3 mN/m[57].

V.1. Développement des morphologies de mélanges non miscibles

D'une façon générale, les mélanges de polymères non miscibles peuvent être assimilés à des systèmes diphasiques où la phase minoritaire est dispersée dans la matrice continue majoritaire. Ainsi, la déformation, la coalescence et la rupture de gouttelettes de polymères dispersés présente donc un intérêt certain du point de vue du développement morphologique de tels mélanges.

a. Cas des systèmes Newtoniens

Tout d'abord, considérons les systèmes Newtoniens. Taylor[58] a été le premier à étudier la déformation de gouttes de polymères newtoniens non miscibles dans un milieu de plus forte viscosité au sein d'un plastographe de type Haake. Les gouttes tendent à former des fils à de faibles vitesses de déformation. Dans le cas de polymères non miscibles, l'établissement de la morphologie stable dépend fortement du temps de mélange, de la composition du système et du rapport des viscosités. Pour caractériser un mélange matrice / phase dispersée, Taylor[58] a défini deux nombres sans dimensions exprimant la déformabilité de la phase dispersée : le rapport des viscosités p et le nombre capillaire Ca.

$$p = \frac{\eta_d}{\eta_m} \qquad \text{et} \qquad Ca = \frac{\eta_m \dot{\gamma} R}{\alpha}$$

Avec η_d et η_m les viscosités de la phase dispersée et de la matrice respectivement, $\dot{\gamma}$ la vitesse de cisaillement, R le rayon de la gouttelette, et α la tension interfaciale du mélange. Le nombre capillaire représente le rapport des forces visqueuses qui tendent à déformer la goutte, sur les forces interfaciales qui tendent à résister à cette déformation. Ces nombres permettent d'estimer si les gouttelettes peuvent se déformer, de façon stable ou non, et se diviser plus petites gouttelettes.

Il peut y avoir déformation de telles gouttelettes dispersées pour des rapports de viscosités inférieurs à 0,2. Pour un rapport de viscosités compris entre 0,2 et 2,2 la gouttelette se déformera et il y aura rupture comme décrit par Rumscheidt et Mason[59]. Par contre au delà de 3,8, la goutte ne se divisera pas sous cisaillement simple mais se déformera selon le mécanisme décrit par Taylor.

Grace[60] montre cependant qu'il peut y avoir rupture de la goutte en élongation à faible déformation, ce qui n'a pas été observé par Taylor en cisaillement simple. En conclusion, pour un système à faible tension interfaciale, plus la goutte est petite plus le cisaillement doit être élevé pour induire une rupture. Celle-ci est d'autant plus aisée que la viscosité de la phase continue est élevée[61]. Mais du point de vue de la déformation et de la rupture d'une phase dispersée l'élongation est plus efficace que le cisaillement.

Sous déformation élongationnelle, de telles gouttes peuvent dans certaines conditions s'allonger et former des fils cylindriques. Selon le rapport des viscosités, dès que l'écoulement est perturbé de tels fils peuvent se rompre en chapelets de petites gouttes[62]. Dans ce cas, un rapport de viscosité et un taux de déformation élevés permettent d'obtenir les gouttes les plus fines[63].

b. Cas des mélanges de fluides viscoélastiques

Dans le cas de fluides viscoélastiques la déformation et rupture de gouttelettes est principalement affectée par l'élasticité des polymères. Malgré les travaux initiés par Van Oene[64], Chin et Han[65], Elmendorp[66], Tsebrenko[67], aucune théorie à l'heure actuelle n'est encore capable de prédire exhaustivement la déformabilité de gouttelettes pour les systèmes viscoélastiques. L'élasticité semble stabiliser les gouttes déformées rendant leur fractionnement plus difficile[68]. Cependant la prédiction de leur déformation et rupture restent encore très complexe et très peu explicitée dans la littérature.

Delaby et al.[69] ont étudié, sur une large gamme de rapports de viscosités, la déformation de gouttelettes thermoplastiques au sein d'une phase continue viscoélastique. Leurs travaux ont été en plein accord avec la théorie newtonienne de Taylor, en particulier dans le cas d'un Ca proche de 1, où la déformation des gouttelettes a affiché une dépendance linéaire avec leur rayon initial.

De plus, Cassagnau et al.[70, 71] ont étudié de façon approfondie l'évolution de la morphologie d'un mélange de deux polymères viscoélastiques immiscibles et l'influence des propriétés élastiques permanentes sur la déformation sous cisaillement de gouttelettes d'EVA réticulé dispersées au sein d'une matrice poly(dimethylsiloxane). En conclusion, leurs travaux ont mis en évidence l'influence de l'élasticité permanente des gouttelettes sur leur déformation sous cisaillement. La déformation des gouttelettes d'élastomère réticulé diminue quand le taux de réticulation augmente, cependant, même après le point de gel, les gouttelettes d'élastomère continuent de se déformer. Toutefois, l'augmentation du rapport des viscosités limite cette déformation qui chute dramatiquement lorsque le taux d'insoluble de la phase élastomère dépasse 60%. De plus, une nette diminution de la relaxation des gouttelettes a été observée quand les propriétés élastiques deviennent supérieures aux forces visqueuses. Une morphologie fibrillaire peut être obtenue en ajustant le taux de cisaillement afin que la réticulation se produise avant la fracturation des fibres d'élastomères en gouttelettes.

De plus, le nombre sans dimension λ_{DC} décrit dans leurs travaux permet d'estimer les tendances morphologiques :

$$\lambda_{DC} = \frac{t_c}{t_{rupture}}$$

Ce nombre adimensionnel est le rapport entre un temps physico-chimique caractéristique de la phase dispersée et un temps de rupture des fibres générées sous cisaillement. Le temps de rupture est caractéristique du système car fonction des viscosités des polymères, de la tension interfaciale du mélange, du rayon des particules, de l'écoulement et de la température. Le temps t_c représente, dans le cas d'une phase dispersée réticulée, le temps nécessaire pour atteindre un taux d'insoluble de 60%.

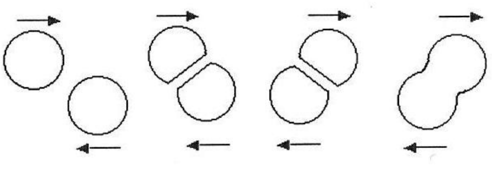
Ainsi :

- Si $\lambda_{DC} << 1$, la morphologie générée sera fibrillaire. Et si $\tan\delta < 0.1$ les fibres seront figées.
- Si $\lambda_{DC} >> 1$, la morphologie sera de type nodulaire. Et si $\tan\delta < 0.1$ la dispersion et la taille des nodules sera conservée lors d'étapes de transformation ultérieures.
- Si $\lambda_{DC} \approx 1$, les fibres dont le taux de réticulation n'est pas suffisant se rompront et conduiront à la formation de nodules sphériques.

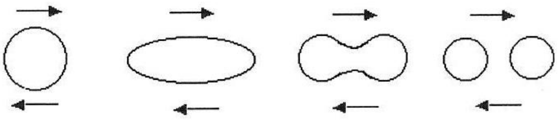
Ainsi l'étude du comportement de systèmes diphasiques est essentielle pour comprendre le processus de dispersion d'une phase au sein d'un matrice polymère lors d'un mélange. Cependant, la stabilisation des morphologies présentant une phase réticulée dispersée repose sur le contrôle de la compétition être le processus de coalescence/rupture et l'état d'avancement de la réaction de réticulation.

V.2. Coalescence et dispersion

La dispersion de fluides immiscibles dépend essentiellement de la compétition de deux mécanismes : la fragmentation et la coalescence toutes deux gouvernées par la rhéologie, les propriétés interfaciales et la composition des mélanges (Figure 9).



(a) coalescence



(b) rupture

Figure 9 – Schématisation des mécanismes de coalescence et rupture de gouttes[71].

Jang et al.[72] ont tout d’abord mis en évidence le phénomène de coalescence dans les mélanges PP/EPDM au repos au cours de recuits. Ils ont aussi observé que le processus de coalescence est augmenté par une courte distance interparticulaire, une basse vitesse de cisaillement, de hautes températures, des concentrations élevées de la phase dispersée et de grandes tensions interfaciales[73, 74]. Inversement, on peut conclure que le phénomène de dispersion est favorisé par de faibles fractions volumiques en phase dispersée, des tensions interfaciales faibles et de grandes vitesses de déformation.

Les travaux de Joubert[75] et De Loor[76] ont apporté des informations intéressantes sur le développement morphologique de mélange thermoplastique / élastomère avant et après réticulation (Figure 10).

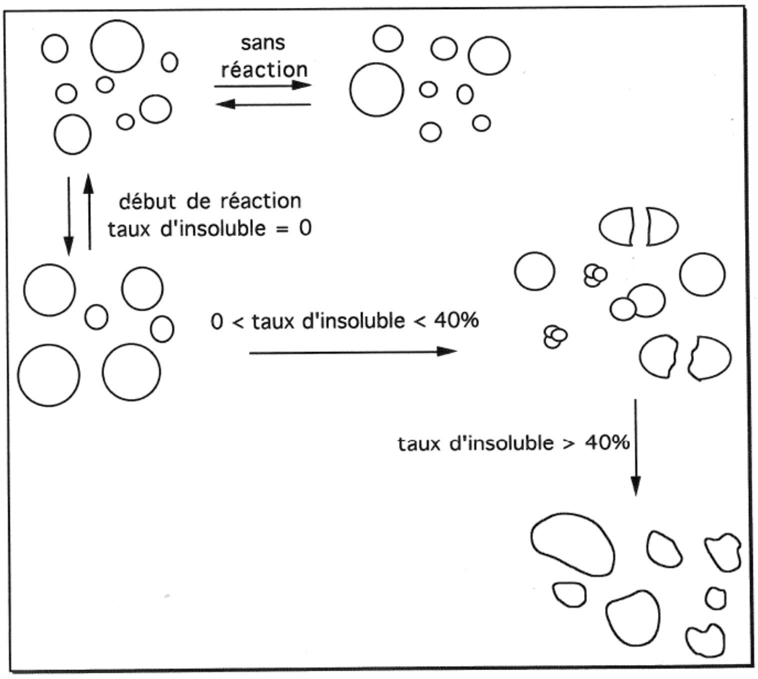


Figure 10 – Mécanismes de stabilisation d’une phase dispersée[76].

Comme indiqué sur la Figure 9, la morphologie de mélange PP / EVA-EMA réticulé sous cisaillement est comme suit :

- avant l’avancement au temps de gel le couplage des chaines élastomères conduit à une augmentation de la viscosité du fait de l’augmentation des masses molaires. La taille des nodules de la phase dispersée augmente donc en conséquence.
- A partir de l’avancement du temps de gel le réseau tridimensionnel se crée et les mécanismes de rupture et dispersion ne sont pratiquement pas détaillés dans la littérature. Cependant la compétition entre la dispersion et la coalescence de la phase

dispersée régule la morphologie selon l'équilibre de Bhowmick et Inoue présenté ci-après.

- Lorsque le taux d'insoluble atteint 40% la morphologie est complètement stabilisée et la taille finale des nodules de la phase dispersée est fixée.

Il faut donc veiller à ajuster le moment de la réticulation afin de fixer la morphologie de la phase élastomère lorsqu'elle atteint l'état de dispersion adéquat.

Bhowmick et Inoue[77] ont quant à eux étudié la vulcanisation de mélanges PP/PA sous cisaillement et ont conclu à un équilibre entre les mécanismes de coalescence et la dispersion (Figure 11).

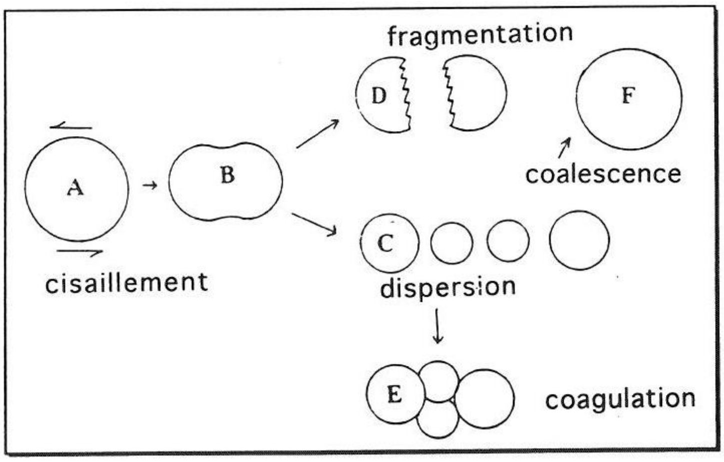


Figure 11 – Modèle d'équilibre des mécanismes de dispersion et de coalescence pendant la réticulation d'un mélange de PP/PA, par Bhowmick et Inoue[77].

Leurs travaux montrent que la réticulation sous cisaillement peut induire une agglomération des particules lors du mélange. Ils concluent aussi que la taille des particules réticulées et dispersées diminue lors des premières minutes de mélange, pour ensuite augmenter. Leur coagulation est d'autant plus importante que la température est élevée et que la proportion d'élastomère est importante. Ils constatent aussi que plus la cinétique de réticulation est avancé plus la dispersion de l'élastomère est grossière. Cependant, ils concluent aussi que la probabilité de coalescence de particules d'élastomère est particulièrement faible dans ce cas car l'inversion de phase conduit théoriquement à la formation d'un système thermodynamiquement stable. Ceci nous permet d'entrevoir la complexité des mécanismes d'inversion de phase et de réticulation dynamique au cours de l'élaboration du Végaprène®.

Corté et Leibler[78] et Macosko et al.[79] ont démontré que le phénomène de coalescence est très nettement diminué par la présence d'un copolymère présentant deux blocs respectivement miscibles dans chacune des deux phases immiscibles**.** Ceci permet d'éviter la formation de grosses gouttelettes nuisant aux propriétés mécaniques et de mise en œuvre du matériau à l'échelle macroscopique. La présence d'un tel copolymère à bloc à l'interface entre les phases dispersée et continue améliore significativement l'adhésion interfaciale des deux phases et permet de stabiliser les dispersions submicroniques essentielles à tout procédé de mise en œuvre.

Le mécanisme global qui gouverne la taille des particules dans le cas de systèmes réticulés dynamiquement a donc été relativement peu étudié. Il ressort des études précédentes que la déformabilité et la dispersion de gouttelettes d'élastomères réticulé est améliorée dans le cas où le rapport des viscosités est proche de 1. De plus, le caractère élastique de l'élastomère réticulé semble stabiliser les inclusions et rendre leur dispersion plus difficile. Plus la vitesse de cisaillement est importante plus la dispersion est homogène et fine. Cependant, la réticulation de la phase dispersée sous cisaillement perturbe les modes de rupture, de dispersion et de coalescence et peut conduire à des particules de formes irrégulières et de fortes tailles. Enfin, un champ d'écoulement élongationnel est plus efficace pour la dispersion surtout dans le cas d'un rapport de viscosité important.

Par ailleurs, ces résultats ont montré que la tension interfaciale joue un rôle primordial et doit être aussi faible que possible, d'où la nécessité de compatibiliser les phases. Ces travaux mettent donc en avant l'utilité de compatibiliser les phases afin de stabiliser une morphologie plus fine, donc plus performante du point de vue propriétés mécaniques.

V.3. Compatibilisation et interface

Il est clair que l'interface entre deux phases de polymères immiscibles est cruciale vis à vis des propriétés du mélange : leur compatibilisation est donc nécessaire afin de diminuer la tension interfaciale[80] et d'affiner la morphologie, la cohésion et les propriétés globales du matériau[81-83]. La taille caractéristique des phases dépend directement de l'interface entre les phases de polymères en question[84], donc de la présence et de la quantité d'agent compatibilisant introduit[85].

Un compatibilisant, présent à l'interface élastomère – thermoplastique, affectera la coalescence et la rupture des particules d'élastomères lors de la stabilisation morphologique du mélange[86]. Globalement, la taille des particules dispersées diminue exponentiellement avec la concentration en compatibilisant jusqu'à une concentration limite[85]. Le compatibilisant influence de ce fait la miscibilité des polymères et la mise en œuvre du matériau, en assurant une meilleure cohésion des phases, et donc de meilleures propriétés mécaniques[82].

La qualité de cette interface entre le phase thermoplastique et l'élastomère est essentielle à tout TPV. Elle est la source même de la conjugaison des propriétés intrinsèques des deux polymères, de l'élasticité et des propriétés mécaniques et de mise en œuvre du mélange. En effet, une bonne adhésion entre les phases est essentielle pour le transfert de contraintes d'une phase à l'autre soit efficace et pour limiter la formation et la propagation de fissures. La partie suivante (i.e. 'Mécanismes de déformation') confirmera l'importance de cette interface.

Dans le cas d'un additif de faible viscosité et miscible avec les deux phases, comme un plastifiant, il faut prendre en compte le phénomène de ségrégation de ces 'petites' molécules. Et puisque la dissipation visqueuse, principale source d'énergie lors de la fusion d'un polymère, est directement proportionnelle à la viscosité et au carré de la vitesse de cisaillement imposée, on peut en déduire que la présence de ce plastifiant ralentit fortement le processus de mélange. Son rôle est donc à la fois essentiel et gênant, et le taux de plastifiant à utiliser doit donc être optimisé à la fois vis à vis de l'élaboration d'un TPV mais aussi bien sur de ses propriétés finales.

Ainsi plusieurs stratégies de compatibilisation sont envisageables[56] :

- ajouter un troisième composé miscible dans les deux autres phases (comme un plastifiant),
- ajouter un copolymère avec une partie miscible dans chacun des deux polymères respectivement, en général un copolymère à bloc ou parfois un copolymère greffé,
- mélanger avec un réactif menant à la modification chimique d'un des deux polymères (compatibilisation réactive) pour formé un copolymère à blocs ou greffé,
- fracturer mécaniquement ou chimiquement des chaînes macromoléculaires de chacune des phases pour créer un copolymère par recombinaison.[87].

Ces stratégies mènent cependant à des résultats significativement différents :

- l’ajout d’un composé ayant une viscosité similaire à celles du thermoplastique et de l’élastomère à la température de mélange facilite la dispersion de l’élastomère et limite la coalescence des nodules une fois dispersés. Mais cela n’est pas suffisant car une bonne adhésion entre ces deux phases est essentielle pour que le transfert de contraintes soit efficace et que le mélange soit parfaitement cohésif.
- L’ajout d’un copolymère à bloc affecte principalement la tension interfaciale donc la taille de la phase dispersée en créant des boucles ou des ponts entre phases améliorant ainsi significativement l’adhésion des deux phases. Ces copolymères à blocs peuvent être introduits avant le mélange en même temps que les autres composés, ou créés lors du mélange ou de la réticulation dynamique[88].
- Les copolymères tri-blocs quant à eux influent directement sur les propriétés mécaniques du mélange final[82].

Dans le cas de mélanges PP/EPDM, il est possible de compatibiliser les phases par le biais d’un copolymère PP-g-EPDM créé lors de l’étape de réticulation sous cisaillement[14]. Des observations MEB de surfaces de rupture d’un mélange vulcanisé de PP/EPDM montrent que les nodules d'EPDM semblent être recouverts de polypropylène ce qui laisse envisager qu’un copolymère greffé PP-g-EPDM puisse être créé lors de la réticulation (Figure 12).

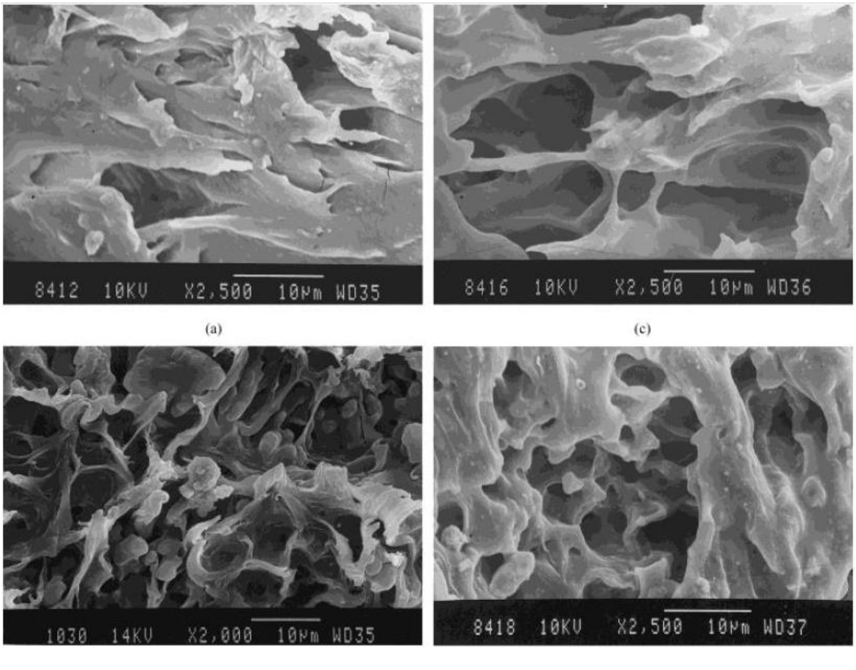


Figure 12 - Clichés MEB d’échantillons vulcanisés de PP–EPDM avec (a)10%, (b) 20%, (c) 30% et (d) 40% d’EPDM[14].

Les auteurs notent que la présence de cette pellicule de copolymère greffé de PP-g-EPDM cause une réduction significative de la taille des particules d'EPDM. Ce polymère greffé renforcerait l'adhésion des phases en assurant une meilleure interface. Cet article montre qu'une proportion bien que relativement faible de ce copolymère à l'interface joue un rôle significatif voir prépondérant du point de vue des propriétés finales, car l'adhésion des deux phases est un des facteurs les plus importants affectant la résistance aux chocs pour ce type de mélange.

Une autre étude intéressante, menée par Kim et al.[82], a été réalisée afin d'améliorer les propriétés mécaniques de mélanges PP/EPDM à l'aide d'un copolymère tri-blocs (PP-g-MAH)-co-[PA-6,6]-co-(EPDM-g-MAH) en guise de compatibilisant (MAH = anhydride maléique). Ce copolymère à blocs améliore notamment la résistance à l'impact à basse température du mélange.

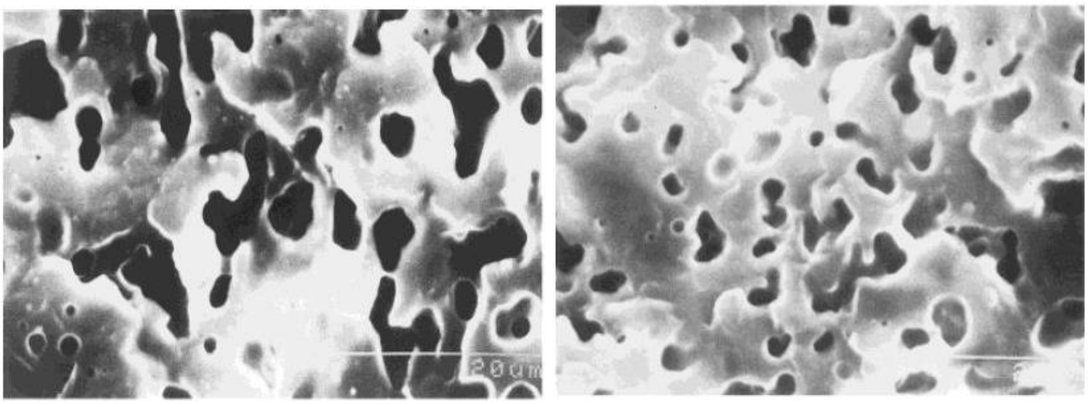


Figure 13 - Clichés MEB de surfaces cryo-fracturées de PP – EPDM, sans compatibilisant à gauche, et avec 2% massique de compatibilisant à droite.

La figure 13 montre que la morphologie globale du mélange ne change pas fondamentalement avec l'ajout du compatibilisant. Cependant, son incorporation augmente nettement le nombre de particules dispersés d'EPDM et améliore significativement l'uniformité de leur dispersion et les propriétés mécaniques du mélange.

V.4. <u>Prédiction morphologique et inversion de phases</u>

Par extension des modèles de déformation de gouttes et de développement morphologique présentés précédemment, la prédiction des morphologies de mélanges immiscibles est désormais possible.

Jordhamo et al.[89] ont été les premiers à proposer une relation semi-empirique à ce sujet :

$$\frac{\eta_1}{\eta_2} \times \frac{\theta_2}{\theta_1} \square 1$$

Avec η_1 et η_2 les viscosités des polymères, et θ_1 et θ_2 leurs fractions massiques. Si ce rapport est supérieur à 1, le polymère 2 sera dispersé dans la matrice constituée du polymère 1, et réciproquement.

Cependant, lors de l'élaboration du TPV, la phase d'EPDM initialement majoritaire en volume réticule pendant le mélange sous cisaillement. La modification des propriétés rhéologiques de la phase élastomère conduit donc nécessairement à des modifications de morphologie. En général, une inversion de phase se produit et l'élastomère se retrouve dispersé au sein de la matrice thermoplastique tout en conservant un caractère plus ou moins continu.

Joubert[75] a proposé une représentation schématique de l'évolution de l'inversion de phase se produisant au cours de la réticulation dynamique (Figure 14).

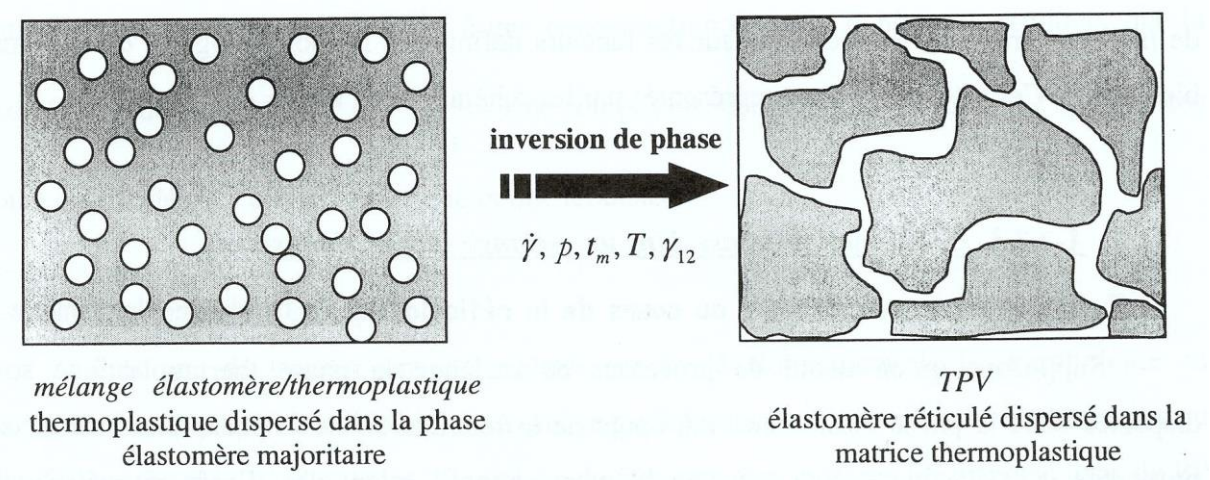


Figure 14 - Représentation schématique du développement de la morphologie au cours de l'élaboration d'un TPV, avec $\dot{\gamma}$ la vitesse de cisaillement, p l'état d'avancement de la réaction, t_m le temps de mélange, T la température de la matière et γ_{12} la tension interfaciale.

Entre ces deux morphologies fondamentalement opposées, le système passe par un état intermédiaire de co-continuité (Figure 15). Les phases en présence peuvent également présenter toutes deux une co-continuité, et celle-ci peut être considérée comme une structure intermédiaire où la phase dispersée devient la phase continue, et la matrice devient une phase dispersée, et caractérise une inversion de phase.

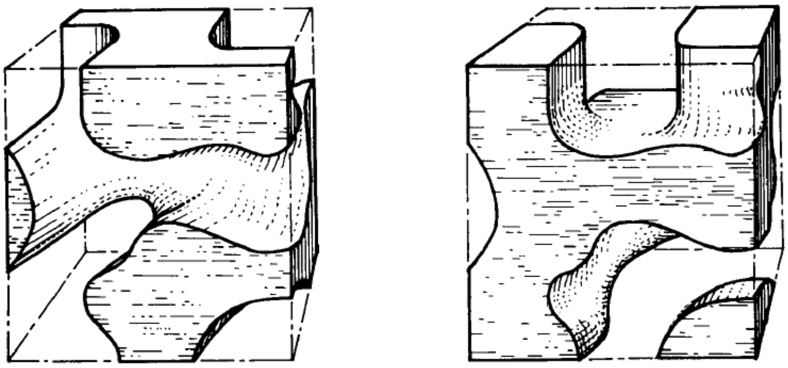


Figure 15 – Modèle de Gergen de structure anisotropique d'un mélange de polymères immiscibles de morphologie co-continue[90].

Au cours de la réticulation, la phase élastomère s'étire de plus en plus jusqu'à se casser en gouttelettes de polymère réticulé. Cette étape conditionne la qualité du matériau car plus l'élastomère est dispersé finement meilleures sont les propriétés finales du TPV[52].

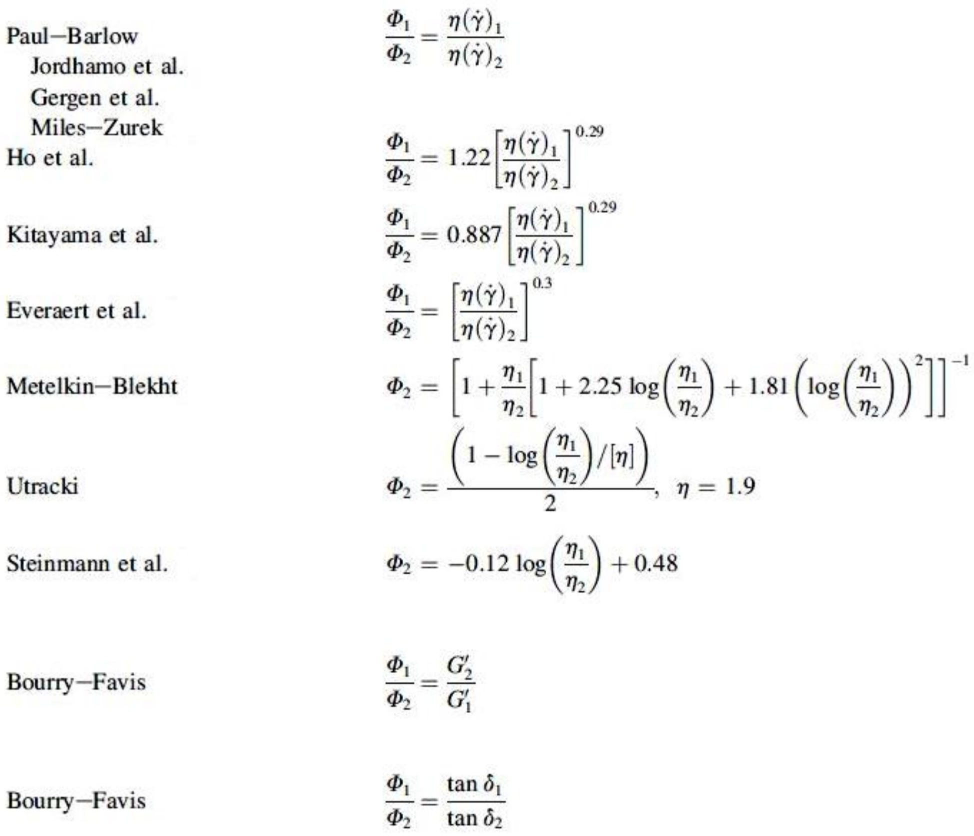
Cette co-continuité des phases est particulièrement importante car elle présente le meilleur équilibre des propriétés, comme par exemple un maximum d'extensibilité et grande rigidité en présence de grandes déformations[87]. D'où l'utilité de savoir prédire la morphologie de ce type de mélanges à l'aide de modèles empiriques.

Il faut donc détecter et contrôler ce mécanisme d'inversion de phase ainsi que les paramètres expérimentaux responsables de cette modification morphologique afin d'obtenir de façon reproductible une morphologie adéquate induisant les meilleures propriétés au TPV[91]. Cette notion de cette co-continuité a été exhaustivement décrite dans la revue de Potsche et Paul[92] qui ont conclu quant à la possibilité de combiner les propriétés des phases en présence par le biais d'une telle morphologie.

Castro et al.[93] ont quant à eux étudié la détection de la co-continuité d'un mélange de polymères immiscibles (POE/PVDF-HFP) d'un point de vue rhéologique, en déterminant deux compositions critiques définissant la zone de co-continuité assimilable à une super structure auto-similaire de dimension fractale.

De plus, Bouilloux et al.[94] ont étudié la détection rhéologique de cette inversion de phase au sein de systèmes réactifs. Leurs travaux ont permis de conclure quant à la stabilité morphologique de la co-continuité et à la largeur de la gamme de compositions induisant une telle morphologie. Leurs recherches ont aussi mis en évidence les limitations liés à la prédiction morphologique du modèle de Jordhamo qui ne s'avère pas toujours approprié dans le cas de tels mélanges thermoplastique / élastomère.

Ainsi, de nombreux modèles semi-empiriques de prédiction morphologique plus perfectionnés ont été décrits dans la littérature afin de tenir compte d'autres paramètres importants en plus de la viscosité et de la proportion des phases comme présentés sur les Figures 16 et 17.



Paul–Barlow Jordhamo et al. Gergen et al. Miles–Zurek	$\frac{\Phi_1}{\Phi_2} = \frac{\eta(\dot{\gamma})_1}{\eta(\dot{\gamma})_2}$
Ho et al.	$\frac{\Phi_1}{\Phi_2} = 1.22\left[\frac{\eta(\dot{\gamma})_1}{\eta(\dot{\gamma})_2}\right]^{0.29}$
Kitayama et al.	$\frac{\Phi_1}{\Phi_2} = 0.887\left[\frac{\eta(\dot{\gamma})_1}{\eta(\dot{\gamma})_2}\right]^{0.29}$
Everaert et al.	$\frac{\Phi_1}{\Phi_2} = \left[\frac{\eta(\dot{\gamma})_1}{\eta(\dot{\gamma})_2}\right]^{0.3}$
Metelkin–Blekht	$\Phi_2 = \left[1 + \frac{\eta_1}{\eta_2}\left[1 + 2.25\log\left(\frac{\eta_1}{\eta_2}\right) + 1.81\left(\log\left(\frac{\eta_1}{\eta_2}\right)\right)^2\right]\right]^{-1}$
Utracki	$\Phi_2 = \frac{\left(1 - \log\left(\frac{\eta_1}{\eta_2}\right)/[\eta]\right)}{2}, \quad \eta = 1.9$
Steinmann et al.	$\Phi_2 = -0.12\log\left(\frac{\eta_1}{\eta_2}\right) + 0.48$
Bourry–Favis	$\frac{\Phi_1}{\Phi_2} = \frac{G'_2}{G'_1}$
Bourry–Favis	$\frac{\Phi_1}{\Phi_2} = \frac{\tan\delta_1}{\tan\delta_2}$

Figure 16 - Listes des modèles semi-empiriques de détection d'inversion de phase[95].

Ces modèles impliquent différents paramètres comme tan δ, divers coefficients empiriques propres à chaque système, mais surtout la vitesse de cisaillement $\dot{\gamma}$.

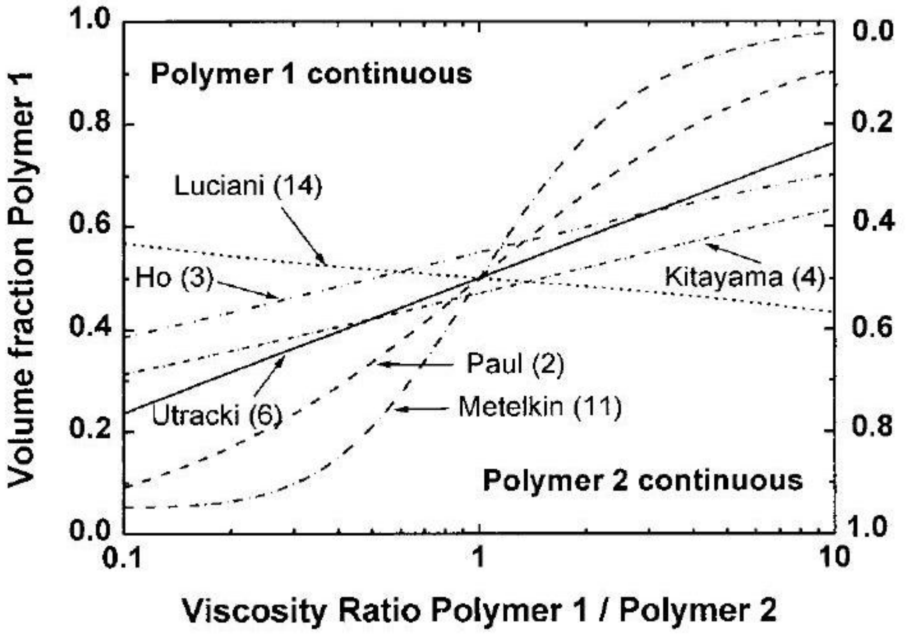


Figure 17 – Différents modèles empiriques décrivant la fraction volumique à l'inversion de phase en fonction du rapport de viscosité de mélanges binaires[92].

Abdou-Sabet[96] a aussi étudié la vulcanisation dynamique d'un mélange PP/EPDM avec une phase élastomère majoritaire. Lors de cette vulcanisation dynamique, il a été prouvé que l'EPDM et le PP subissent une inversion de phase qui permet de maintenir la plasticité du mélange. En début de réaction, deux phases co-continues sont générées. Puis au fur et à mesure que la réticulation progresse, la phase élastomère continue, sous l'influence d'un cisaillement intensif, de s'étirer jusqu'à se briser pour former des petites gouttelettes. Le PP forme alors la phase continue dans laquelle la phase élastomère est dispersée. Il a été conclu qu'un haut degré de réticulation de la phase élastomère empêche le processus de rupture des 'filaments' en plus petites particules et la réduction de l'aire interfaciale par formation de sphères. Il semblerait donc qu'il faille parfaitement disperser l'élastomère partiellement réticulé avant de la réticuler totalement. Cela fera l'objet d'une étude détaillée dans la suite de ce manuscrit (cf. chapitre V). Quantitativement, peu de travaux existent exceptés ceux de Joubert et al.. Cela tient principalement au fait qu'il est difficile d'exprimer physiquement la viscosité d'un système réticulé.

V.5. Morphologies typiques des TPVs

Les TPV peuvent présenter un large panel de morphologies. Van Duin et al.[4] ont élaboré des mélanges PP/EPDM, réticulés dynamiquement à l'aide d'une résine phénolique, aux morphologies particulièrement intéressantes (Figure 18).

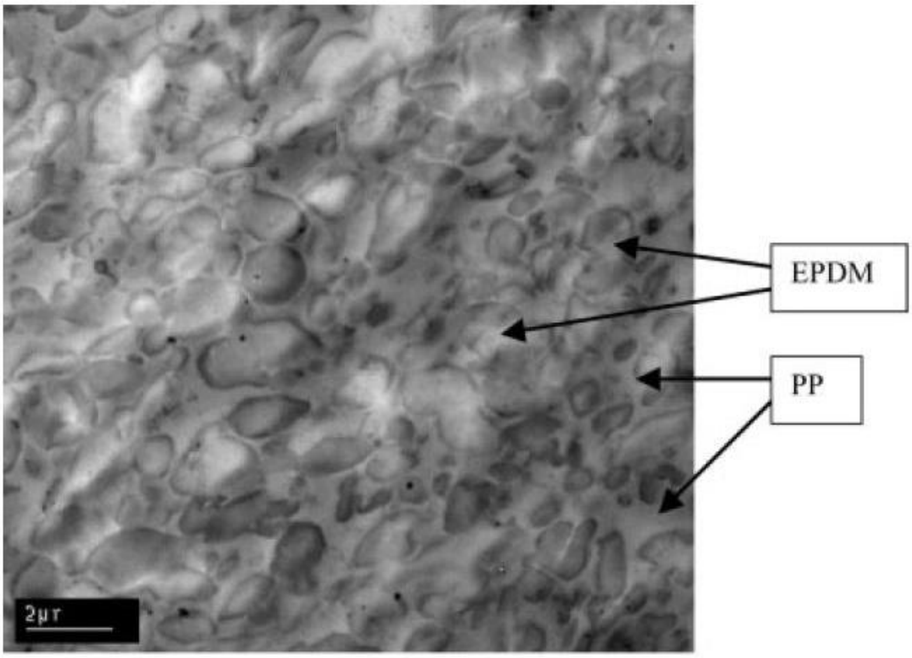


Figure 18 – Cliché MET d'un TPV à base de PP/EPDM plastifié[4].

La morphologie de ce TPV est en fait constituée d'une phase d'EPDM dispersée dans le PP bien que ce mélange semble afficher à priori une co-continuité des phases. Ce type de morphologie, présentant une phase d'EPDM totalement réticulé et dispersé finement sous forme de nodules de tailles inférieures à 2µm dans la matrice thermoplastique, confère à l'ensemble les propriétés mécaniques propres aux TPV.

Bhadane et al.[51] ont quant à eux abouti à la schématisation de la structure de la phase d'élastomère au sein de ce type de mélange PP/EPDM. Le facteur important est le taux d'insoluble de l'élastomère, et les auteurs mettent en avant des micro-gels de structures primaires et secondaires (Figure 19).

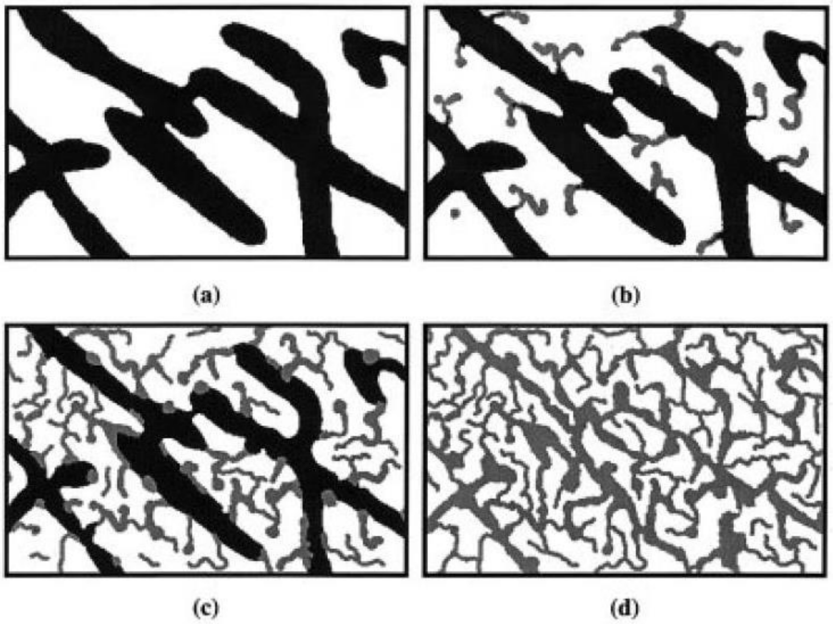


Figure 19 – Morphologies schématiques de mélanges PP/EPDM à 40/60 avec (a) le mélange non réticulé, (b) réticulé à 25%, (c) réticulé à 50%, (d) réticulé à 100%[51].

La réticulation sous cisaillement induit la formation de micro-gels d'élastomère interconnectés. Cette structure tout à fait particulière ne peut être obtenue, pour ce genre de système, que par le biais d'une réticulation sous cisaillement qui permet d'assure la cohésion structurelle du matériau en présence d'une phase élastomère est entièrement réticulée.

VI. Propriétés mécaniques et mécanismes de déformation

VI.1. Influence de la réticulation dynamique

Ponsard-Fillette et al.[22] ont étudié l'influence d'une réticulation dynamique sur els propriétés de traction de mélanges PP/EPDM et ont conclu qu'un mélange réticulé sous cisaillement présente un allongement à la rupture plus important que l'échantillon non vulcanisé, et sa contrainte à la rupture est nettement améliorée.

La résistance aux chocs est aussi une propriété mécanique complexe qui reflète l'absorption de l'énergie d'impact selon différents processus précédant la rupture du matériau. Jain et al.[14] ont montré que la dureté et la résistance aux chocs de la plupart des thermoplastiques peuvent être considérablement augmentées par l'incorporation d'une phase dispersée d'élastomère réticulé (Figure 20).

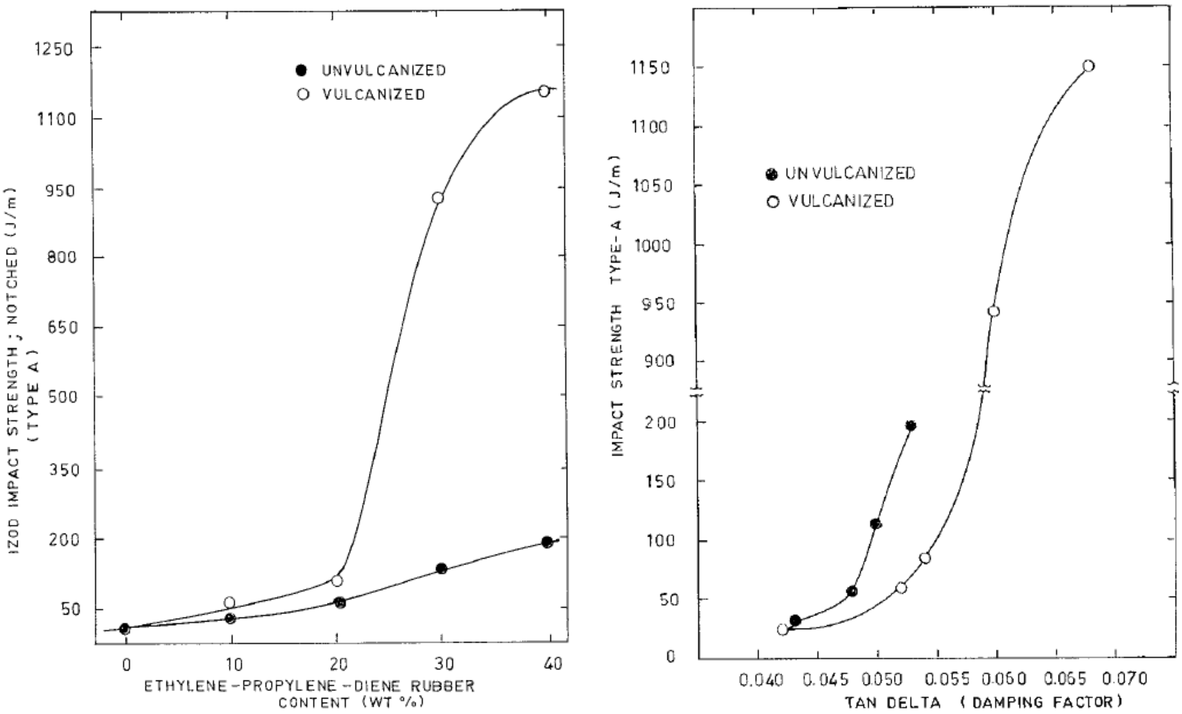


Figure 20 – Effet de la réticulation dynamique et de tan δ sur la résistance mécanique de mélanges PP/EPDM[14].

Ces travaux ont montré une amélioration très nette de la résistance à l’impact de mélange PP/EPDM réticulé sous cisaillement en comparaison avec un mélange identique non réticulé. De plus, la proportion de la phase élastomère ainsi que le caractère plus ou moins élastique de l’élastomère réticulé jouent, bien évidemment, un rôle prépondérant sur la résistance aux chocs du matériau. On peut attribué ces résultats au fait que la phase caoutchouteuse dispersée fait office de sites de concentration et de dissipation de contraintes. Cette phase élastomère induit une relaxation des efforts aux interfaces des domaines polyoléfine - élastomère. Par conséquent, la nucléation des fissures et la déformation de la matrice sont significativement réduites et la dureté du matériau est nettement améliorée comme confirmée par la figure 21.

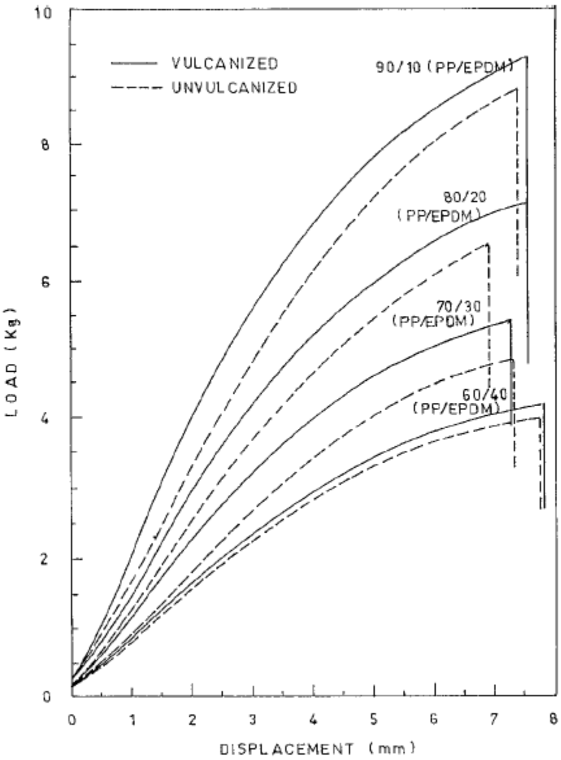


Figure 21 – Effet de la réticulation dynamique et de la proportion des phases sur de mélanges PP/EPDM[14].

La charge plus élevée requise pour propager une fissure dans les mélanges vulcanisés indique une adhésion entre le PP et d'EPDM nettement améliorée par l’étape de réticulation dynamique. D’une façon générale, les mélanges vulcanisés ont de meilleures propriétés mécaniques dues à l’augmentation de l'adhésion des phases et à la réduction des cavités dans la matrice de PP[14]. Toutefois, pratiquement aucune étude de relaxation et recouvrance élastique de tels mélanges n’a été reportée dans la littérature et nos travaux auront pour but d’apporter plus d’informations dans ce domaine (cf. Chapitre III).

VI.2. <u>Mécanismes de déformation des TPV</u>

Il a été démontré auparavant dans ce chapitre que les propriétés rhéologiques et mécaniques des TPV sont intimement liées à leur morphologie[97], bien que ces relations microstructure/propriétés et mécanismes de déformation soient encore de nos jours bien peu explicités dans la littérature. Les processus d’absorption et de dissipation de l’énergie sont donc rigoureusement différents pour chaque type de morphologie ce qui requiert une caractérisation de chacun des systèmes afin de pouvoir corréler les propriétés mécaniques dynamiques aux morphologies en question.

Yang[98] a aussi analysé le mécanisme de déformation d’un TPV à base de PP et d’EPDM réticulé et dispersé. Même à des déformations élevées la matrice est localement préservée dans les limites élastiques et se comporte comme un adhésif formé in situ entre les particules d’élastomères interconnectées. Ce comportement constitue une des clés du mécanisme de recouvrance élastique de mélanges diphasiques mais n’est que brièvement décrit dans la littérature.

Les travaux de Groeninckx[99] ont aussi apporté des résultats particulièrement intéressants sur les TPV du type nylon-6 / EPDM. Pour ce système, composé d’une phase continue thermoplastique semi-cristalline et de nodules d’élastomère réticulé dispersés finement, leurs études en microscopies à force atomique et en transmission ont révélé une déformation et plastification fortement inhomogènes de la matrice. Lorsque soumis à une déformation, la plastification s’initie dans les zones les plus fines de la matrice. De plus, même pour de larges déformations, les zones les plus épaisses de la matrice ne sont pratiquement pas déformées, donc très peu sollicitées : ces domaines plus massifs jouent le rôle de point d’adhésion entre les phases et assurent la transmission de la contrainte d’une phase à l’autre. Et lorsque la déformation est supprimée, la phase élastomère déformée exerce une contrainte inverse du à son caractère élastique ce qui assure la recouvrance du matériau.

Plus récemment, Boyce et al.[100, 101] ont mis en évidence le rôle important de la co-continuité sur le mécanisme de déformation globale d’un TPV (Figure 22).

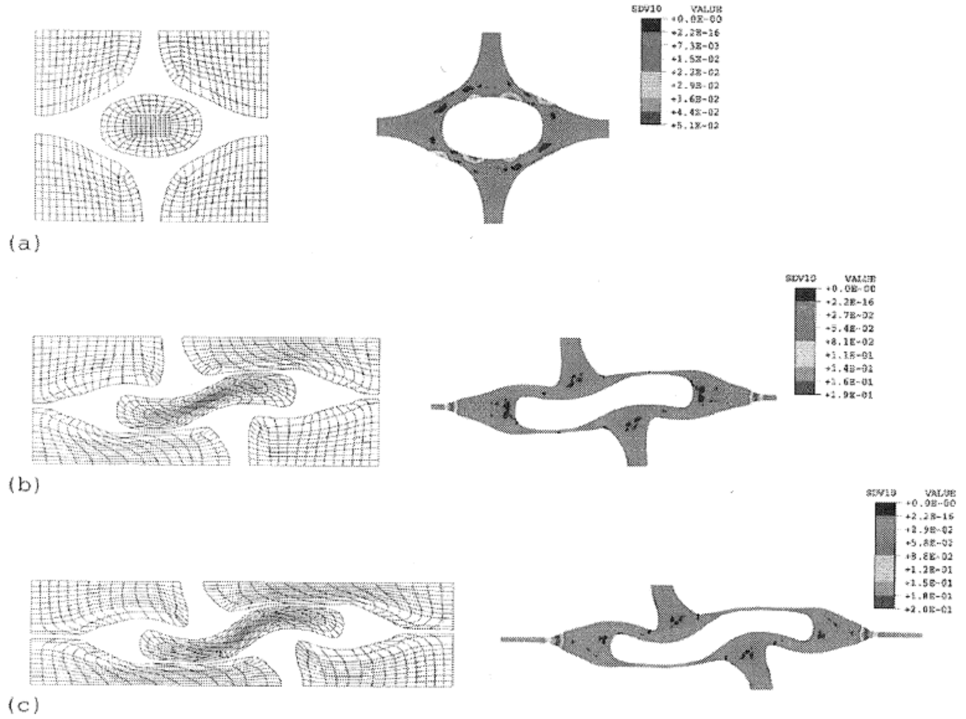


Figure 22 – Modélisation des microdéformations d’une matrice co-continue thermoplastique / élastomère (phase thermoplastique en gris) possédant une large quantité de plastifiant et assimilable à un TPV, pour des déformations vraies de (a) -0.10, (b) -0.50 et (c) -0.70[100].

Ces travaux montrent l’importance de la taille caractéristique de la co-continuité des phases. Cette structure peut subir de grandes déformations en sollicitant et plastifiant peu la matrice thermoplastique compte tenu de son volume. La quasi-totalité du thermoplastique n’est alors que très peu déformée, et seuls les brins les plus fins se plastifient très largement dès les preiers instants de la déformation. La phase continue d’élastomère se déforme ensuite très largement et assure le comportement caoutchoutique à l’ensemble. Au final, les parties les plus massives de la phase thermoplastique ne se déforment pas ou très peu : ces domaines pivotent et se réarrangent dans l’espace alors que la phase élastomère subit seule la déformation imposée de façon réversible. De plus l’asymétrie de ce type de morphologie peut induire une réduction importante de la plastification de la phase thermoplastique : dans ce cas la rotation des domaines massifs sera plus importante, la plastification totale sera réduite et la recouvrance élastique après suppression de la déformations sera nettement améliorée. Ceci montre clairement l’importance de la co-continuité et de l’interface entre les deux phases polymères. Une telle sollicitation ne peut être assurée que s’il y a transmission de la contrainte au sein du matériau, ce qui sera d’autant plus le cas que l’adhésion des phases sera de bonne qualité.

Van Duin[4] a récemment proposé un modèle intéressant de déformation de TPV à phase élastomère dispersée et réticulée (Figure 21). Lors d'une contrainte en élongation, la phase amorphe de PP s'oriente, puis, lors de la relaxation, les nodules d'EPDM relaxent jusqu'à un certain point. Des études AFM ont montré que lors de l'élongation du TPV la couche thermoplastique de PP située à l'équateur des nodules d'EPDM se plastifiait mais était 'remise à sa place' lors de la rétraction du nodule d'EPDM (Figure 23).

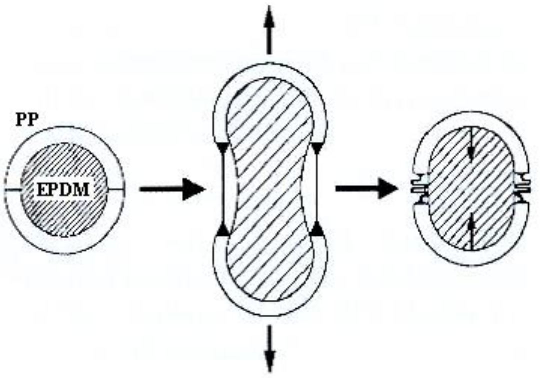


Figure 23 - Représentation schématique de la déformation élongationnelle puis relaxation d'une phase caoutchouteuse dispersée au sein d'une phase thermoplastique[4].

Cette constatation a été validée par des analyses par éléments finis et donne une information de taille quant à l'explication de l'élasticité permanente des TPVs. L'interface joue donc un rôle particulièrement important : la déformation de ces gouttelettes et la plastification du PP enrobant les nodules d'EPDM dépendent alors de la qualité de l'interface et du taux de réticulation de l'EPDM. Plus l'interface sera bonne plus la contrainte imposée à la matrice sera transférée aux nodules, donc plus ils subiront la contrainte totale à la place de la matrice. Et plus l'EPDM sera réticulé moins les nodules se déformeront donc moins le PP se plastifiera. Ceci peut expliquer la possibilité de recyclage de ce type de matériau car, par augmentation de la température, on peut théoriquement effacer les bandes de striction et les zones cristallines du PP sans trop le dénaturer et ainsi le remettre en œuvre.

La compréhension des relations entre la structure et les propriétés des TPV du type PP/EPDM réticulé dynamiquement doit encore progresser pour assurer la maitrise des processus conduisant à des matériaux optimisés. Or, l'étude de leurs morphologies en particulier leur évolution au cours du processus d'élaboration a été relativement peu traitée. Ces morphologies et mécanismes impliqués dans l'élaboration et le comportement dynamique des TPV constituent ainsi un champ de recherche complexe et captivant.

Conclusion

Cette étude bibliographique permet de cerner la problématique liée à l'élaboration d'un mélange de deux polymères immiscibles et, de surcroît, vulcanisé dynamiquement.

Les propriétés élastiques et de mise en œuvre de mélanges PP/EPDM réticulés sous cisaillement dépendent de nombreux paramètres et mécanismes interdépendants, les principaux étant : la nature et proportion des constituants, les paramètres opératoires et le choix du procédé, le timing d'introduction de l'agent réticulant, le rapport des viscosités des phases en présence et son évolution lors de la réticulation de la phase élastomère, la cinétique de réticulation, l'influence de la densité de réticulation sur le développement morphologique, la diffusion du plastifiant et des charges, l'inversion de phases, la compatibilisation éventuelle des phases, la cristallisation du thermoplastique après élaboration, etc.

Etant donné le nombre de ces paramètres et la complexité des mécanismes impliqués dans cette élaboration, il n'existe pas à ce jour de théorie unifiée les prenant en compte dans leur ensemble. Nous avons donc choisi d'étudier des systèmes simplifiés en décomposant le procédé d'élaboration au lieu de considérer l'élaboration d'un TPV dans son intégralité. Nos travaux ont donc pour but d'individualiser, autant que faire se peut, les mécanismes impliqués afin de nous affranchir de leurs interactions, dans l'optique de mieux les comprendre et d'estimer leur influence sur le développement morphologique de ces mélanges.

Ce manuscrit propose ainsi de répondre à plusieurs questions qui restent encore sans réponses à l'heure actuelle, en particulier concernant les relations structure – propriétés des TPV du type PP/EPDM. L'élaboration de ce type de TPV repose sur un savoir faire empirique acquis au fil des années et jalousement protégé. Cependant de nombreuses zones d'ombre subsistent et une approche scientifique permettra d'améliorer la compréhension de ces systèmes.

Tout d'abord, le chapitre II présentera brièvement les matériaux et techniques expérimentales utilisées. Le comportement viscoélastique de l'EPDM, la structure de son réseau et son comportement de relaxation / recouvrance ne sont pratiquement pas décrits dans la littérature. Le chapitre III apportera des résultats nouveaux sur cet élastomère plastifié grâce à l'étude et à la modélisation exhaustives de sa structure et de son comportement viscoélastique en cisaillement et en compression.

Ensuite, compte tenu du peu de travaux relatifs aux morphologies et comportements mécaniques des TPV du type PP/EPDM, le chapitre suivant apportera de nouvelles informations quant à la structure physique de ce type de mélanges. Plus particulièrement, l’augmentation de l’élasticité de l’EPDM n’induit pas forcément une amélioration significative de l’élasticité globale du mélange PP/EPDM, confirmant une fois encore que cette corrélation structure – propriétés est encore loin d’être clairement explicitée. Dans cette optique, le chapitre IV de ce manuscrit apportera des informations utiles quant à la compréhension de l’influence de la morphologie et de la structure de ces mélanges sur leur relaxation de contraintes et recouvrance élastique.

Enfin, comme nous l’avons souligné, du point de vue rhéologique les mécanismes de déformation, de dispersion et de coalescence d’élastomère réticulé en présence d’une phase thermoplastique ne sont que très peu abordés dans la littérature. Le cinquième et dernier chapitre de ce manuscrit traitera donc ce thème via une approche novatrice : l’étude de la dispersion d’EPDM plastifiés et réticulés de façon variable dans du PP en diverses proportions. Une comparaison des morphologies et propriétés mécaniques de ces mélanges (préparés à partir d’EPDM pré-réticulé) sera faite avec des mélanges réticulés sous cisaillement, nous permettant ainsi d’estimer l’importance et les conséquences de ce procédé d’élaboration.

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Chapitre II

Matériaux et Techniques Expérimentales

Chapitre II – Matériaux et Techniques Expérimentales

I. Matériaux utilisés

I.1. L'EPDM Vistalon 8800

L'EPDM est obtenu par polymérisation de l'éthylène, du propylène et d'un diène par catalyse métallocène. C'est l'un des caoutchoucs synthétiques les plus utilisés à l'heure actuel. L'incorporation statistique du diène permet d'obtenir des produits insaturés et réticulables. Les pourcentages massiques sont généralement compris entre 45 et 80% d'éthylène, et entre 1 à 15% de diène[1]. La structure même de l'EPDM influe ainsi directement sur sa réactivité aux agents réticulant, donc sur ses propriétés finales et, a fortiori, sur celles du TPV.

La gamme de température d'utilisation des EPDM s'étend de -40 jusqu'à 200°C et leur tenue thermique est relativement bonne (200°C pendant 5 heures, et jusqu'à 130°C pendant 1000 heures). L'avantage de cet élastomère réside en partie dans son prix modeste et ses propriétés mécaniques particulièrement bonnes après réticulation. Son excellente tenue au vieillissement climatique fait de cet élastomère une référence dans le secteur de l'automobile. Il peut accepter des taux de charge et de plastifiant très élevés, ce qui permet d'obtenir un excellent rapport qualité - prix. Sa tenue aux solvants et aux différents produits pétroliers est en revanche médiocre.

L'EPDM utilisé est le 'Vistalon 8800' (ExxonMobil Chemical). Ce terpolymère est élaboré à partir de 53.5% (massiques) d'éthylène et de 10% de diène ici le 5-éthylidène-2-norbornène (Figure 1). Ce terpolymère est caractérisé par un pourcentage massique relativement faible d'éthylène et taux élevé de diène particulièrement important du point de vue de la réticulation.

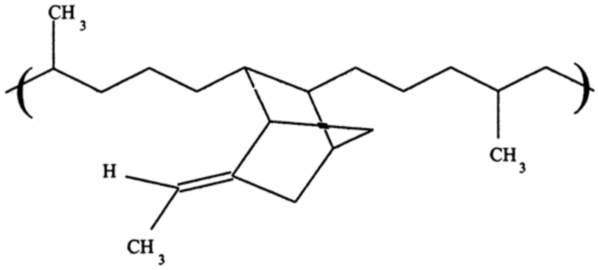

Figure 1 – Motif de répétition du terpolymère d'éthylène-propylène-diène à base d'éthylidène-norbornène.

Ce polymère commercial contient originellement 13% d'huile en masse, sa masse volumique est de 0.87g.cm^{-3}, sa viscosité Mooney ML(1+4) de 73 à 125°C et sa température de transition vitreuse d'environ -85°C. Sa caractérisation rhéologique est reportée Figure 2.

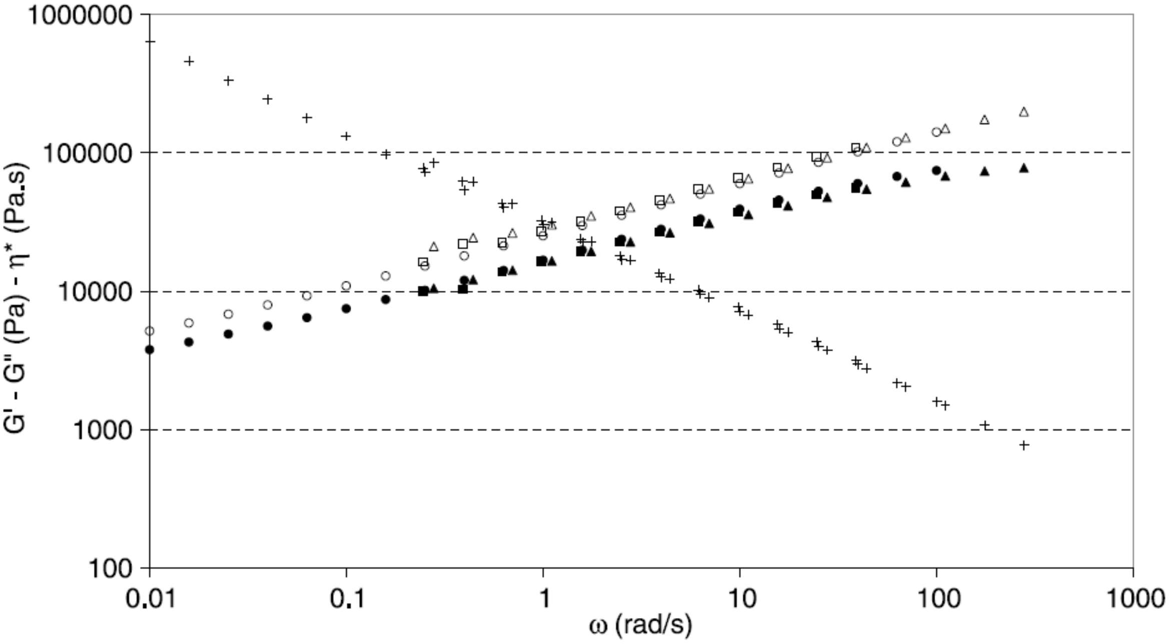

Figure 2 – Balayage en fréquence de l'EPDM Vistalon 8800 à 200°C (courbes maîtresses), avec G' le module élastique (symboles ouverts), G'' le module visqueux (symboles fermés) et η* la viscosité (+)[2].

I.2. Le polypropylène PPH3060

Le thermoplastique utilisé dans nos études est le 'PPH3060', un polypropylène de masse molaires moyennes $M_n = 72000$ g.mol^{-1} et $M_w = 384000$ g.mol^{-1}, synthétisé par polymérisation du monomère de propylène par catalyse hétérogène Ziegler-Natta. Cet homopolymère est fortement cristallin, sa température de fusion est de 162°C. Sa masse volumique est de 0.905 g.cm^{-3} à 20°C, et sa transition vitreuse se situe aux alentours de -20°C. Son MFI est de 1.8 g /10min (230°C, 2.16kg)[2]. La caractérisation rhéologique à 200°C de ce PPH3060 est reportée sur la Figure 3.

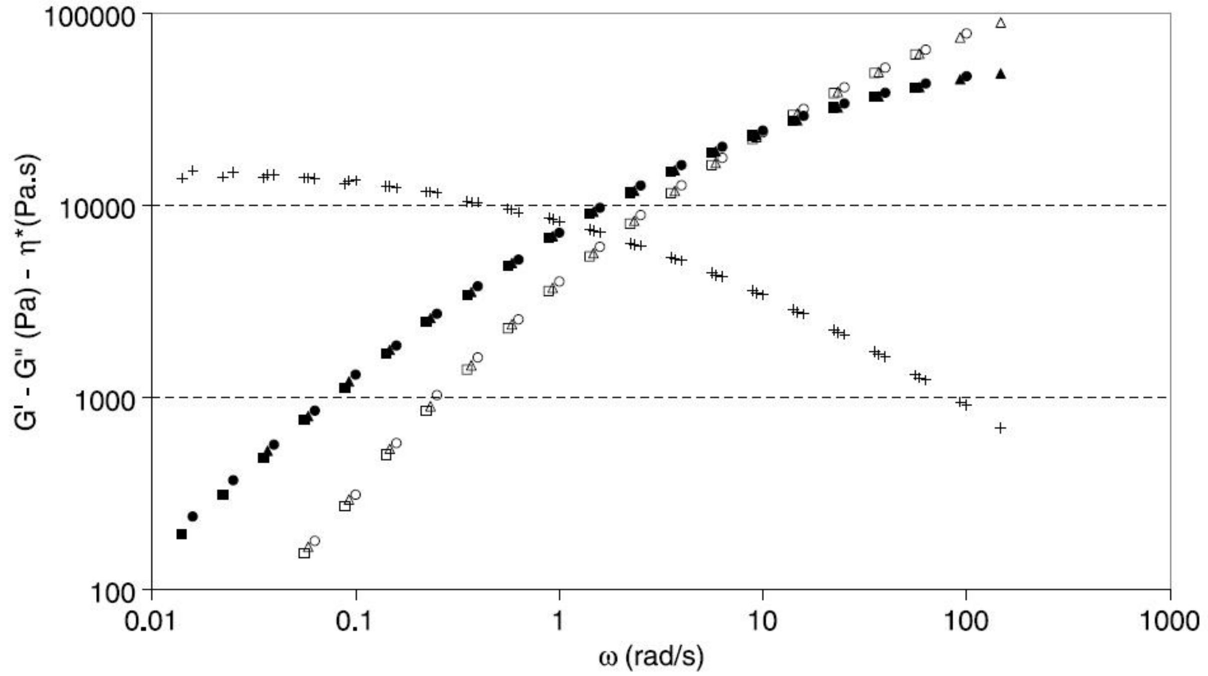

Figure 3 – Balayage en fréquence du PPH3060 à 200°C (courbes maîtresses), avec G’ le module élastique (symboles ouverts), G’’ le module visqueux (symboles fermés) and η* la viscosité (+)[2].

I.3. Le plastifiant

Le plastifiant utilisé est une huile paraffinique ‘Torilis 7200’ (Arkema) de masse volumique 0.90 g.cm^{-3}. Sa viscosité est de 32 mm²/s à 100°C. Cette huile est soluble dans le THF et l’acétone (cf. partie ‘Taux d’insoluble’).

I.4. Système de réticulation

L’agent réticulant utilisé se compose d’un résine phénolique ‘SP 1045’ (Schenectady) et d’un catalyseur : le dichlorure d’étain ($SnCl_2$). Cette résine phénolique est élaborée par condensation d’un alkylphenol et d’un formaldéhyde avec des ponts di-méthyl éther liant les unités phénoliques. Ces résines phénoliques sont généralement classées en deux catégories : les résols et les novolaques en raison du rapport molaire phénol / aldéhyde. La famille des résols, dont la résine SP 1045 fait partie, est caractérisée par la présence de groupes réactifs du type méthylol et d’unités diméthylène-éther, alors que les résines novolacs ne présentent pas de groupes méthylol réactifs et ne peuvent donc pas être considérés comme des agents réticulants.

II. Process utilisé

L'élaboration en discontinu des différents EPDM et des mélanges PP/EPDM a été réalisée grâce à un mélangeur interne de type Haake équipé d'un malaxeur interne Rheomix 600. Ce réacteur isochore de 50 cm^3 permet d'imposer un malaxage de type tangentiel en enregistrant la température du mélange ainsi que le couple moteur assurant une vitesse de cisaillement imposée (Figure 4).

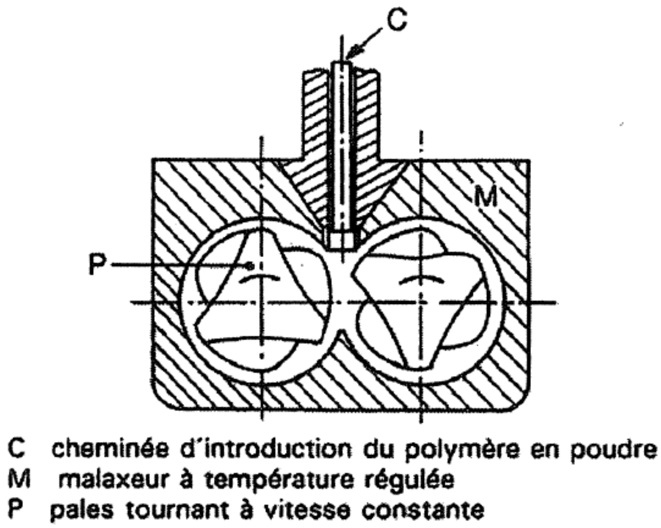

Figure 4 – Représentation schématique d'un mélangeur interne Haake Rhéomix 600[3]

Toutes les préparations ont été mises en forme sous presse, à des températures et pendant des durées variables, sous forme de plaques de dimensions : 50 x 90 x 1 mm^3 qui ont pu être caractérisées au rhéomètre, en DMA ou par microscopies. Les détails et conditions des différentes préparations liées aux trois volets de cette étude sont rappelés dans les chapitres correspondants (cf. Chapitres III à V).

III. Recouvrance élastique

Le principe du test de Déformation Rémanente après Compression est d'évaluer la capacité élastique d'un échantillon cylindrique à recouvrer sa dimension initiale après avoir été soumis à une déformation constante pendant une durée déterminée, à une température donnée.

Du point de vue industriel, ce test est normalisé. Dans le cas par exemple des normes ASTM D 395 (ISO R 815, NF T 46011, NMRPS 523) ce test consiste à placer un échantillon compressé à 25% dans un four pendant 3 jours à 150°C, puis de sortir l'échantillon et de le laisser refroidir pendant 30 minutes, puis de déduire, par différence entre la taille initiale et la taille finale, la déformation résiduelle ou son complémentaire la recouvrance élastique du matériau.

Dans nos conditions de laboratoire ce test a été effectué sur un DMA de Texas Instrument (DMA 2980) sur des échantillons cylindriques de 4 mm de diamètre et 1.5 mm de hauteur. Les essais DRC menés ont consisté à imposer une déformation par compression de 25% pendant 10 heures à 100°C, puis une période de 10 heures de recouvrement de la déformation avec une force de contact de 0.02N toujours à 100°C (cf. Figure 5). Ce test, contrairement à la procédure industrielle, tenait compte du coefficient de dilatation du matériau : la déformation de 25% était imposée une fois que le matériau était stabilisé en température. Le test se déroule donc ainsi :

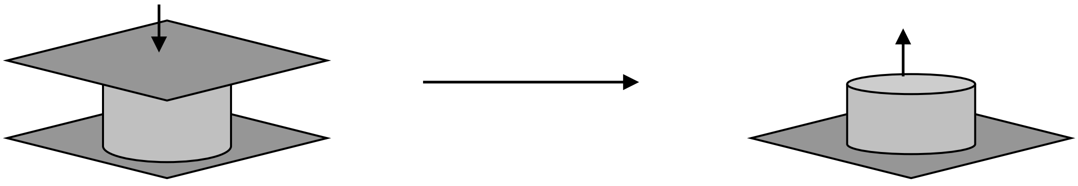

Figure 5 – Représentation schématique du test de DRC.

La déformation rémanente après compression peut être facilement déterminée par :

$$DRC = \frac{l_0 - l_1}{l_0 - l_2} = \frac{1}{\varepsilon_{0,n}} \times \frac{l_0 - l_1}{l_0}$$

Avec : l_0 la hauteur initiale de l’échantillon, l_1 la hauteur de l’échantillon après avoir subi la déformation qui lui a été imposée, l_2 la hauteur de l’échantillon lors de du test de déformation imposée et $\varepsilon_{0,n}$ la déformation nominale imposée de 0.25. L’échantillon est parfaitement élastique si sa DRC vaut 0 : dans ce cas il recouvre exactement sa taille initiale.

Les aspects viscoélastiques d’un tel test ont récemment été explicités par Cassagnau et al.[4, 5]. La contrainte appliquée et la déformation subie par l’échantillon ont les allures présentées sur la Figure 6.

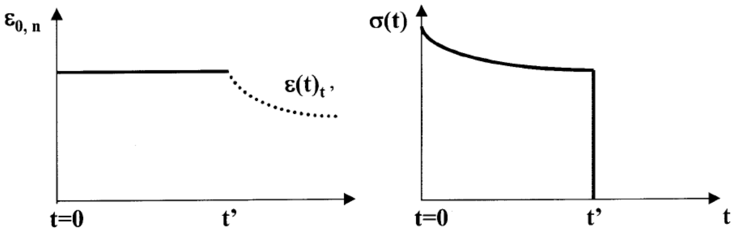

Figure 6 – Profils viscoélastiques de la déformation et de la contrainte du matériau lors test du test de DRC.

Au temps t = 0 la déformation est imposée et le matériau relaxe on peut ainsi suivre, par le biais de la force nécessaire pour appliquer la déformation en question, l'évolution du module de relaxation du matériau. De plus, dans le domaine de déformation linéaire la superposition de Boltzmann est applicable[4] :

$$\varepsilon(t)_{t'} = \int_{-\infty}^{t} \frac{\delta\sigma(u)}{\delta(u)} \times D(t-u).du$$

Avec $\sigma(u)$ la fonction contrainte-relaxation. Pour : $u < 0$ on a $\sigma(u) = 0$; Pour $0 \leq u \leq t'$ on a $\sigma(u) = \varepsilon 0.E(u)$ avec $\varepsilon_0 = \ln(1+ \varepsilon_{0,n})$ et E(u) le module d'Young de relaxation, et enfin pour $t'<u$ $\sigma(u)=0$.

La déformation imposée induit une relaxation des chaînes macromoléculaires, puis une recouvrance élastique après suppression de la contrainte qui permet d'estimer le caractère viscoélastique du matériau. Ce phénomène est directement lié au mécanisme moléculaire de relaxation et de diffusion des extrémités de chaînes pendantes[4]. Après suppression de la déformation le matériau exerce une pression sur le plateau supérieur en contact avec l'échantillon, et la déformation résiduelle peut être suivie, donnant accès au profil de recouvrance élastique de l'échantillon. Ainsi, contrairement au test industriel normalisé, les profils du module de relaxation et de la recouvrance élastique du matériau peuvent être enregistrés.

IV. Caractérisations microscopiques

La caractérisation microstructurale par microscopies électroniques à balayage et en transmission permet d'observer les morphologies de ces mélanges en vue de les comparer aux modèles de prédiction morphologique et à leurs propriétés mécaniques.

IV.1. Microscopie Electronique à Balayage

Chaque échantillon a tout d'abord été cryofracturé, ou surfacé à froid par microtomie, dans de l'azote liquide, afin de présenter une surface aussi lisse que possible, puis recouvert d'un dépôt homogène d'or de 15 à 20 nm par métallisation plasma. La phase d'EPDM a été sélectivement extraite grâce à un bain dans le THF pendant 7 jours, suivi de plusieurs rinçages avec ce même solvant. Après séchage, la qualité de l'extraction était vérifiée par pesée des échantillons. L'observation microscopique a été réalisée à l'aide d'un MEB Hitachi S800 à une tension de 18kV.

IV.2. Microscopie Electronique à Transmission

Les échantillons doivent tout d'abord être microtomé en lamelles de 55nm d'épaisseur à froid, i.e. en dessous des Tg des polymères afin de ne pas déformer le mélange. Les lamelles sont ensuite déposées sur des grilles en cuivre (Mesh 300). Ces lamelles sont ensuite marquées : l'utilisation d'oxydes d'osmium ou de ruthénium permet de fixer un métal sur les fonctions diènes de l'élastomère, ce qui induit un marquage efficace[6]. L'observation s'effectue grâce à un microscope électronique en transmission (MET) TEM Philips CM 120 : sur les clichés la phase EPDM ressort ainsi noire, alors que le polypropylène est d'apparence très claire.

V. Taux d'insoluble et gonflement

La densité de réticulation des échantillons peut être déterminée par l'intermédiaire de leur taux de gonflement du gel dans un non solvant. La mesure du taux de gonflement est une méthode fiable qui permet de quantifier le taux d'insolubles correspondant au taux de polymère réticulé n'ayant pas été dissout. Ces taux d'insolubles et de gonflement permettent d'accéder à la densité de réticulation à partir des modèles de dynamique moléculaire, point qui sera plus amplement explicité dans le chapitre III. Deux méthodes principales de mesure ont été utilisées :

- Par diffusion de THF :

Etant donné la très bonne interaction EPDM – THF, cette première méthode de détermination du taux d'insoluble de l'EPDM a reposé sur le principe de la diffusion du THF et l'extraction de l'huile et de l'EPDM non réticulé par diffusion des macromolécules hors du réseau gonflé. Chaque échantillon a été immergé, en 5 exemplaires, pendant 7 jours dans du THF, et rincé chaque jour afin d'assurer l'extraction totale de l'EPDM non réticulé et de l'huile présents dans ces mélanges. Les échantillons ont ensuite été séchés sous vide pendant une journée puis pesés.

Dans le cas de préparations d'EPDM plastifié plus ou moins réticulée, il est possible de déterminer le taux de gonflement de ces réseaux par suivi de la perte de masse de l'échantillon gonflé de solvant, et à l'aide de la formule suivante :

$$G = \frac{1}{\upsilon_2} = \frac{(Mg - Mp)/\rho_{THF} + Mp/\rho_{EPDM}}{Mp/\rho_{EPDM}}$$

Avec : ν_2 la fraction volumique de polymère à l'équilibre de gonflement, Mg la masse de polymère gonflée, Mp la masse de polymère insoluble (sèche après extraction), et ρ_{THF} et ρ_{EPDM} les masses volumiques du solvant et de l'élastomère respectivement.

Concernant les mélanges PP/EPDM, ce type de mesure a aussi permis de tester qualitativement certaines morphologies: dans le cas où le PP est dispersé au sein d'une phase continue d'EPDM pas ou très faiblement réticulé, la dissolution de l'EPDM conduit à l'écroulement du matériau. Cependant, pour tous les mélanges comportant une phase de PP il est impossible de déterminer le gonflement de la phase élastomère étant donné la présence de PP insoluble dans le solvant en question.

- Par distillation soxhlet

La seconde méthode de détermination du taux d'insoluble consiste cette fois-ci non pas à extraire uniquement l'EPDM non réticulé et le plastifiant comme par diffusion du THF, mais à dissoudre en plus le PP par rinçages successifs à reflux de l'échantillon par un mélange azéotropique (de toluène/xylène à 90/10%) à 115°C pendant 5 jours dans un soxhlet.
Cette méthode n'est convenable que dans le cas ou la phase élastomère est entièrement réticulée, car une durée pareille à 115°C conduit à la réticulation de l'élastomère.

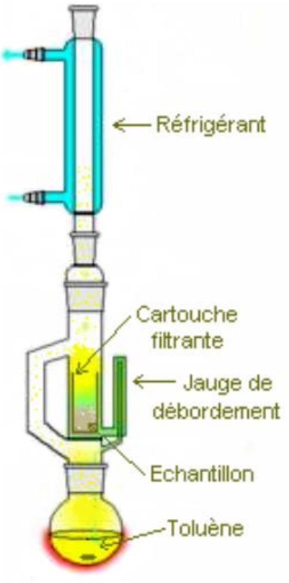

Figure 7 – Schéma d'un soxhlet.

Les techniques expérimentales complémentaires (suivis rhéologiques, méthodes de compoundage, etc.) sont détaillées dans les parties expérimentales respectives aux trois chapitres qui suivent.

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Chapitre III

Viscoelasticity of randomly crosslinked EPDM networks

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Chapitre III – Viscoelasticity of randomly crosslinked EPDM networks

Abstract

The network structure of plasticized EPDM compounds, crosslinked with resol at different concentrations, was studied by means of rheological methods consisting in oscillatory shear tests, to determine the equilibrium modulus Ge, and long-time relaxation tests in compression followed by strain recovery (a protocol that also yielded values of the compression set of the samples). Ge results were analyzed with respect to the phenomenological model of Langley and Graessley which takes into account the contribution of crosslinks and trapped entanglements to the shear equilibrium modulus. A correction was introduced in order to take into account the presence of plasticizer. The measurement of the soluble polymer fraction in the different samples allowed a more detailed characterization of the networks to be carried out, following a molecular approach by Pearson and Graessley. This method enabled to calculate the crosslink density and trapping factor, but also to compute the probability φ1 for an un-crosslinked polymer unit to belong to a dangling chain. This probability was shown to increase as resol concentration, and then crosslink density, decreased. The empirical Chasset-Thirion equation was used to model the long-time relaxation data for each sample.

Chasset-Thirion parameters were interpreted by Curro and Pincus within a theoretical framework based on the idea that the longest relaxation times are associated with the pendent chains of the network. The relaxation times, obtained from the fitting of experimental relaxation moduli, dramatically increased as the crosslink density decreased. This result corroborates the evolution of φ1 : both tend to demonstrate that in the present compounds, the decrease of crosslink density is accompanied by an increase of the number and length of the dangling chains, leading to increasing relaxation times. The large soluble fraction and long pendent chains of samples showing the lowest crosslink densities were responsible for their poor elastic recovery. The relaxation data were used to model the elastic recovery of the compounds and predict their compression set profiles. Very satisfactory agreement was obtained between experimental data and computations.

Keywords : EPDM networks; Viscoelastic properties; Dangling chains

I. Introduction

Ethylene-propylene-diene (EPDM) terpolymers are elastomeric materials which combine a saturated polymer backbone with residual unsaturations as side groups. As a consequence, they are more resistant to oxygen, ozone, UV and heat than commodity polydiene elastomers. Their resistance to swelling in apolar fluids, such as oil, is however poor. The dienes used in commercial EPDMs are very few : 5-ethylidene-2-norbornene (ENB), dicyclopentadiene and 5-vinylidene-2-norbornene are currently the only ones. Most EPDM applications require its crosslinking. This is achieved by using mainly three types of crosslinking agents : sulfur, peroxides and alkylphenol-formaldehyde resins (resols). Peroxide is gradually gaining importance at the expense of sulfur, essentially because of the high thermal stability of the C-C intermolecular bonds formed in co-agent-assisted peroxide crosslinking of EPDMs. This matches the growing high-temperature demand of end-users. Resols also provide high temperature stability and are employed preferentially in thermoplastic vulcanizates (TPVs), which generally comprise a polypropylene phase which would deteriorate if peroxides were used.

The mechanisms of the different reaction schemes implemented for EPDM crosslinking have been derived from studies either aimed at modeling the rubber crosslinking chemistry by use of low molar weight model olefins, or at direct analysis of the crosslinked material. However, due to the low unsaturation content of EPDM, the use of spectroscopic techniques initially suffered from analytical sensitivity problems. These were overcome with technological evolutions, allowing infrared and solid state NMR spectroscopies to become the main direct analytical techniques for crosslinked elastomers. For instance, infrared spectroscopy was proved to be very valuable in analyzing the mechanism of co-agent-assisted peroxide vulcanization of EPM and EPDM [1-3]. Various examples of ^{13}C solid state NMR-based studies of EPDM networks can also be found in literature, either investigating sulfur [4,5] or peroxide crosslinking [6,7]. As far as resol crosslinking is concerned, few studies have been published, mostly relying on model systems [8]. Practically, resol cure is generally activated in order to achieve sufficiently high cure rates and degrees of crosslinking. This consists in introducing an acid species (e.g. stannous chloride, or an acid released by another chemical) that enhances cure rate via a carbo-cationic mechanism [9].

From an academic point of view, the chemistry of EPDM crosslinking is now understood satisfactorily, and the different mechanisms are summarized in [9]. However, the kinetics of EPDM crosslinking is usually studied with rheometers, and interpretation in terms of standard chemical reaction kinetics is therefore not straightforward. Moreover, the effects of the additives entering EPDM formulations (oil, fillers and other chemicals) on the crosslinking reaction are not yet characterized completely. However, proton NMR T_2 relaxation analysis of sulfur-vulcanized, oil-extended EPDM specimens very interestingly enabled several relationships to be established between sample composition, molecular mobility and the network density [10].

The traditional methods for analyzing rubber networks are equilibrium swelling measurements and viscoelastic or mechanical testing. The analysis of such properties has been practiced for long to demonstrate the existence of different network features and has supported the development of the first theoretical models like the affine [11] or the phantom network models [12]. In the former, the shear modulus is given by :

$$G_e^{\mathrm{affine}} = \nu\, R\, T = \frac{\rho\, R\, T}{\bar{M}_c} \qquad (1)$$

where ν is the density of elastically active chains and $\bar{M}_c$ the average molar weight of these chains. An elastic chain is defined as a chain attached to the network at each of its two ends. For the phantom model, the junctions (crosslinking points) are free to fluctuate and the shear modulus is thus lower than in the case of the affine network :

$$G_e^{\mathrm{phantom}} = (\nu - \mu)\, R\, T \qquad (2)$$

where μ is the density of junctions.

The phenomenological model developed by Langley [13] and Dossin and Graessley [14] involves an additional term accounting for the topological contributions. According to the entanglement interpretation of the topological contributions, a portion of the restrictions on configurational rearrangements of macromolecules become permanently trapped when a network is formed and therefore are able to contribute to the equilibrium elasticity. The modulus can be expressed as :

$$G_e^{\mathrm{Langley-Graessley}} = (\nu - h\,\mu)\, R\, T + G_e^{\max}\, T_e \qquad (3)$$

where h is an empirical parameter between 0 and 1. T_e is the fraction of trapped entanglements in the network, i.e. the proportion of the maximum concentration of topological interactions that contribute to the modulus. $G_e^{\max}$ is the maximum topological contribution. It is expected to be very close to G_N^0, the plateau modulus of the un-crosslinked, high molar weight polymer. More recently, the slip-link model [15,16] refined the modeling of entanglements as slip-links joining polymer chains together and likely to act as additional crosslinks.

Discrepancies between theory and experiment still remain and the role of chain entanglements, network defects such as dangling chains, and network heterogeneities, is certainly a key issue. Ferry [17] suggested that the molecular mechanism responsible for the long time relaxation process is the diffusion of dangling chain ends in the presence of entanglements. The contribution of the latter to the elastic modulus was illustrated for example by Patel et al. [18], by means of mechanical testing and equilibrium swelling measurements. These workers compared "ideal" polydimethylsiloxane networks (formed from pure difunctional PDMS, which yielded perfect networks without pendant chains) with imperfect ones having an equivalent value of ν but containing many pendant chains, created by using monofunctional PDMS mixed with the difunctional species. NMR can also be considered for characterizing the statistical structure of randomly crosslinked materials, as demonstrated for instance by Viallat et al. [19] who investigated the mechanisms of swelling and related changes of chain segment conformation in EVA/EMA gels in presence of increasing concentrations of solvent.

Of course the viscoelastic behavior of vulcanizates has been investigated intensively in relation to their network features. The introduction of polymer dynamics concepts allowed some progress in the molecular theories developed for such vulcanizates. A molecular interpretation of the long-time relaxation of elastomers, based on results by De Gennes [20] for the reptation of a single branched chain with topological constraints, was first given by Curro and Pincus [21]. Their model is based on the retraction of pendent chains in a crosslinked network with topological constraints (entanglements). It predicts that a polymer network containing a random distribution of dangling chain ends leads to a relaxation modulus having a power law dependence on time [21,22], as in the phenomenological Chasset and Thirion equation [23]. Indeed, Chasset and Thirion postulated in the 1960's that an excellent representation of the isothermal relaxation modulus data for many rubbers can be given by :

$$E(t) = E_{\infty}\left[1+\left(\frac{t}{\tau_0}\right)^{-m}\right] \qquad (4)$$

for long times t. E_{∞} is the equilibrium modulus, and m and τ_0 are material parameters. So, Curro and co-workers provided an *a posteriori* theoretical background to this empirical equation and supported the conjecture of Ferry [11] that dangling chain ends lead to extremely long viscoelastic processes. Curro and Pincus theory predicts that the model parameter m is proportional to crosslink density, which was found to be in agreement with some experimental data on natural rubber. However, this point was discussed and criticized by McKenna and Gaylord [24]. In the following decade, end-linked elastomers like polydimethylsiloxanes were preferred for studying the terminal relaxation behavior of networks with dangling chains since, contrary to randomly crosslinked networks, the former allow to decouple the effect of crosslink density from that of the molar weight of pendent chains. This enabled some studies to focus on the dependence of the Chasset-Thirion exponent m with the molar mass and the distribution of molar masses of pendent chains or, for instance, with their number of entanglements [25,26]. Consistent trends were observed in both studies, showing that m is inversely related to the mass average molar mass of the pendent chains (and then, the number of entanglements per dangling chain).

As far as industrial development is concerned, the relaxation mechanisms in the long time limit are of great importance because they define the elastic properties and creep behavior of crosslinked elastomers. Among numerous other experimental procedures, the compression set test is commonly carried out. It reflects the elastic recovery properties of elastomeric materials. However, through a viscoelastic analysis like that of Joubert et al. [27], who followed the molecular approach developed by Curro and coworkers [21,22], the results can be discussed on the basis of molecular mechanisms in the long relaxation times and can therefore be correlated to the structure of the crosslinked network. Indeed, in Joubert's paper, ethylene-vinyl acetate samples crosslinked by two methods could be clearly distinguished from the elastic recovery point of view with respect to their microstructure.

Upon literature overview, it is striking that, in the case of EPDM, viscoelastic analysis is not very developed. Actually, despite its intensive use in industrial applications, EPDM is a complex polymer whose microstructure has often been said to contain "microgels", i.e. microcrystalline regions, which make rheological analysis even more critical. Therefore, the majority of studies devoted to it rely on NMR spectroscopy, as previously mentioned. This technique allows network density analysis in terms of chemical crosslinks as well as temporary and trapped entanglements. It is also possible with the T_2 relaxation method to estimate the amount of highly mobile chains, i.e. extractable material and network defects as dangling chains and chain loops. In the case of plasticized EPDM compounds, increasing oil content causes the decrease of entanglement density [10]. EPDM network density was shown to largely influence the mobility of oil molecules, which is all the more hindered as the network density is higher. These observations emphasize the interest of NMR spectroscopy as a complementary technique to rheology for the investigation of the structural characteristics of rubbery networks such as topology, heterogeneity (molar mass distribution of network chains) and amount of defects, which all could largely influence volume average chain dynamics and macroscopic properties.

Thus, the aims of the present paper are i) to characterize the structure of oil extended EPDM networks by performing classical physico-chemical and viscoelastic measurements in relation with relevant molecular models, in the purpose of ii) analyzing the role of entanglements and dangling chain ends and iii) modeling their long time relaxation behavior to be able iv) to predict compression set data from relaxation data.

II. Experiments

II.1. Materials

Experiments were carried out with EPDM Vistalon 8800 (ExxonMobil Chemical), in which the diene species is ethylidene norbornene (ENB). The following values of molar weight were measured : $\bar{M}_n$=160000 g/mol and $\bar{M}_w$=310000 g/mol. The molar content of each component in the terpolymer was assessed by ^{13}C NMR : 59.5 mol % ethylene, 38.3% propylene and 2.2% ENB. Vistalon 8800 actually comprises neat EPDM with a specific gravity of 0.86 g.cm^{-3}, extended with 13% (w/w) paraffinic oil. This results in a total specific gravity of 0.87 g.cm^{-3} and a Mooney viscosity ML$_{(1+4)}$ of 73 at 125°C. Additional paraffinic oil (Torilis 7200, TotalFinaElf, France) was incorporated to Vistalon 8800 to mimic industrial compositions. The specific gravity of this plasticizer is 0.90 g.cm^{-3} at 20°C. Its proportion in the binary EPDM/plasticizer mixture was set to the industrial standard for most samples, i.e. 60 wt.% or phr (grams per hundred grams of Vistalon 8800). The corresponding volume fraction of plasticizer (initially present + added) is 0.44.

Radical crosslinking of EPDM was carried out by means of an octylphenol-formaldehyde resin (SP1045, Schenectady International, USA) called resol in the following. The reference amount of resol was 4% w/w (or phr) on EPDM basis and 0.6 phr $SnCl_2$ were used for crosslinking catalysis. In order to vary the degree of crosslinking from the standard formulation, the materials were prepared with diverse amounts of curing resin : 1, 1/4, 1/7, 1/10 and 1/30 of the reference quantities of resol, and an uncrosslinked sample was made for comparison (0 phr resol). All samples were prepared with a constant content of 0.6 phr of stannous chloride $SnCl_2$. In the following, materials crosslinked with the regular amount of curing additives will be named "reference" samples (REF), whereas the others will be referred to via the corresponding ratio of crosslinking agent (RES0, RES1/4, RES1/30 ...)

The polymer and chemicals were kindly supplied by Hutchinson (Chalette-sur-Loing, France). They were used as received from the supplier.

II.2. Sample preparation

The blends of the polymer, processing oil and curing system were prepared in an internal batch mixer (Haake Rheomix 600, Thermo Electron), at the temperature of 120°C. The following protocol was adopted : first, the polymer was introduced (at time t=0) into the cavity and sheared by itself for 5 minutes at 120 rpm in order to ensure thermal homogenization. The plasticizer was then poured in and the two components were mixed for the necessary time to reach torque stabilization. Prior to introducing the curing system, the temperature and rotation speed were decreased (80°C and 50 rpm, respectively) and torque stabilization was waited for, again. The curing system (resin+catalyst) was then introduced and mixing was allowed to go on until torque started to increase. The blend was rapidly dumped in order to prevent the crosslinking reaction from occurring inside the mixer.

After dumping, test samples of every composition were compression moulded into 1 mm-thick sheets for 5 minutes at 110°C (no crosslinking occurred during this operation). Some of them were aimed at viscoelastic measurements for monitoring the crosslinking reaction at 200°C, and assessing the reaction time and material thermal stability. Then, the other samples were crosslinked during molding in press at 200°C for different times corresponding to the completion of reaction.

All samples were stored away from light at room temperature.

II.3. Measurements of the polymer soluble fraction

The total soluble weight fraction in the crosslinked samples was extracted with tetrahydrofurane using standard procedure, over 96 hours with several renewals of the solvent. Since this soluble fraction includes all the plasticizer initially present in the sample, the soluble polymer weight fraction w_s could be expressed with respect to the mere sample polymer content, after subtraction of the plasticizer amount.

II.4. Viscoelastic measurements in oscillatory mode

All specimens (un-crosslinked and crosslinked) were tested in the form of 1 mm-thick disks on a Rheometrics RMS800 rheometer under nitrogen atmosphere, using either 13 mm or 25 mm parallel plate geometry (depending on the torque level), in the linear viscoelastic regime. The extent of the linear viscoelastic domain was determined by means of strain sweeps as illustrated in Figure 1.

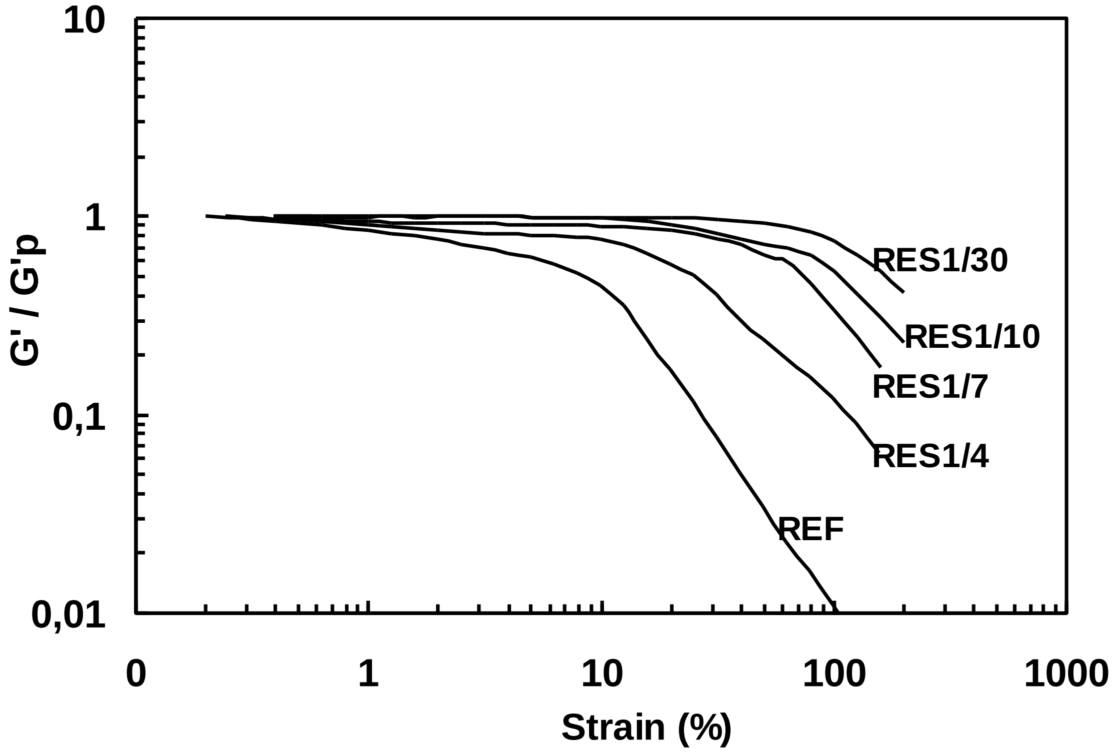

Figure 1 - Evolution of the normalized storage modulus G'/G'$_p$ with shear strain (200°C, 6.28 rad.s^{-1}). G'$_p$ is the low-strain plateau modulus.

It can be noticed that the maximum strain for linear viscoelasticity is at least 20-30% for samples RES1/30, RES1/10 and RES1/7, whereas RES1/4 and REF exhibit non-linear behavior at strains exceeding ca. 10 and 1%, respectively. The evolution of the viscoelastic properties of the un-crosslinked polymer upon addition of plasticizer was examined in a previous paper [28] and is illustrated in Figure 2.

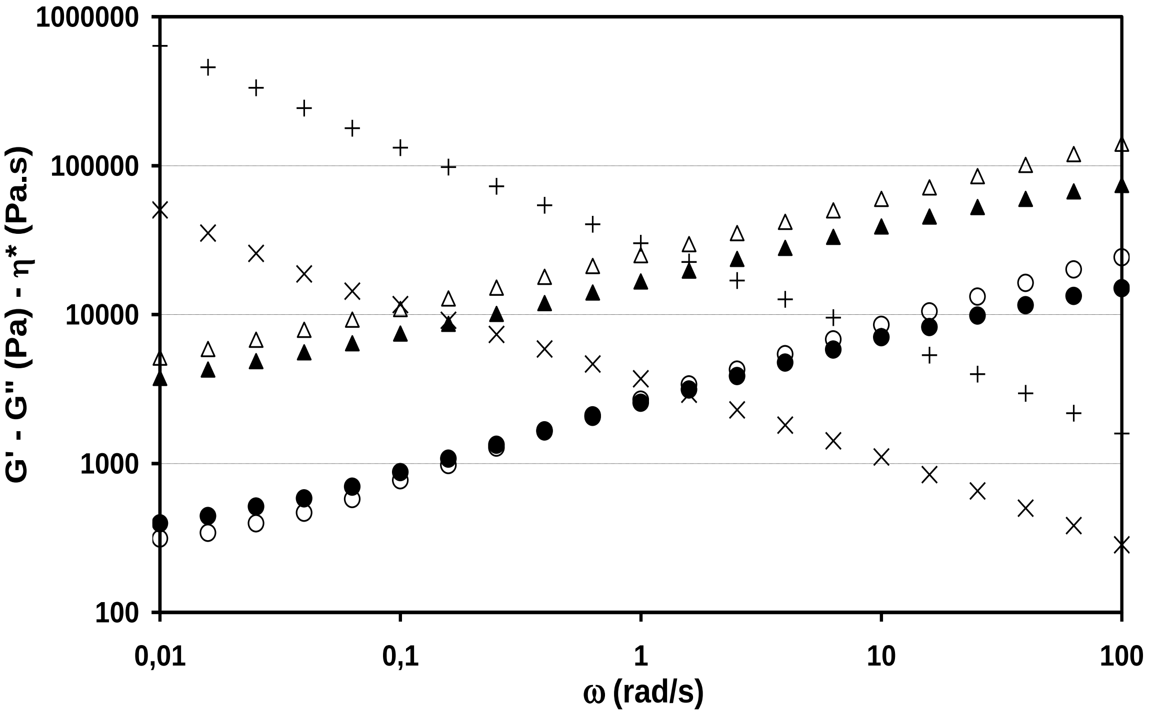

Figure 2 - Viscoelastic behaviour of un-crosslinked EPDM in the linear domain at 200°C : G' (open symbols), G" (closed symbols) and η* (crosses). △, ▲ and + : non-plasticized EPDM Vistalon8800. ○, ● and × : EPDM Vistalon8800 plasticized with 60phr oil (volumic fraction of EPDM : ϕ=0.56).

The evolution of the dynamic moduli G' and G" and of the loss tangent tanδ during crosslinking of the polymer matrix was followed by time sweep oscillatory shear experiments ($\omega = 6.28$ rad.s^{-1}) at 200°C. The time at which no further significant variation of the moduli occurred was considered as the time necessary for the chemical reaction to be completed and therefore determined the duration of the molding operation for the samples to be cured directly after being dumped from the batch mixer. At the end of each of the time sweep experiments, a frequency sweep was performed in order to characterize the network formed. The value of the equilibrium modulus G_e was determined from the low frequency plateau exhibited on G' plots.

II.5. Long time relaxation measurements and compression set tests

Cured samples were submitted to a compression set test, with a dynamic mechanical analyzer (DMA 2980, TA Instruments, USA) allowing relaxation experiments, according to the following protocol. A 4 mm-diameter, 1.3 mm-high cylindrical sample was placed between the plates and submitted to a compression strain of 25% for 10 hours (sample initial height and deformation were controlled very precisely on the apparatus), while recording the stress relaxation. At the end of this time, the stress was instantaneously removed, allowing for strain recovery, which was monitored for another 10 hours. The test temperature was 100°C. It must be reminded that under 25% strain, all the samples except for REF and RES1/4 remained within their linear viscoelastic domain.

III. Modelling of the elastic modulus of the networks

It must be noted that eq.(1) to (3) were developed for "dry" networks and have to be modified for networks which contain a soluble species acting as a diluent. The expression for the modulus of the "dry" network after extraction is similar to the one derived by Flory [11] for a network swollen in a solvent, and can be written :

$$G_e / RT = (\nu - \mu)\,(1 - u_{sol})^{1/3} \qquad (5)$$

for a phantom network. u_{sol} is the volume fraction of the soluble species. As mentioned previously, the characteristics of the networks were derived from the experimental determinations of the equilibrium modulus G_e and the soluble fraction. We consider the phenomenological model developed by Langley, Dossin and Graessley, as presented in eq.(3). Values of ν, μ and T_e can be calculated from the polymer sol fraction w_{sol} as will be explained later. However, our EPDM networks also contain large amount of plasticizer and are thus swollen by this extractable component which acts as a diluent. This is not taken into account unless corrections are introduced for the plasticizer into both contributions to the modulus. Consequently, on the one hand, the network contribution (ν-hμ) RT must be corrected by $\theta^{1/3}$, where θ is the polymer volume fraction of the compound, analogous to (1-u_{sol}) in eq (5). On the other hand, the entanglement contribution is also altered by the presence of oil and in that case the effect is that of a diluent in an entangled, un-crosslinked polymer. This point was addressed in a previous paper [28].The terminal viscoelastic parameters of this EPDM in presence of the same plasticizer were derived from the bulk polymer ones with a correction based on the free volume theory. This correction is of the form $\theta^{2.25}$, as shown with different polymer systems [29,30], in agreement with the founding theoretical work by Daoud et al. [31].

Finally, the shear modulus of the network in presence of a plasticizer can be written :

$$G_e = (\nu - h\,\mu)\,R\,T\,\theta^{\frac{1}{3}} + G_e^{max}\,T_e\,\theta^{2.25} \qquad (6)$$

The parameters ν, μ and T_e can be calculated using the theoretical relations established by Pearson and Graessley [32,33], as described hereafter. In our case, the soluble polymer fraction, w_s, has been measured. From this knowledge, the extent of reaction p (= fraction of crosslinkable moieties effectively involved in crosslinks) can be computed from the following equation :

$$p = b\,(w_s^{\frac{-1}{(b+1)}} - 1)\,/\,(r_n\,\xi) \qquad (7)$$

with $\xi = (1 - w_s)$ and $b = r_n / (r_w - r_n)$, where r_n and r_w are the number average and weight average of crosslinkable reactive sites, respectively.

A randomly chosen un-crosslinked polymer unit is connected to the network in either of the following manners : it can be connected to the gel along only one of the two paths leading away from it (probability ψ_1) or along both paths (probability ψ_2).

The probability ψ_2 can be computed as follows :

$$\psi_2 = 1 - 2\varepsilon + (1 + p r_n \xi / b)^{-b-1} \qquad (8)$$

where $\varepsilon = \left[1 - (1 + p r_n \xi / b)^{-b}\right] / p r_n \xi \qquad (9)$

and then : $\psi_1 = 2\,(1 - \varepsilon - \psi_2) \qquad (10)$

Finally, ν, μ and T_e are available through :

$$\nu = \frac{\rho}{2\,M_0}\,p\left[3\psi_1\psi_2 + 2\psi_2^{\,2}\right] \qquad (11)$$

$$\mu = \frac{\rho}{2\,M_0}\,p\left[2\psi_1\psi_2 + \psi_2^{\,2}\right] \qquad (12)$$

$$T_e = \psi_2^{\,2} \qquad (13)$$

M_0 is the molar weight of the molecular segment between two consecutive reactive sites, i.e. between two ENB moieties. The following value was obtained from the ENB % and from the molar weight of the terpolymer : M_0 = 1520 g/mol.

r_n and r_w could then be derived : $r_n = \frac{\bar{M}_n}{M_0}$ and $r_w = \frac{\bar{M}_w}{M_0}$.

IV. Modelling of the viscoelastic properties in the long-tim range : relaxation and strain recovery

Although of real interest from an industrial point of view, the compression set property is scarcely addressed on real systems from a computational point of view. However, it can be treated in a viscoelastic framework as demonstrated by Joubert et al. [27]. Here, we performed similar calculations based on the relaxation data. It must be noted that the development of a constitutive model is beyond the scope of the present paper, therefore the equations implemented for modeling the stress and strain response of our materials were taken from linear viscoelastic theory. It is clear that, as mentioned in section 2.5, this is only an approximation for samples RES1/4 and REF. This will be considered in the discussion of the results (see section 5.4). The computational method is described below.

As mentioned in the introduction, the Chasset-Thirion equation (eq. 4) can be used quite satisfactorily to model the relaxation modulus of rubbers in the long-time range. So, we determined for each sample the values of the three Chasset-Thirion parameters (E_∞, τ_0 and m) by fitting the experimental data from the relaxation stage of the compression set test. The time range over which the fit was performed was taken between 10 minutes (Chasset-Thirion model is *a priori* not well suited for short times) and 600 minutes (beginning of the strain recovery stage). However, it was noticed that, in most cases, the fit remained very satisfactory below 10 minutes.

Fitting this data by a mathematical equation enabled us to extrapolate the modulus evolution to times longer than 600 minutes, which was made necessary for the strain recovery modeling. Indeed, the calculation of the evolution of the residual strain during the 10 hours following the suppression of the stress required to calculate the creep compliance. The latter was derived from the relaxation modulus by solving the integral convolution equation relating the relaxation modulus E(t) and the creep compliance J(t) in linear viscoelasticity :

$$t = \int_0^t E(u).J(t-u)du \qquad (14)$$

following the stepwise numerical method based on trapezoid approximation described in [34]. Then, once E(t) and J(t) were determined over the whole time domain (0-1200 minutes), the Boltzmann superposition principle was used to derive the evolution of strain as follows :

$$\varepsilon(t) = \int_{-\infty}^{t} \frac{d\sigma(u)}{du}.J(t-u)du \qquad (15)$$

where σ is the stress. $\sigma(t)=\varepsilon_0.E(t)$ for t<t' (t'=600 min) and $\sigma(t)=0$ for t<t'.

So,

$$\underset{t>t'}{\varepsilon}(t) = J(t).\sigma(0) + \int_{0}^{t'} \frac{d\sigma(u)}{du}.J(t-u)du + \int_{t'}^{t} \frac{d\sigma(u)}{du}.J(t-u)du \qquad (16)$$

which yields, after integration by parts and rearrangement :

$$\frac{\varepsilon(t)_{t>t'}}{\varepsilon_0} = J(t).E(0) + \int_{0}^{t'} \frac{dE(u)}{du}.J(t-u)du - E(t').J(t-t') \qquad (17)$$

The evolution of the residual strain, and thus of the compression set, can then be calculated over the whole recovery stage of the compression set experiment, i.e. from time t'=600 minutes to 1200 minutes. From a practical point of view, the calculations were performed with the Mathcad7® software (Mathsoft Inc./Parametric Technology Corp., USA).

V. Results & Discussion

V.1. Viscoelastic properties of the crosslinked samples at 200°C

The temperature chosen for crosslinking was 200°C and only the influence of resol amount on viscoelastic properties was studied in the parallel plate rheometer. Figure 3 exhibits the evolution of the storage modulus G' with time for all samples containing the crosslinking agent.

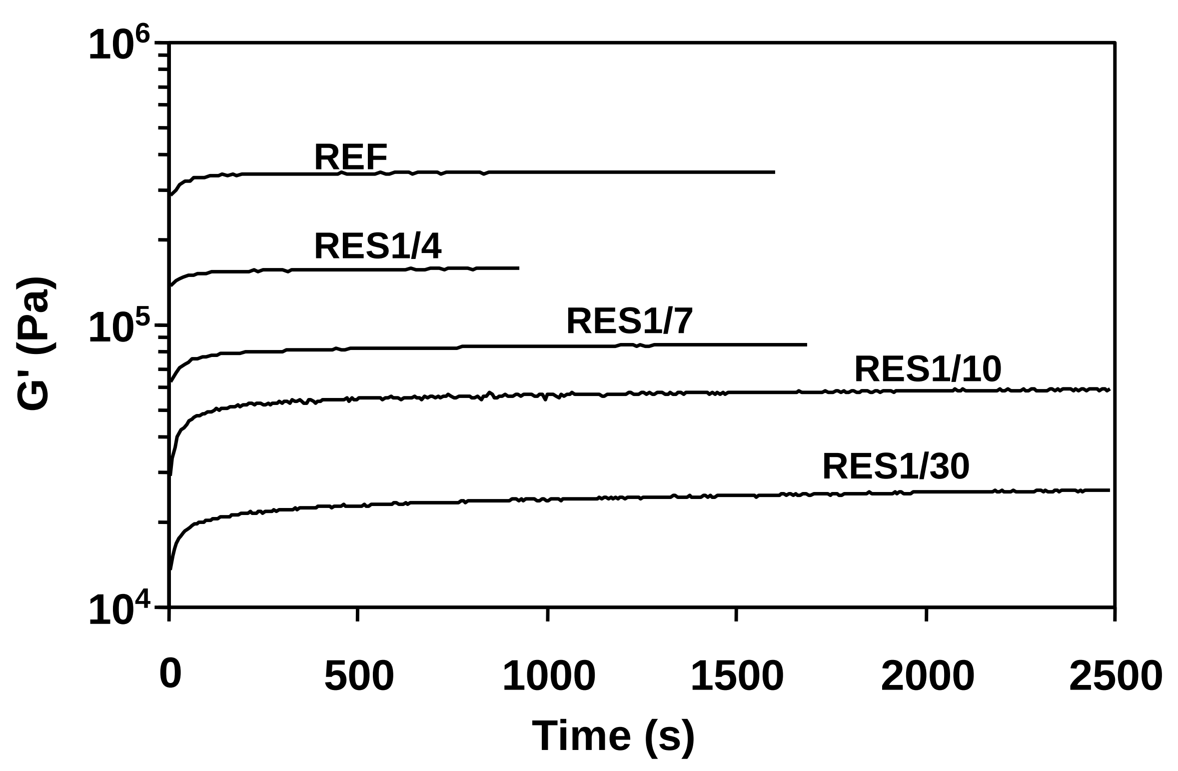

Figure 3 - Evolution of G' with time for the samples during crosslinking (200°C, 6.28 rad.s^{-1}, linear viscoelastic domain).

All recordings exhibit a plateau at long times which expresses the complete reaction and thermal stability. The very beginning of the crosslinking reaction is difficult to capture because it starts as soon as the specimen is placed between the rheometer plates until it reaches the set temperature. Nevertheless, it is clear that the time needed by the modulus to reach a plateau is all the longer as resol concentration is low. It can be seen that the modulus regularly increases as resol input is increased. The frequency sweeps performed after reaction completion yielded the low frequency G' (and so G_e) and tanδ values reported in Table 1.

Resol proportions (with respect to reference)	tanδ	G_e (Pa)
1	0.01	$3.3\ 10^5$
1/4	0.07	$9.8\ 10^4$
1/7	0.12	$5.8\ 10^4$
1/10	0.18	$3.4\ 10^4$
1/30	0.40	$2.0\ 10^3$

Table 1 - Linear viscoelastic parameters of EPDM networks crosslinked at 200°C with different proportions of resol. Oscillatory measurements were carried out at 200°C.

Improvement of the "perfect" nature of the network can be inferred from the decreasing tendency of tanδ when the amount of curing system increases, as a consequence of the enhancement of the degree of crosslinking (shortening of the elastic chains between crosslinks). A quasi-linear relationship can be noticed between G_e and resol concentration, which supports the conclusion that the crosslinking agent efficiency does not depend upon its concentration.

V.2. Determination of the network characteristics according to Pearson and Graessley's approach

As explained in Section 3, the known density of crosslinkable sites on the polymer backbone (yielding r_n and r_w) and the measured soluble polymer fraction in the formed network (oil subtracted) w_s, enabled us to derive all the structural parameters which, within the framework of Pearson and Graessley's theoretical approach of randomly crosslinked tetrafunctional networks, reflect the evolution of the structure when increasing the concentration of the curing agent. Table 2 presents the values of w_s, from which p, ψ_1 and ψ_2 are computed. The network characteristics ν, T_e, ν/μ and the empirical parameter h from Langley and Graessley's model are then derived.

Specimen	w_s (*)	p	ψ_1	ψ_2	ν $^{(*)}$ $mol.m^{-3}$	T_e	$\frac{\nu}{\mu}$	$p' = \frac{\text{nb of crosslinks}}{\text{nb of diene moieties}}$	h
REF	0.002	0.229	0.08	0.92	124	0.85	1.93	0.122	0.62
RES1/4	0.011	0.080	0.20	0.79	39	0.63	1.84	0.040	0.59
RES1/7	0.038	0.041	0.32	0.65	17	0.42	1.75	0.018	0.56
RES1/10	0.104	0.023	0.44	0.46	6.5	0.21	1.67	0.007	0.53
RES1/30	0.300	0.012	0.50	0.20	1.25	0.04	1.58	0.002	0.51

(*) expressed with respect to volume of polymer without taking plasticizer into account

Table 2 - Structural parameters for the different specimen, as computed from the theoretical relations derived by Pearson and Graessley [33].

The value of the ratio between the number of chemical crosslinks, and the number of diene moieties (i.e. of reactive sites) available in the volume considered, called p', is also given for comparison purposes with p. Determining p' required to calculate the concentration of crosslinkable sites (i.e. ENB moieties), which could be derived from the knowledge of the

ENB content of the terpolymer. This also allowed to calculate the average molar weight of the chain segments between two consecutive reactive sites, M_0, involved in eq.(12). So, on the one hand, p is obtained from a theoretical background relying only on the knowledge of the soluble polymer fraction. On the other hand, p' is derived from the whole computation originating from p and therefore allows a cross-checking of the results concerning the chemical network.

Figure 4 displays the evolutions of the major structural parameters, namely ν, T_e, ψ_1 and ψ_2, with the increasing concentration of resol used (expressed in phr).

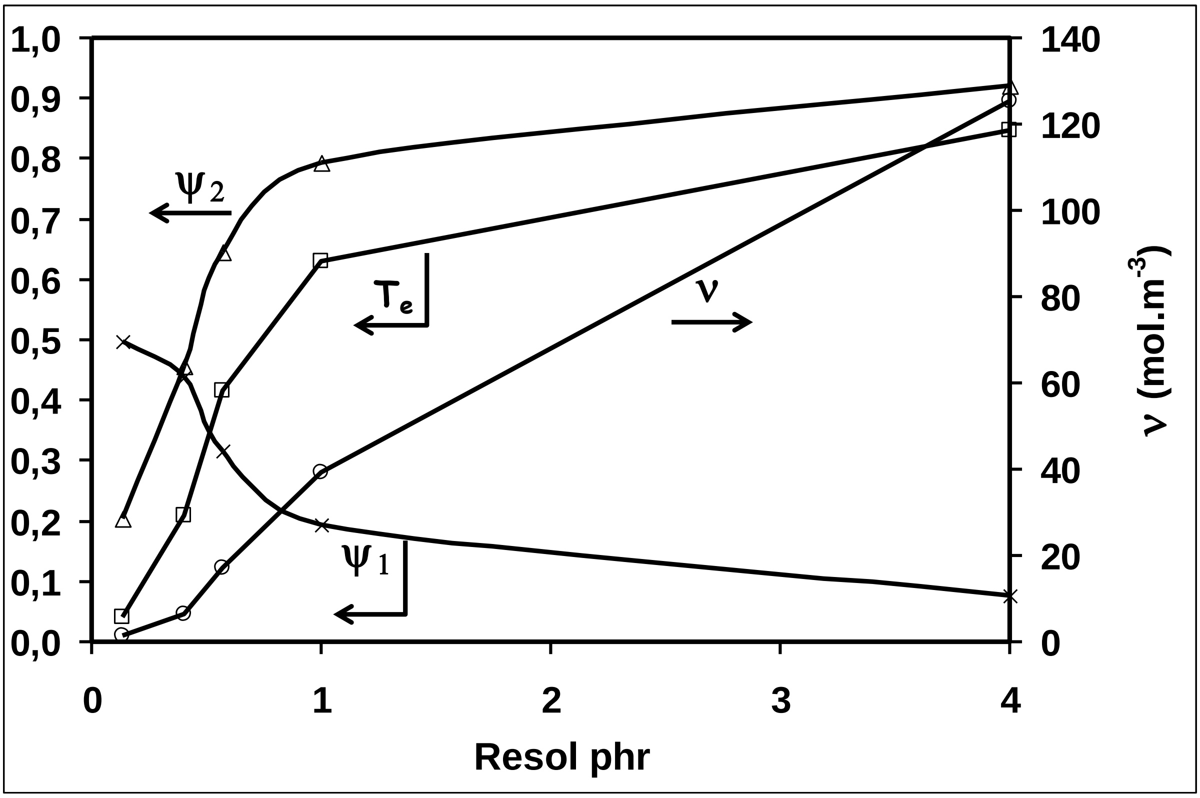

Figure 4 - Evolution of the network structural features with the proportion of crosslinking agent. The computed parameters are ν (o) and T_e (□) from Langley and Greassley model (eq. 3), derived from ψ_1 (x) and ψ_2 (Δ), as introduced by Pearson and Graessley (eq. 8 to 13).

Logically, the crosslink density ν and the proportion of trapped entanglements T_e, which is linked to the probability ψ_2, increase with the resol fraction. Simultaneously, the probability of forming dangling chains decreases. However, whereas ν follows an almost linear evolution with the crosslinking agent fraction, T_e exhibits a dramatic increase with resol phr while it remains lower than about 1/5th of the reference concentration, and much slower afterwards. This was expectable, considering that from a certain network density, the long range chain mobility is highly hindered (60% of trapped entanglements) and then the possibility for a chain to "escape" from getting crosslinked to others largely decreases.

Table 2 shows that the μ/ν ratio increases with increasing the curing agent concentration and tends towards 2, which is the theoretical value for tetrafunctional network. This is an indication of the network evolving towards a more and more "perfect" structure when increasing crosslink density and concomitantly decreasing dangling chain occurrence (ψ_1). This evolution towards a tetrafunctional network containing supposedly less defects is supported by the comparison of p' and p : indeed, it can be seen that the ratio p'/p gets all the nearer to 0.5 as resol phr increase. For an ideal tetrafunctional network, p' should be strictly equal to p/2, since one chemical crosslink involves two norbornene moieties. Here, the matching of p' with p/2 improves for samples closer to reference.

The last column of table 2 presents the values of the empirical parameter h, whose determination was carried out as follows. Considering eq.(6), it can be seen that plotting the values of G_e/T_e vs. $\frac{\nu RT}{T_e}$ should yield a straight line whose slope and intercept are $\left(1-\frac{h\,\mu}{\nu}\right).\theta^{1/3}$ and $G_N^0\,.\,\theta^{2.25}$ respectively. Actually, we performed a linear regression over the values, after discarding those for sample RES1/30 which were out of range, and obtained a slope of 0.56 (correlation coefficient R^2=0.94). This enabled us to compute h for each sample (from experimental G_e). It can be noticed that h increases with resol fraction. As mentioned by Pearson and Graessley, h is difficult to establish theoretically, but it should be near 1 for highly entangled networks. So our results are consistent with this statement, and show, as could be expected, that the higher the crosslinking density, the higher the entanglement density, due particularly to entanglement trapping.

At the same time as the slope, the intercept was calculated, yielding a numerical value of G_N^0 for the non-plasticized polymer, which could not be measured from rheological tests on un-crosslinked materials. Here, $G_N^0 = 2.1\times10^5$ Pa, and $G_N^0\,.\,\theta^{2.25} = 5.7\times10^4$ Pa, which would represent the plateau modulus of the plasticized material. Considering the shapes of the plots in figure 1, these values are quite realistic, but it must be noted that for such a platicized polymer, if a plateau existed, it would probably occur at very high frequencies.

Now, the whole set of Langley and Graessley's model parameters were available for recalculation of the equilibrium modulus, $G_{e\ calc}$ according to eq.(6). The correlation of G_e and $G_{e\ calc}$ is reported in figure 5.

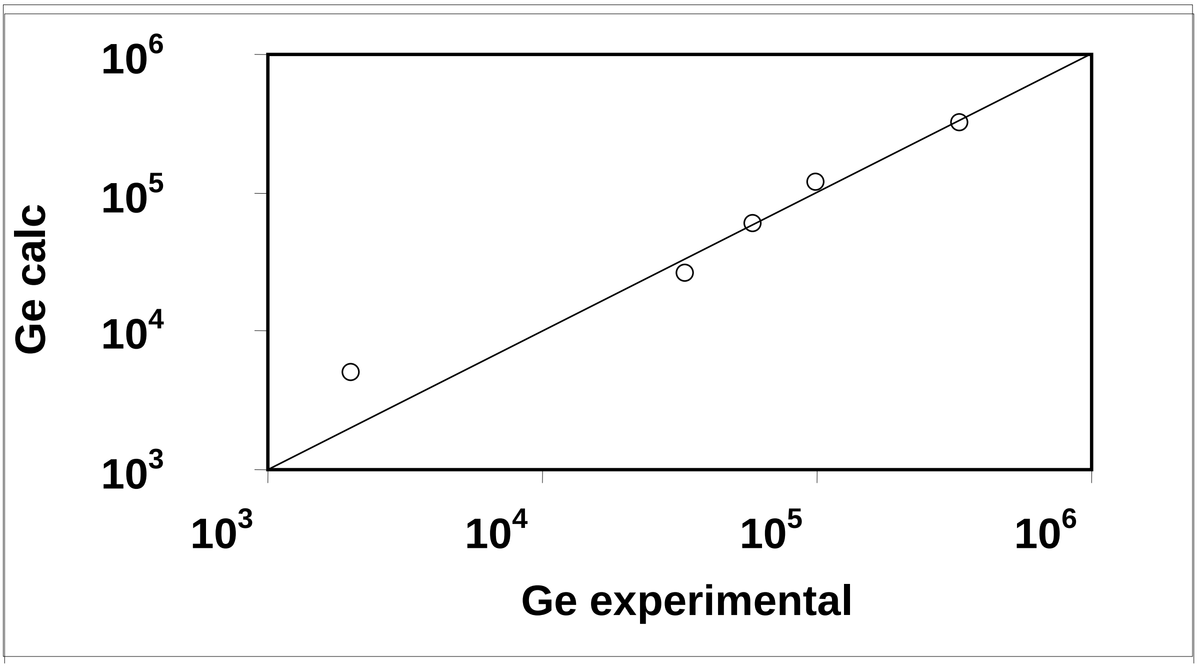

Figure 5 - Comparison of computed shear equilibrium modulus (eq. 6) and experimental data at 200°C.

Very satisfactory agreement can be observed (slope of the regression is 0.97 and R^2=0.99), which validates our approach that relies on a rubber network theory expressing the topological contributions from the permanently entangled chains, and also refers to another theoretical background based on the free volume concept to account for the diluting effect of the plasticizer. However, it must be noted that the effect of the concentration of the latter is not addressed in the present work, although it is likely to be of great influence towards the crosslinking kinetics, due to the modified polymer chain mobility, and so presumably towards network structure.

V.3. Long-time relaxation behavior at 100°C

As mentioned in section 1, network defects have long been shown to mainly affect the long-time behavior of rubber vulcanizates. In evaluating our samples for elastic recovery after prolonged strain at hot temperature (100°C), the compression stage of the test was analyzed from the viscoelastic point of view, since it corresponds to conditions of relaxation under constant strain over 10 hours.

The recordings of the modulus of the different samples are plotted in figure 6.

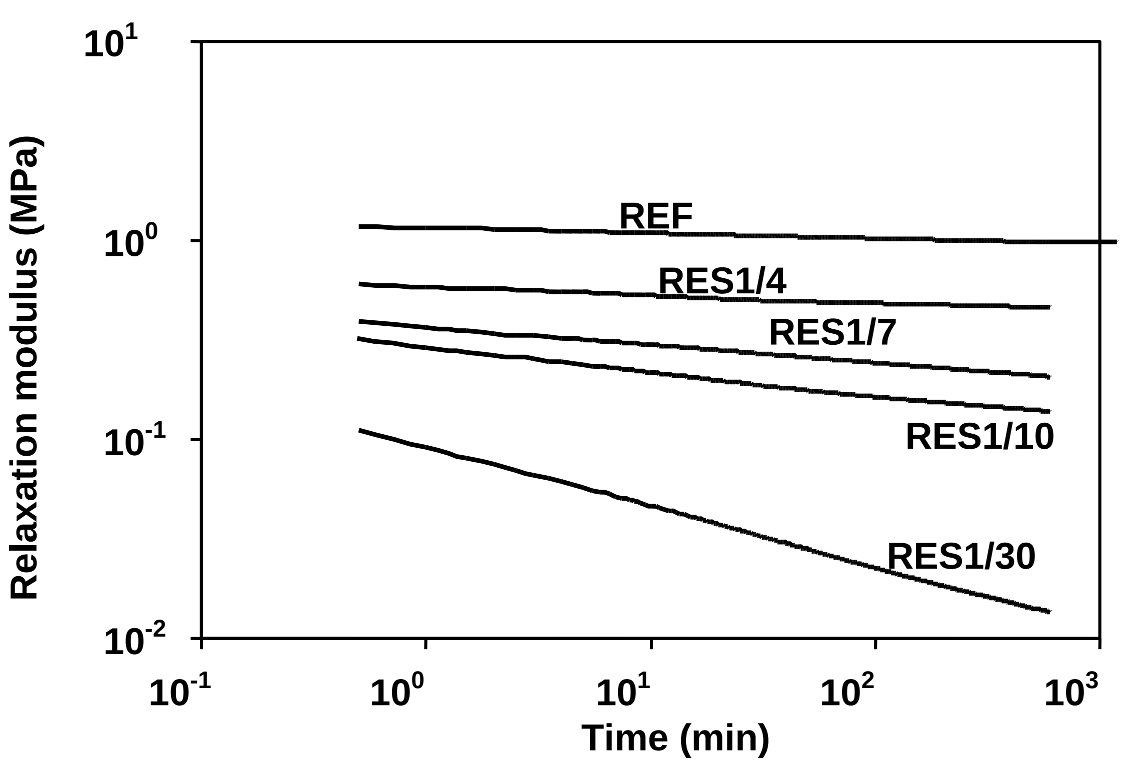

Figure 6 - Evolution of the relaxation modulus measured over 10 hours at 100°C, under 0.25 compressive strain.

It is apparent that these relaxation curves are not positioned in the same manner as those for G_e with respect to resol concentration. Whereas G_e was evolving quasi-linearly with the latter, the relaxation plots of the least crosslinked materials (RES1/30, RES1/10, RES1/7) are quite close to one another and exhibit a different pattern from those of samples RES1/4 and REF. For quantitative comparison purposes, the data was fitted with Chasset and Thirion equation, so that E_∞, τ_0 and m were determined for each specimen. These values are reported in Table 3.

Specimen	E_∞ (Pa)	τ_0 (min)	m
REF	$6.3\ 10^5$	0.09	0.067
RES1/4	$2.6\ 10^5$	13	0.070
RES1/7	$1.2\ 10^5$	104	0.170
RES1/10	$7.0\ 10^4$	512	0.184
RES1/30	$4.0\ 10^3$	8000	0.348

Table 3 - Fitted parameters of Chasset-Thirion equation for the shear stress relaxation of plasticized EPDM networks (strain = - 0.25).

Interestingly, the orders of magnitude of E_∞ and τ_0 follow a significant evolution and exhibit some similarities which support the preceding remarks concerning two "groups" of materials. Some gap is observed between the equilibrium relaxation moduli of samples REF and RES1/4 on the one hand, and those of the 3 remaining samples on the other hand. This has of course to be related with the presence of un-crosslinked chains (cf. w_s) and with increasing amount of dangling chains (cf. ψ_1) for the 3 latter. Although it is all the slower as the dangling end is longer, the relaxation is possible and the modulus keeps on decreasing consequently towards very low values of E_∞. The higher crosslink density and trapping factor of REF and RES1/4 are responsible for moduli which remain over 2.10^5 Pa, i.e. much higher than the level of the estimated plateau modulus of the un-crosslinked plasticized polymer.

The characteristic relaxation times τ_0 are worth paying some attention to, although their magnitude cannot be compared with published data for similar systems. Only their evolution between the different samples can be commented. Again, this evolution is very consistent with the supposed role of the dangling chains. The extreme values of τ_0 are about five decades apart. As shown in the works by Curro and Pincus, which refer to natural rubber with zero soluble fraction, the relaxation of a dangling chain (i.e. a chain linked to the network by only one of its extremities) is assimilated to the reptation of star-like molecules, whose relaxation times evolve exponentially with their molar mass. So, from a qualitative point of view, our results demonstrate that for imperfect networks such as our low crosslinked samples, the long time relaxation mechanisms are largely emphasized, supposedly due to the presence of long dangling chain ends.

The exponents m from Chasset Thirion equation cannot be compared to published data neither, and the analysis of the crosslink dependence of m can not be carried out with the Curro and Pincus approach. Indeed, the decrease of m when resol quantity is increased, which is observed in the present study, is opposite to the proportional relation derived by these authors in their theory. The major reason for this discrepancy is certainly that our networks, which contain both plasticizer and soluble polymer fractions, do not fit into the assumptions of the Curro and Pincus theory.

V.4. Compression set at 100°C

The relaxation experiments described above were followed by a 10 hour recovery stage, during which the evolution of strain was continuously recorded. The experimental data, expressed in terms of compression set (i.e. % of residual strain) and residual strain, are reported in figure 7 and in table 4 for the different materials.

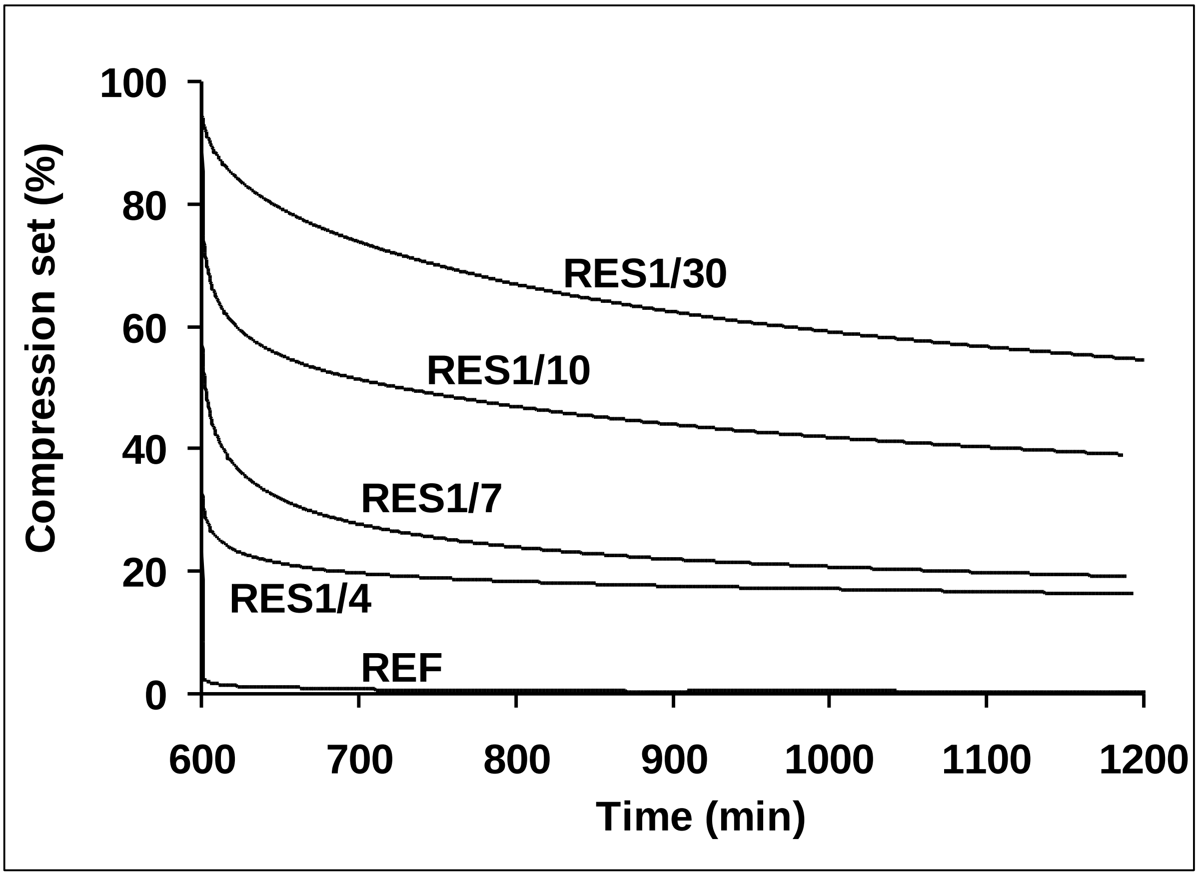

Figure 7 - Evolution of the compression set (i.e. $\frac{\text{residual strain}}{\text{initial strain}}$%) during strain recovery monitored at 100°C, over 10 hours after release of the compressive stress at t=600 min.

Specimen	Experimental Compression set (%)	 Strain (-)	Modelled Strain (-)
REF	0.4	0.001	0.002
RES1/4	16.3	0.041	0.040
RES1/7	19.2	0.048	0.058
RES1/10	39.1	0.097	0.098
RES1/30	54.6	0.137	0.140

Table 4 - Compression set and residual strain after 10 hour compression at constant strain (-0.25), followed by 10 hour recovery, at 100°C.

It is shown that only the reference material has an almost 0% residual strain after 10 hours of recovery. All other materials are still evolving after 10 hours, and no stable state is reached. Obviously, compression set is all the smaller as the crosslinked network is denser and contains fewer defects. Consequently, the results concerning samples RES1/10 and RES1/30 consist in compression sets of around 40% and over, which correspond to total residual strains above 10%. The bad performance of these materials is certainly to be linked to uncrosslinked chains and to network defects such as long dangling chains, which do not contribute to the permanent network and are able to relax during the compression stage, then providing no elastic contribution during the recovery stage.

The results of the compression set modeling are illustrated in figure 8 through the evolution of residual strain in time.

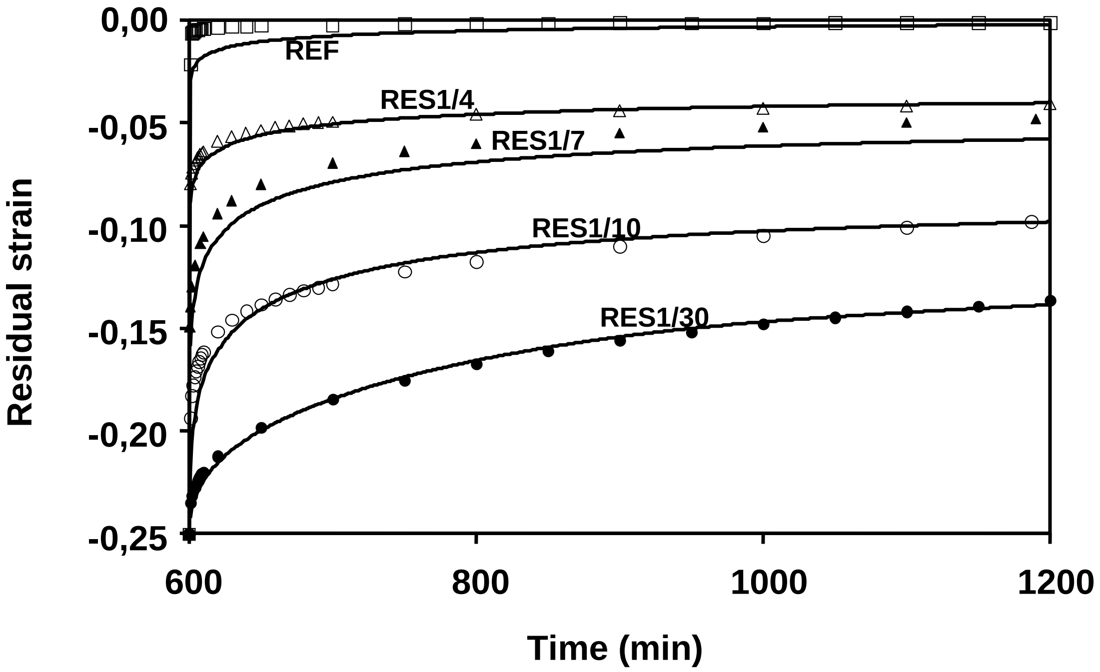

Figure 8 - Comparison between residual strain computed from eq. 17 and measured data during recovery at 100°C. Symbols : experimental ; solid lines : model.

It is clear that the model is able to capture the general trends of the materials recovery behavior. Slight discrepancies are observed, which certainly originate from different factors depending on the specimen, although of course the principle itself of the computation contains several approximations and sources of error which can affect all samples : the fitting of the experimental data of modulus and extrapolation, the trapezoid approximation in the creep compliance calculation, the numerical resolution of the integral term in eq (17), etc.

More specific points can be discussed. As far as the reference sample is concerned, the nominal strain applied (-0.25) was mentioned to be out of the linear viscoelasticity range, which is most likely to explain the underprediction of the model. However, even for those samples which remained in their linear domain, the model underpredicts the strain at the beginning of the recovery process. In this case, the reason is more likely to be the lack of accuracy on the modulus values at the very first instants of relaxation. Indeed, during the relaxation test, firstly the strain could obviously not be applied strictly instantaneously, and secondly, the data acquisition started after some delay. The consequence is that the value of the initial modulus, E(t=0) had to be somewhat extrapolated. Computations for the first instants of recovery have been observed to be sensitive to experimental error on E(t=0). On the other hand, some extrapolation was also necessary at long times, from 600 to 1200 minutes, for recovery modeling purposes. This extrapolation was provided by fitting the data with the Chasset-Thirion model which obviously can induce some inaccuracy and affect the quality of the results in the long time range. This is probably what can be noticed on the plot corresponding to the RES1/7 sample.

Nevertheless, it can be concluded that the compression set test can be predicted from the mere knowledge of the material relaxation behavior. The agreement with experimental data is satisfactory. These results are quite original in the field of industrial compounds such as, among others, plasticized EPDM networks.

VI. Conclusions

Plasticized EPDM compounds were crosslinked by means of octylphenol-formaldehyde resin (resol) whose concentration was adjusted by a factor up to 1/30 in order to induce large variations of the crosslink density. A significant increase of the soluble polymer weight fraction was observed along with the decrease of the crosslink density. Viscoelastic measurements in oscillatory mode were carried out in order to determine the equilibrium modulus G_e and to support a characterization of the network features based upon the phenomenological model of Langley and Graessley whose parameters are ν, the concentration of active chains, μ, the concentration of junctions and T_e, the fraction of entanglements trapped when the network was formed. The knowledge of the polymer molecular characteristics and the soluble fraction in the different samples allowed the determination of the extent of reaction and of the probabilities for an uncrosslinked polymer unit to be linked to the network by only one or by two paths. The former case corresponded to pendent chains. Then, ν, μ and T_e could be calculated. This provided a complete characterization of the networks, showing that the lower the crosslinking agent concentration, the higher the trapping factor, the more numerous and the longer the pendent chains. Such chains have long been known to be responsible for long time relaxation mechanisms in elastomeric networks, according to considerations based on the reptation theory. Therefore, relaxation experiments were performed over long times, followed by elastic recovery monitoring. By fitting the relaxation data with the Chasset - Thirion equation, its parameters could be computed, especially τ_0, the characteristic time for the longest relaxation mechanisms. A dramatic increase was observed in τ_0 as the resol concentration decreased. This is another evidence of the presence of long dangling chains, which lead to very poor recovery properties of samples having low crosslink densities.

With these results, the aims of the present study were reached insofar as, from common physico-chemical and viscoelastic characterizations, several network parameters were quantified, and the role of entanglements and dangling chains could be proved through some features of the viscoelastic response of these networks. In addition, predictions of the compression set data were made possible by using the Chasset-Thirion equation to model and extrapolate the relaxation data in time. A very satisfactory agreement could be achieved between calculations and experiments. The method adopted here is somewhat original since it provides some theoretical background to the interpretation and prediction of an engineering property.

Acknowledgement

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Chapitre IV

Co-continuous Morphology and Stress Relaxation Behaviour of Unfilled and Silica Filled PP/EPDM Blends

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Chapitre IV – Co-continuous morphology and stress relaxation behaviour of unfilled and silica filled PP/EPDM blends

Abstract

These researches aimed at bringing significant and useful information regarding the morphologies and relaxation behaviour of PP / EPDM blends as detailed morphological studies of such uncrosslinked blends are still lacking in the literature. This work allowed a fruitful study of the correlation between their morphology and final mechanical properties, especially concerning their relaxation behaviour. In particular, among all the expected morphologies, the co-continuity is virtually undescribed in the literature whereas it is surely one of the most interesting one regarding the confinement effect of two continuous phases having such a low interfacial tension. The experimental conditions leading to such an atypical morphology have been thoroughly described, and its final properties have shown amazing results especially regarding the relaxation and strain recovery behaviours encountered during compression set experiments. As a matter of fact, these experiments highlighted interesting industrial properties related to such a particular morphology : uncrosslinked co-continuous blends reveal a final strain recovery of nearly 40% after a 25% strain applied for 10 hours at 100°C which could be discussed on the basis of several physical and rheological considerations. Additionally, the study of the stabilisation of such a morphology has also brought interesting results. Finally, we have also studied the influence of hydrophilic and hydrophobic silica nanoparticles on such a specific morphology and its correlated compression set properties.

Keywords : PP/EPDM blends, morphology, relaxation, silica nanoparticles

I. Introduction

The study of one of the most currently used elastomer / thermoplastic blends on the market, the ethylene-propylene-diene (EPDM) / polypropylene (PP) blend, is a subject of great importance having many relevant consequences on the process of industrial thermoplastic vulcanisates (TPVs)[1]. As a matter of fact, the blending of PP with yet uncrosslinked EPDM has an undisputable impact on the forthcoming and yet not well understood dynamic crosslinking, and the elaboration of such a complex material also involves several mechanisms like the oil diffusion [2, 3], phase inversion[4], phase compatibilisation[5], cristallisation[6], morphology stabilisation[7] as well as processing[8-10] and rheological[11-15] considerations related to this reactive melt blending[16-19] as all these aspects highly matter on the final blend properties[20].

As a matter of fact, in the case of such polymer blends, there is a direct correlation between the final morphology and the mechanical properties of the material[21]. The initial morphology of such a blend, prior to the crosslinking step, also has a drastic impact on the final TPV morphology as it is set to endure the forthcoming modifications induced by the crosslinking, which leads to a drastic increase of the viscosity of the elastomeric phase and thus to some severe structural and morphological modifications. This provokes relevant consequences on the final mechanical properties especially in the case of such immiscible polymers showing a very weak interfacial adhesion. It is therefore very important, from a industrial as well as from an academic point of view, to challenge all possible morphologies in order to optimise its potential properties. Furthermore, a better understanding of the initial morphology is a real issue towards the final properties of those widely used thermoplastic vulcanisates and is necessary in order to optimise the combination of their elasticity and excellent processability.

Concretely, detailed morphological and mechanical studies of uncrosslinked PP / EPDM blends, especially in presence of silica nanoparticles, are still lacking in the literature. This paper thus aims at adding up relevant information on such uncrosslinked polymer blend relaxation behaviour which can show particularly interesting profiles during compression set experiments.

Hence, one of the challenges in understanding exhaustively the correlation between the morphology and the final mechanical properties is, obviously, to characterize exhaustively all possible morphologies, especially the most interesting one property-wise : the co-continuity.

As a matter of fact, only a few studies have been carried out on this matter, and many researches are still ongoing on an international level, raising an increasing interest world-wide. For instance, Bhadane et al.[22, 23] conducted very interesting studies on the co-continuity stabilization and phase separation of a two immiscible polymer blend. They also identified and characterized elastomeric network structures within dynamically crosslinked thermoplastic / elastomer blends. Sarazin et al.[24] brought new results on the stabilization of co-continuous morphologies with mixing time wheareas Mekhilef et al.[25] described the phase inversion and the boundaries of co-continuous morphology domains on a theoretical as well as on an experimental point of view. Omonov et al.[26, 27] clearly summed up and generalised the detection and characterisation of the co-continuous domains[26] as well as the stability[27] of two immiscible polymer blends, and Willemse et al.[28] and Li et al.[29] studied the aspects related to the interfacial tensions on the morphology and its stabilization for several polymer blends. Additionally, on a more rheological point of view, Carrot et al.[30, 31] carried out fruitful researches on the gel and co-continuity detections, and Veenstra et al.[32] described the co-continuity of co-polymer / thermoplastic blends. Thus, over the last few years, many scientists have brought up relevant information and raised complex questions around the co-continuous morphology of such thermoplastic / elastomer blends which, in the end, have hardly been studied although this kind of blend actually allows a deep understanding of the correlation between atypical morphologies and their surprising related mechanical properties[33, 34].

Furthermore, despite all these researches, the relaxation behaviour and the strain recovery of such blends have virtually been unstudied. In addition, the incorporation of silica nanoparticles has also led to interesting conclusions as its incorporation within such thermoplastic / elastomer blends has shown a drastic impact on the morphology and final properties[35-39]. However, once again, very few studies of the relaxation behaviour of such nanoparticle-filled blends have been reported in the literature, and this paper therefore tends to address some information on that matter.

Hence, we will first focus on describing and explaining the main morphologies of such blends, and will aim at closely examining the atypical co-continuous morphology and its behaviour during compression set experiments. The stabilization of this co-continuity and the progressive demixion of both phases are, most importantly, one of the key results later presented in this paper. Finally, it also seemed interesting and innovative to estimate the impact of the incorporation of hydrophilic and hydrophobic silica nanoparticles on the co-continuous morphology and its compression set profiles.

II. Exprimental Part

II.1. Materials

Isotactic PP (PPH 3060) was supplied by Total Petrochemicals, showing a melt flow index MFI = 12g / 10min. Its molecular weights are $\overline{M_n}$ = 67,300 g.mol^{-1} and $\overline{M_w}$ = 273,000 g.mol^{-1}. Experiments were carried out with Vistalon 8800 (ExxonMobil Chemical), a material that comprises 53.5 %w/w of ethylene and 10 %w/w of EPDM. The following values of molecular weights were measured : $\bar{M}_n$=160,000 g.mol^{-1} and $\bar{M}_w$=310,000 g.mol^{-1}. This terpolymer, having a specific gravity of 0.86 g/cm^{-3}, is originally oil-extended with 13%wt. of paraffinic oil, which yields a total specific gravity of 0.87 g.cm^{-3} and a Mooney viscosity $ML_{(1+4)}$ of 73 at 125°C. Additional paraffinic oil (Torilis 7200, TotalFinaElf) was incorporated to the Vistalon 8800 to mimic industrial compositions. The specific gravity of this oil is 0.90 g.cm^{-3} at 20°C. Its proportion in the PP/EPDM/plasticizer blend was set to 60 phr (grams per hundred grams of rubber) for all blends. The corresponding volume fraction of oil (initially present plus added to the formulation) is 0.445 with respect to the elastomeric phase.

Two types of nanosilicas (SiO_2) were used. A hydrophilic pyrogenic silica, Aerosil A200, with a specific surface area of 200 m^2/g and a hydrophobic nanosilica, Aerosil® R805, having a specific surface area of 150 m^2/g and treated with trimethoxyoctylsilane. The two types of silica are aggregates of primary spherical particles having an average diameter of 12 nm. Both of them were kindly supplied by Degussa Corp.

II.2. Compounding procedure

The blends made of polymers, processing oil and, eventually, of silica nanoparticles, were prepared in an internal batch mixer (Haake Rheomix R600 of 50 cm^3), at a temperature of 200°C. No compatibiliser has been used in order to avoid any interaction between the two immiscible phases. The following protocol was thus adopted : first, the EPDM was introduced into the batch blender and sheared for 2 minutes at 120 rpm in order to ensure the fragmentation and thermal homogenization of the thermoplastic elastomer. The oil was then poured in at 5 rpm in order to avoid any drawbacks of oil and to allow a proper oil diffusion

within the elastomer. After torque stabilization, the PP, and eventually the silica, was poured in and the components were mixed at 50 rpm until torque stabilization. The blends were rapidly dumped in order to prevent the crosslinking reaction from occurring inside the mixer. Over such a short period of time we have proven that the EPDM does not self crosslink by thermal degradation. The samples were then compression molded into 1.5 mm thick sheets for 3 minutes at 200°C and then left to cool to room temperature. This protocol has been thought to ensure that no degradation crosslinking occurred during the blend elaboration. This has been verified by insoluble measurements and rheological experiments which did not reveal any insoluble fraction nor any significant modification of the EPDM. All samples were stored away from light at room temperature prior to testing.
Table 1 sums up the four most relevant blends which have been studied in this work.

Blend	%w/w of PP	%w/w of EPDM	%w/w of Plasticizer
1	80%	10.9%	9.1%
2	50%	27.2%	22.8%
3	30%	38%	32%
4	10%	48.9%	41.1%

Table 1 – Blend Compositions

The fraction of plasticizer includes both the 60phr of paraffinic oil and the fraction of processing plasticizer originally included in the Vistalon 8800.

II.3. Polymer extraction prior to microscopic characterizations

To ensure a full EPDM and plasticizer extraction, samples were put in fresh tetrahydrofuran solvent for 7 days at room temperature, and were stirred regularly. All samples were washed several times a day with fresh solvent in order to ensure the complete swelling, dissolution and diffusion of the EPDM. The samples were then dried in a vacuum oven at 80°C for 24 hours. Weighing of the dry samples allowed us to ensure that the entire EPDM phase as well as the plasticizer had been fully removed.

II.4. Dynamic Mechanical Analysis

A Texas Instrument Dynamic Mechanical Analyser (DMA 2980) has been used to perform the compression set experiments in stress relaxation mode. The blends were first moulded into cylindrical samples of 4 x 1.5 mm^3, then sustained an imposed 25% relative strain for 10 hours at 100°C, followed by a strain recovery period of 10 hours with a contact force of 0,02 N. This test was thought to take into consideration the thermal dilatation of the materials. Both relaxation and strain recovery profiles were recorded.

II.5. Morphology characterization

The morphology of these blends was first observed using a Hitachi S800 Scanning Electron Microscope (SEM). The samples were first cryofractured in liquid nitrogen to avoid any plastification and morphology alteration. The EPDM phase was selectively extracted as previously described. The fractured surfaces were sputter-coated with gold in order to deposit a 50 nm homogenous conductive layer. Additionally, Transmission Electron Microscopy (TEM) was another helpful means of characterization for such blends. All blends were observed using a Philips CM120 microscope after ultra cryo-microtomy. Samples, taken in triplicate throughout the whole material, were ultra-microtomed into 50 nm thin films at –110°C using a crystal blade to ensure that no phase deformation occurred (as these sample preparations were realised below both the PP and EPDM glass transition temperatures). Samples were then marked using a Ruthenium oxide solution which induced an oxidation and fixation of the metal on the diene functions of the EPDM thus showing dark on TEM micrographs due to the diffusion of the electrons by the fixed metal[40]. All micrographs were made on the microscopes of the Technological Centre of Microstructures of the University of Lyon 1.

III. Results & Discussion

III.1. Blend morphologies

The primary objective was to sum up all possible PP/EPDM blend morphologies prior to exhaustively describing and studying the most interesting one property-wise.

As any would expect, Blend 1 shows a continuous PP matrix with micrometric and submicronic EPDM nodules whose size varies from 50 nm to 1 µm as seen in Figure 1.

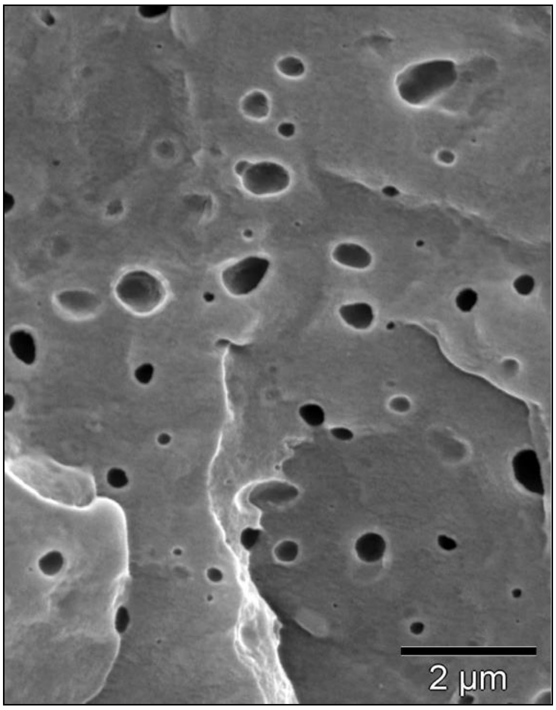


Figure 1 - SEM micrograph of Blend 1 after 2 minutes of blending.

Blend 2 has shown a morphology very similar to Blend 1 with a continuous PP phase but with clearly thicker dispersed nodules of EPDM as we can see in Figure 2.

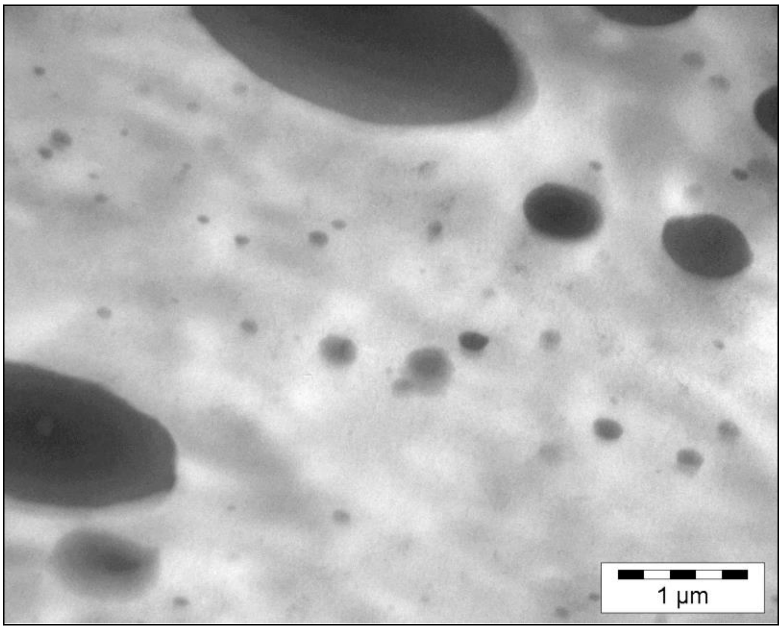
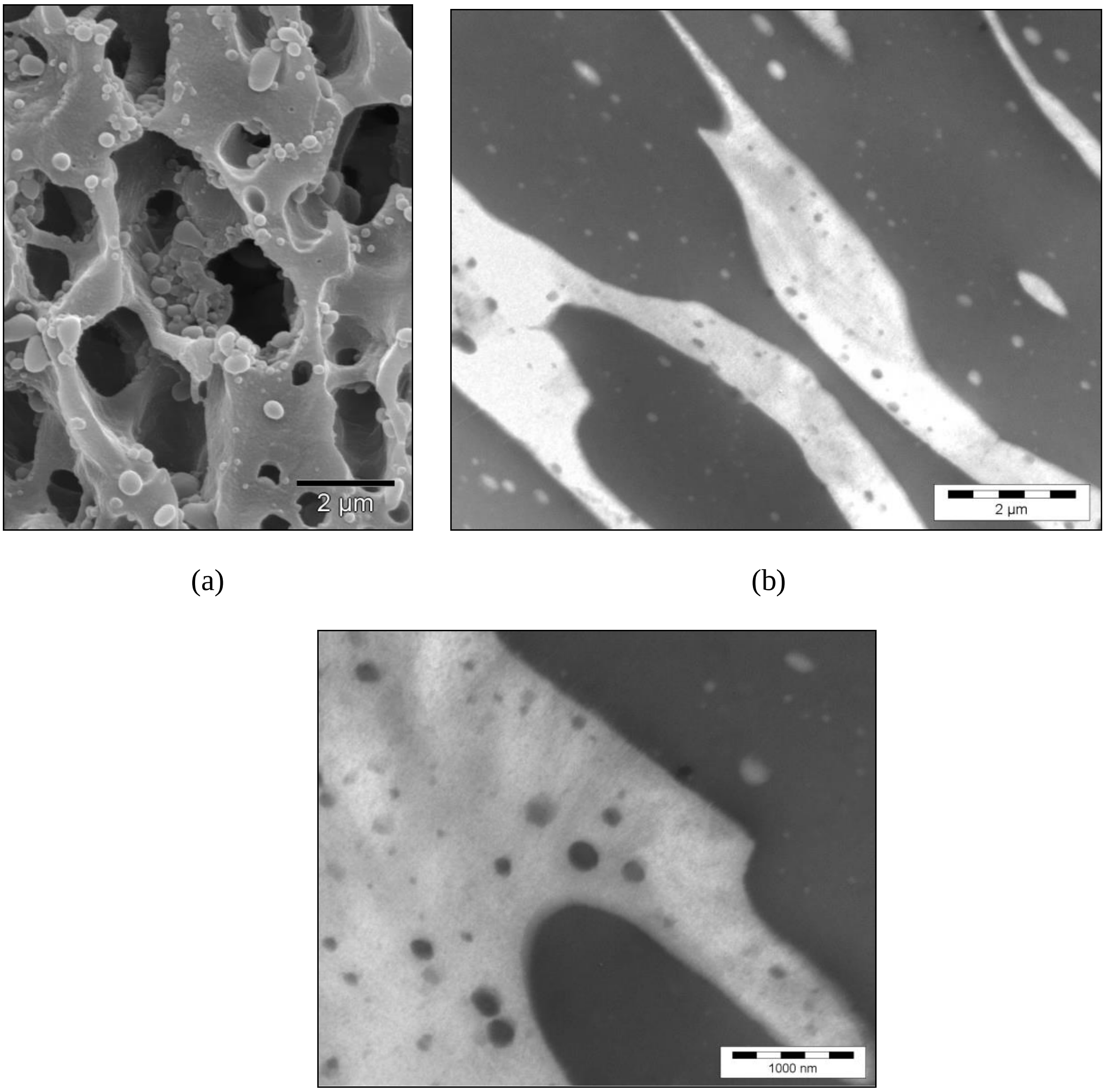


Figure 2 - TEM micrograph of Blend 2 after 2 minutes of blending.

The size of the EPDM nodules is increasing with the EPDM fraction and now ranges from around 100 nm to 5 µm. The dispersion of the EPDM within the PP is thus less effective when increasing the EPDM fraction. According to the compositions of these blends, this trend is in total agreement with all semi empirical models predicting the morphology of two immiscible polymer blends[26].

Blend 3 composition was thought to show a continuous morphology of both phases. Looking at Figure 3, this blend is surely the most interesting one regarding its morphology.



(a) (b)

(c)

Figure 3 - a) SEM and b, c) TEM micrographs of Blend 3 after 2 minutes of blending.

As we can see both on the SEM (Figure 3a) and the TEM micrographs (Figures 3b and 3c), with this precise composition and processing this blend shows a very fine and homogeneous co-continuity whatever the scale : nodules of PP can be observed in the EPDM phase, and vice versa, proof of a genuine co-continuity. The size of the two continuous phases is around

2 µm with nodules of one phase included into the other of dimensions varying from 50 to 500 nm.

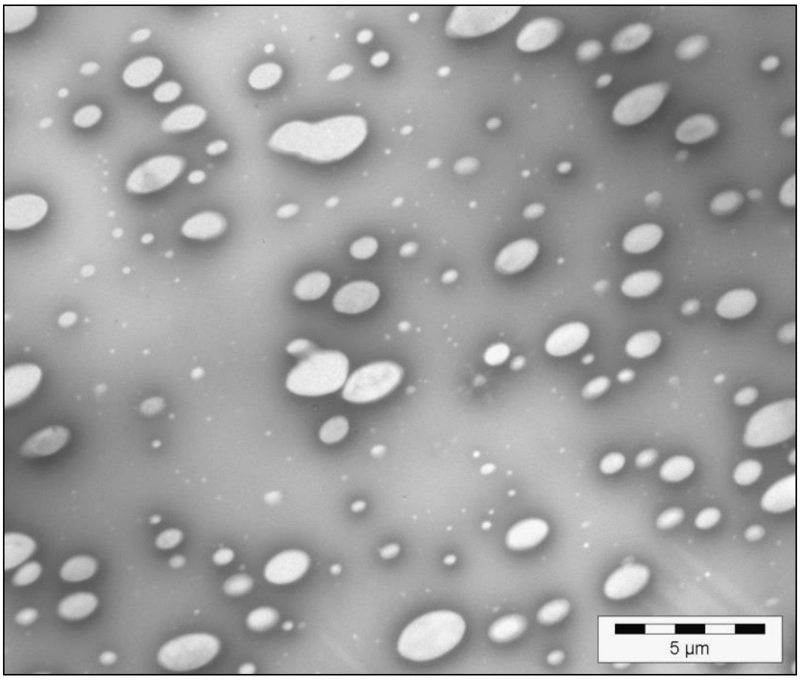


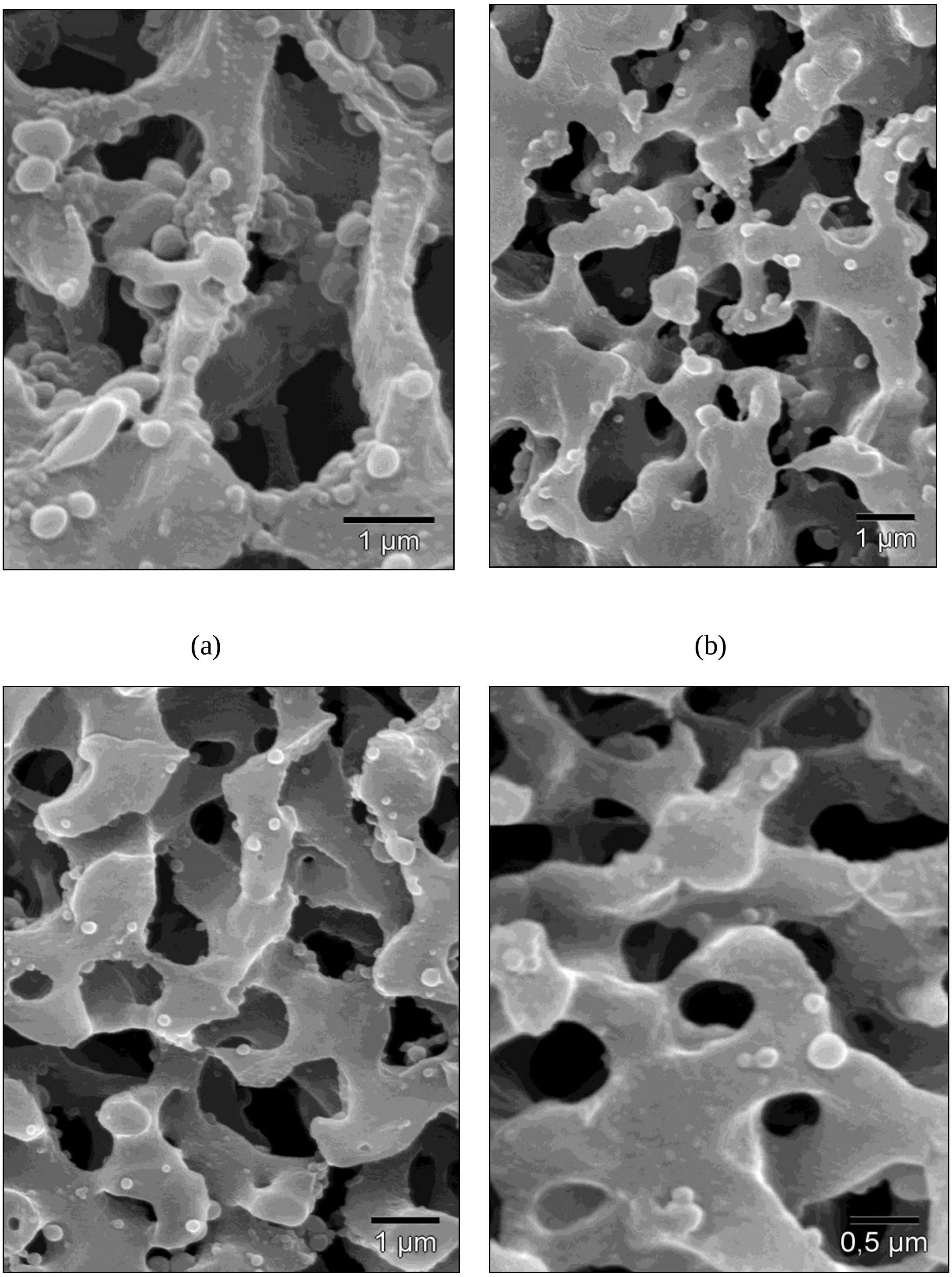
Figure 4 - TEM micrograph of Blend 4 after 2 minutes of blending.

Finally, as observed in Figure 4, Blend 4 shows the exact negative of Blend 1 morphology with a dispersed PP phase within a continuous EPDM phase, with PP nodule size ranging from 100 nm to 3 µm.

III.2. Co-continuity stabilization

By taking samples within the blender at various time after introducing all the components we managed to follow the evolution of the morphology with the time of mixing.

First of all, Figure 5 clearly demonstrates that, as Favis[24] concluded, the co-continuity is formed within the first minutes of blending.



(a) (b)

(c) (d)

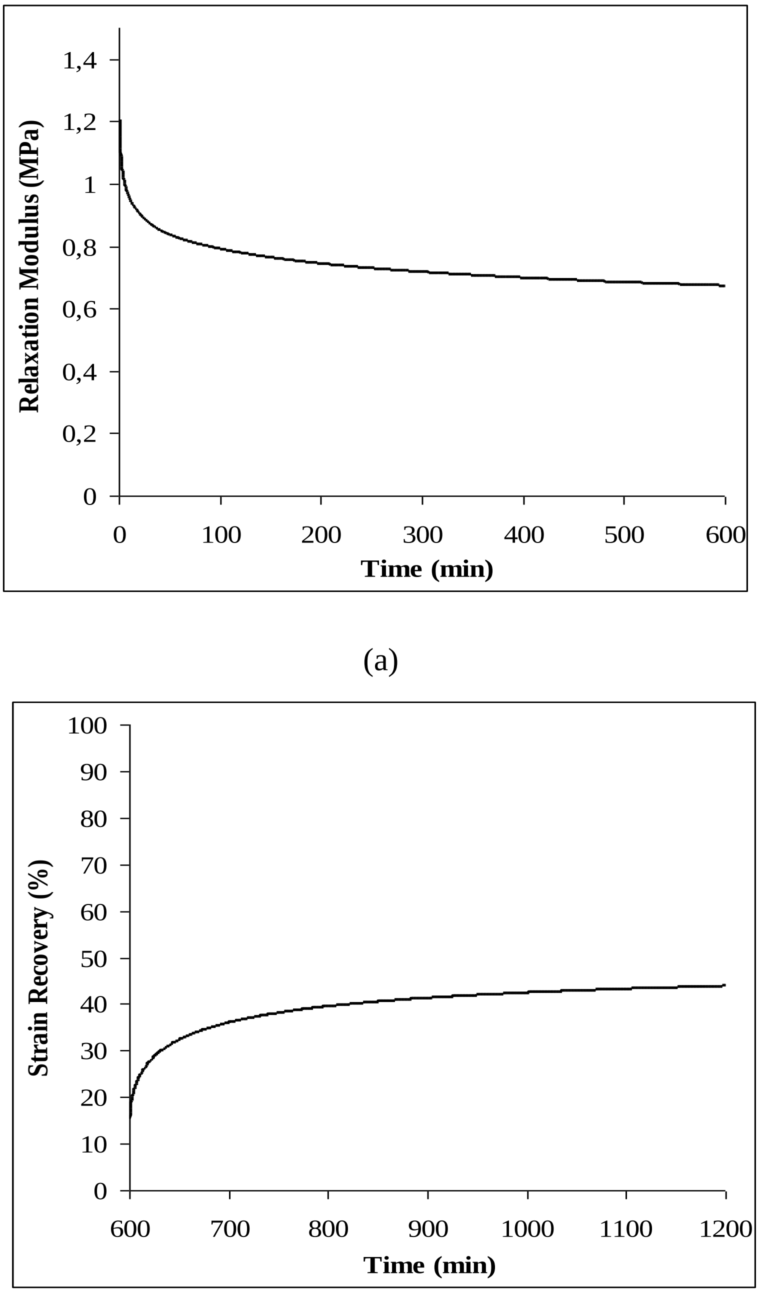
Figure 5 - SEM micrographs of Blend 3 after a) 3, b) 10, c) 18 and d) 45 minutes of mixing.

Nevertheless, for this system and under these experimental conditions, the time of blending also plays an important role on the phase separation and stabilisation. We can notice in Figures 5a to 5d that, during blending, the more time passes the less nodules there are of one phase into the other, and the thicker the continuity becomes. The nodules of PP and EPDM included in the large co-continuous phases slowly migrate towards their main phase to finally show two nearly perfectly demixed phases. The intensive shearing finely and rapidly disperses one phase into the other and the finest co-continuity is actually achieved within the first couple of minutes. But both phases segregate one another with the increasing mixing time which, despite such an intensive shearing, leads to two nearly perfectly separated co-continuous phases. It has to be said that we can invalidate the assumption that such intensive shearing at 200°C might involve a slight crosslinking of the EPDM phase via degradation, thus an increase of the EPDM viscosity, which might perturb the co-continuity equilibrium. Indeed, it is clear that such a period of time does definitely not induce any relevant insoluble fraction, which allows us to discard this hypothesis. Therefore, such time dependence of the morphology stabilization has to be due to the very low interfacial tension between both phases which actually induces some yet small but still significant evolution of the morphology with the time of blending.

III.3. Viscoelastic properties of the co-continuous blend

III.3.1. Structure and viscoelastic behaviour

Contrarily to the other blends, Blend 3 (sampled after 2 minutes of mixing) showed a surprising compression set profile as shown in Figure 6.



(a)

(b)

Figure 6 – a) Relaxation modulus evolution during the 10 hours of compression at 25% strain, and b) Strain recovery profile after suppression of the strain of Blend 3. Test temperature : 100°C.

After 10 hours of compression at 25% strain and 100°C (see relaxation profile in Figure 6a), the blend showed an incredible strain recovery (Figure 6b) whereas we expected this blend to flow as none of the phases were crosslinked, thus no chemical network was present. Furthermore, a plastic deformation, non reversible by nature, of the PP phase could be expected at such a strain.

As one may see in Figure 6b, this blend actually presents a significant strain recovery after suppression of the deformation despite the fact that the EPDM is uncrosslinked. This has, obviously, been confirmed over several samples taken throughout the same batch, and on other identical blends re-prepared afterwards. Admittedly, a period of 10 hours of compression at 100°C might induce a slight degradation of the EPDM which, even in the absence of crosslinking agent, would naturally lead to the partial crosslinking of the elastomeric phase although ensuring a relatively poor strain recovery due to the very low crosslink density this could create. Nevertheless, the insoluble fraction of the sample, even after enduring the compression set experiment, was carefully checked and confirmed to be virtually equal to 0%, thus confirming for sure that this elastic behaviour could not be attributed to any chemical network.

Therefore, other physical considerations must be taken into account to explain such an atypical elastic behaviour. First of all, as the elasticity of such a blend can not be attributed to any chemical network and knowing that, if tested separately, both the PP and the uncrosslinked EPDM polymers totally relax under these conditions and do not show any strain recovery, this material actually has to present a physical network induced by its particular morphology. In fact, the inner nature of such a morphology, made of the dual co-continuous PP and EPDM phases, plays a predominant role on the macroscopic elasticity. Hypothetically, such a structure could allow slight and very localised deformations of the thin amorphous zones of the PP phase which, in this case, may not deform and plastify irreversibly but could store some part of the deformation to restore it after suppression of the compression. To validate this hypothesis, several samples of Blend 3 were first cut out from the main batch then soaked several times into THF for 10 days in order to dissolve and extract all the uncrosslinked EPDM co-continuous phase as well as the paraffinic oil present in the formulation. Once the EPDM and the plasticizer had been extracted, the residual PP continuous phase, totally unmodified during this operation, was submitted to the same compression set experiment, and its relaxation and strain recovery profiles were rigorously determined in the same conditions as before.

The residual and yet unmodified PP matrix showed a relaxation behaviour similar to the one of Blend 3 but with, obviously, a much lower initial relaxation modulus as the material lacks the EPDM and plasticizer in its volume. Most importantly, we can see in Figure 7 that the PP structure induces a significant and nearly instantaneous strain recovery, yet not as much important as the one of Blend 3, although the entire EPDM and plasticizer fractions were extracted.

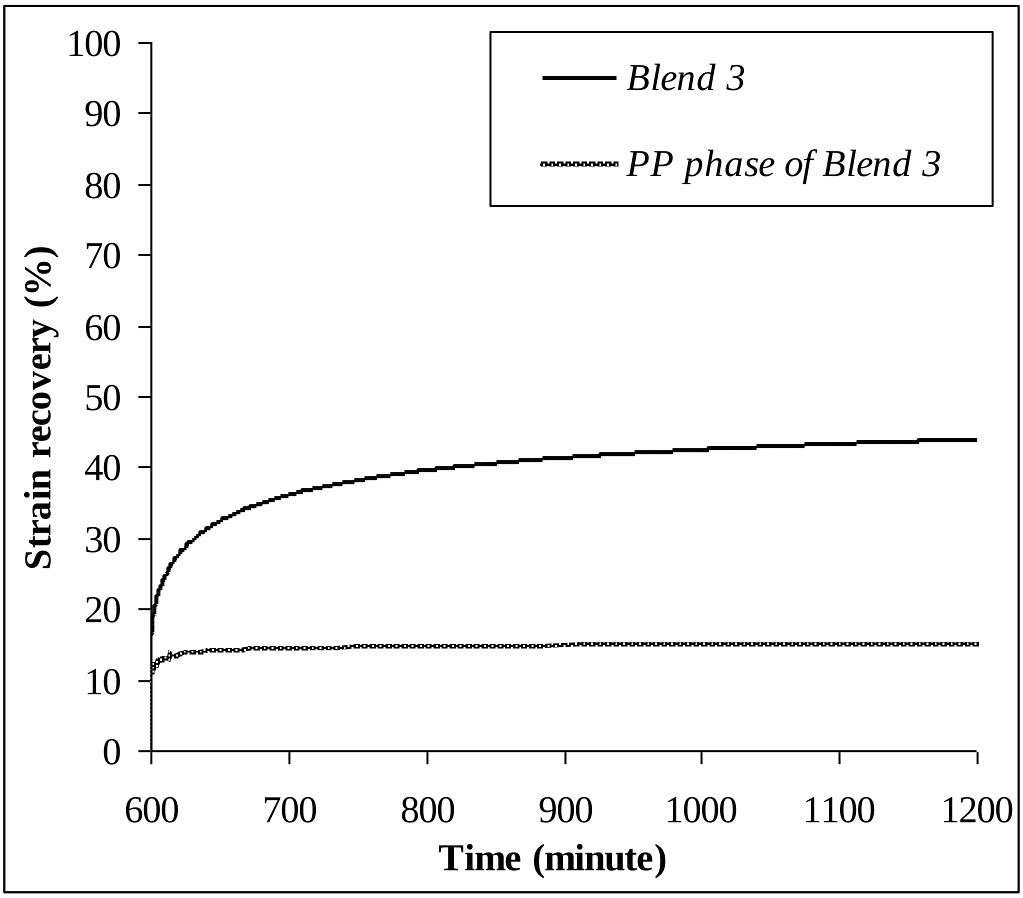


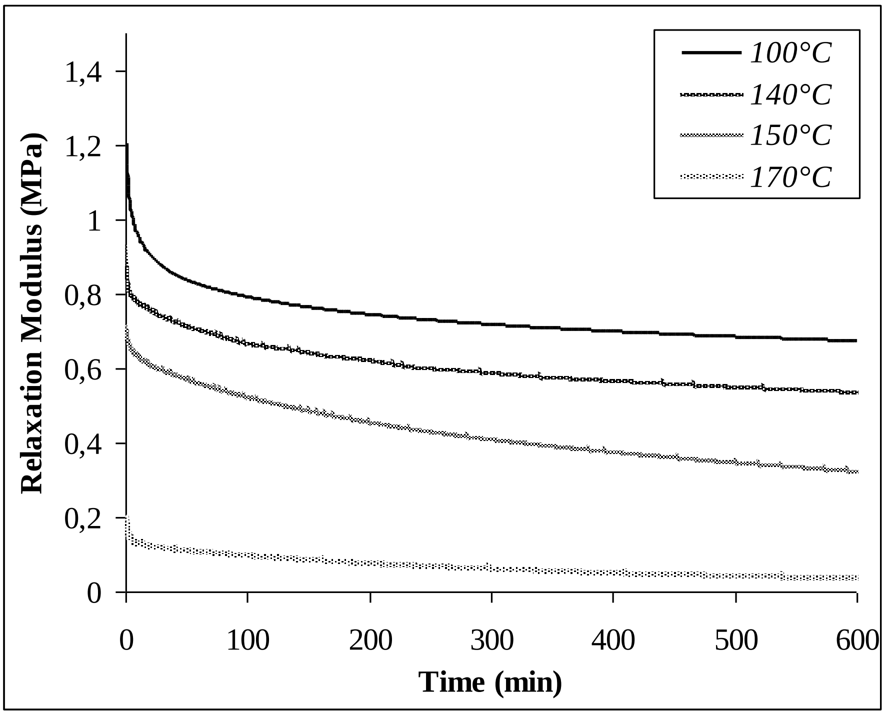
Figure 7 - Strain recovery of the PP phase of Blend 3 at 100°C and 25% strain.

This residual PP phase acts like a physical network similar to a “sponge-like” microstructure as, even after extraction of 70% of its mass (i.e. the EPDM plus the plasticizer) the compression set experiment gives an impressive 15% recovery nearly instantaneously after the suppression of a 10-hours compression. This particularity is very interesting as it shows that the PP structure can also play an active role on the global elasticity of such blends, whereas most assumptions stipulate that the EPDM crosslinking density is the main contribution.

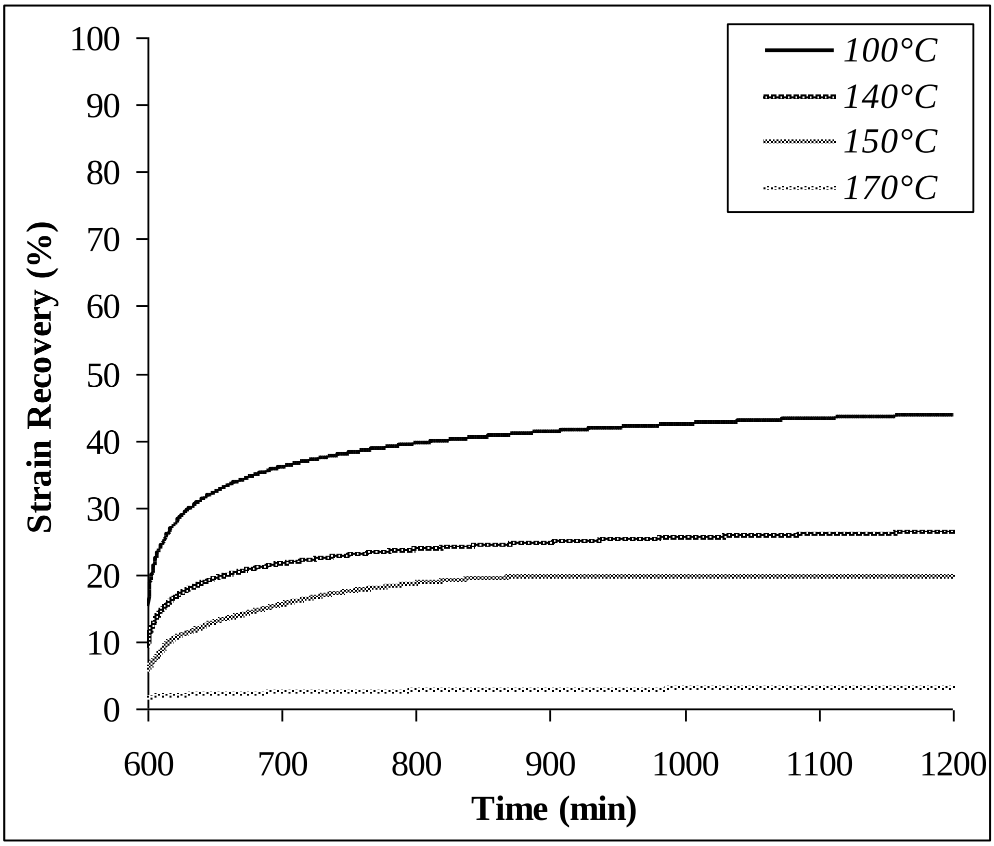
By extrapolation, we can understand that if the PP phase is largely predominant in the blend, like in Blends 1 and 2, its large continuous phase, having nodules of EPDM dispersed in it, is far from being similar to a thin and flexible microstructure as seen above. In this case the PP plastifies at very low compression strains and the reversibility of the deformation is thus immediately disabled, thus any uncrosslinked blends having a main thermoplastic continuous phase may not recover from a non linear deformation. On the other hand, if the EPDM is the only continuous phase with the PP phase dispersed in it as in Blend 4, the fact that it can relax indicates that the phases can actually flow exhaustively. This creep behaviour is due to the physical nature of the polymers which, with such a microstructure, can diffuse the stress within the sample volume avoiding any possible stress accumulation, thus forbidding any potential strain recovery.

As a first step in understanding the atypical elastic behaviour of Blend 3, and in order to confirm the existence and contribution of a physical network, we submitted this Blend 3 to a series of compression set experiments (25% during 10 hours) at various temperatures to see if the melting of the PP phase would induce a drastic fall of the strain recovery.

As we can see in Figures 8a and 8b, when Blend 3 is submitted to compression set experiments at temperatures near the melting point of the PP phase, its relaxation modulus as well as its strain recovery drastically drop.



(a)



(b)

Figure 8 – a) Relaxation modulus, and b) strain recovery profiles of Blend 3 over 10 hours of compression followed by 10 hours of recovery, as a function of the temperature.

The structure of the PP is altered by the fusion of the PP crystallites and the physical network collapses, highlighting the importance of the cristallinity of the thermoplastic phase on the elastic behaviour of such blend. Thus, the cristallinity, just as well as the amorphous fraction of the thermoplastic phase, plays an active role on the strain recovery. At temperatures above 150°C, the presence of a slight residual relaxation modulus and strain recovery can be explained by the fact that the EPDM can slightly self crosslink by degradation of the polymer chains over 10 hours only above 160°C. Nevertheless, this crosslinking happens under compression and its impact is extremely low as it represents alone a very weak 3% strain recovery at 170°C. Thus, the fact that the physical network is ruined by the fusion of the PP crystallites induces a severe modification of the microstructure which provokes a profound drop of the elasticity of the blend. Thus, these results prove that the PP phase microstructure and its cristallinity play an active role on the elastic behaviour of such blends having a multi-scale co-continuous morphology, results which are in total agreement with the literature[18]. Furthermore, Boyce et al.[41] highlighted the importance of the co-continuity of the phases in TPVs on the global elasticity of the blend. Even though their researches were carried out on a crosslinked co-continuous elastomeric phase, they showed that this phase could sustain large deformation without altering the thermoplastic matrix. The quasi-totality of the thermoplastic phase does not endure any major deformation due to the structure of the material and the interface between both phases. Taking this into account, such a co-continuous morphology is thus definitely the most appropriated one regarding TPVs applications as they combine the processability of the thermoplastic, the elasticity of the elastomeric blends, and a physical network which may endure some relatively significant stress without retaining major irreversible deformations.

However, the aim of this paper is not to study the mechanical deformation of such a morphology under compression : the mechanisms involved in the deformation of TPVs are still being investigated thanks to mathematical simulations, nevertheless their complexity is still far from being fully explained.

Moreover, the presence of a physical network itself does not entirely explain the elasticity of this co-continuous blend. We thus have to consider additional contributions as, for instance, the confinement of both phases within such a thin morphology. Hence, the elastic properties of this type of blends could also partially depend on the confinement of these polymers present at micronic, submicronic and, eventually, nanometric dimensions. The relaxation of such polymers present at such small dimensions can potentially be obstructed by a confinement of the polymer chains induced by the three dimensional continuity structure of each phase, reducing the mobility, thus the relaxation, of the elastomer when the material undergoes a significant strain outside its linear viscoelactic domain. Within such a structure, the polymer may not relax freely and stress accumulates between the confined phases as the strain is applied. The material structure does not allow it to relax totally and freely, and the accumulated stress release contributes to the elasticity of the network as soon as the applied stress is removed.

It was actually shown that such a confinement effect could be directly implicated in the morphology stabilisation of polymer blends and could potentially matter on the final physical properties[42]. The inner nature of such an effect is particularly complex and even if this has been studied for several years many important researches are still ongoing on an international level. Such an effect has, for instance, been observed in the case of a PP/EPDM blend at 80/20% w/w presenting submicronic nodules of EPDM dispersed in the PP matrix : Zumbrunnen[43] concluded that the shearing and mixing of molten polymers could actually lead to the formation of nanometric and confined polymer morphologies with specific properties, highlighting the fact that such a confinement could have a significant impact on the final macromolecular blend properties. This confinement effect, combined with the inner structure of the PP physical network, actually leads to the creation of an elastic network. Contrarily to a chemical network of a commonly crosslinked EPDM, here the co-continuous thermoplastic matrix is tightly combined and constrained within the co-continuous elastomer phase at every scale, making a complex structure which acts like a proper network at macroscopic scales.

Even though both these first two contributions have to be taken into consideration, these can not be the only explanations for this particular relaxation and strain recovery behaviours. In fact, we can not further discuss without taking into account the presence of a residual inner stress caused during the mixing and, more particularly, during the moulding of the blend. Even if the structure relaxes partially, there is still some residual stress which will inevitably induce a slight elastic recovery as the confined phases tend to resist against the residual pressure applied during the moulding process as the two phases are contracted and support a significant stress and deformation. As a matter of fact, this effect is virtually unquantifiable and can not be fully eliminated prior to testing even by leaving such blends at 100°C for several hours. Although, we can affirm that the relaxation modulus evolution as well as the strain recovery profile of such a blend left at 80°C for 24 hours prior to testing, in order to remove most of the inner mechanical stress accumulated during the processing and moulding, are virtually identical to the neat Blend 3, confirming that this effect does not have much of a relevancy in this kind of experiments.

Thus, in the case of such a co-continuous thermoplastic / elastomer blend, there is a synergy of mechanisms. The co-continuous structure perturbs the deformation and relaxation of both constrained phases. In this case, the inner structure of the PP, even though highly crystalline, can actually afford a relatively important elastic deformation thanks to the thin amorphous zones which plastify far less than the rest of the matrix and can recover some part of the applied deformation after suppression of the compression. Additionally, inner residual stress between phases surely amplifies the effect of these two contributions. As a matter of fact, a similar mechanism has been described in the literature by Van Duin in the case of such blends made of a crosslinked elastomer and a thermoplastic phase[18] submitted to an elongation strain which showed that even though the thermoplastic matrix was elongated and plastified, the interaction with the elastomeric phase could actually allow the thin PP structure to recover some part of the deformation. Therefore, nothing forbids us to consider a similar deformation and strain recovery mechanism in the case of an uncrosslinked co-continuous blend under compression.

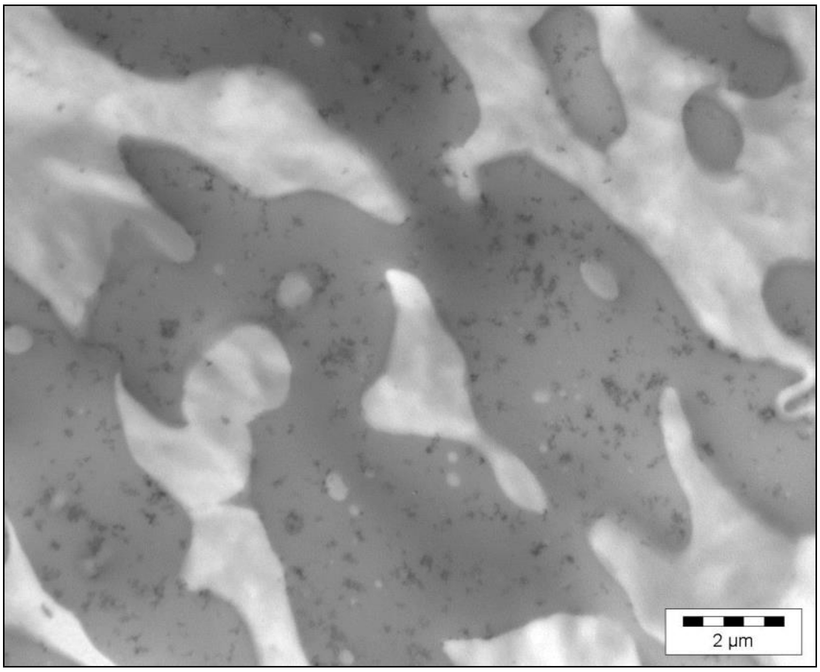
III.3.2. Influence of silica nanoparticles

The incorporation of silica nanoparticles into the composition of such co-continuous blends was first thought to help us understand the mechanism of relaxation and strain recovery of this type of blend, and to balance the importance of each previous consideration on the overall strain recovery mechanism.

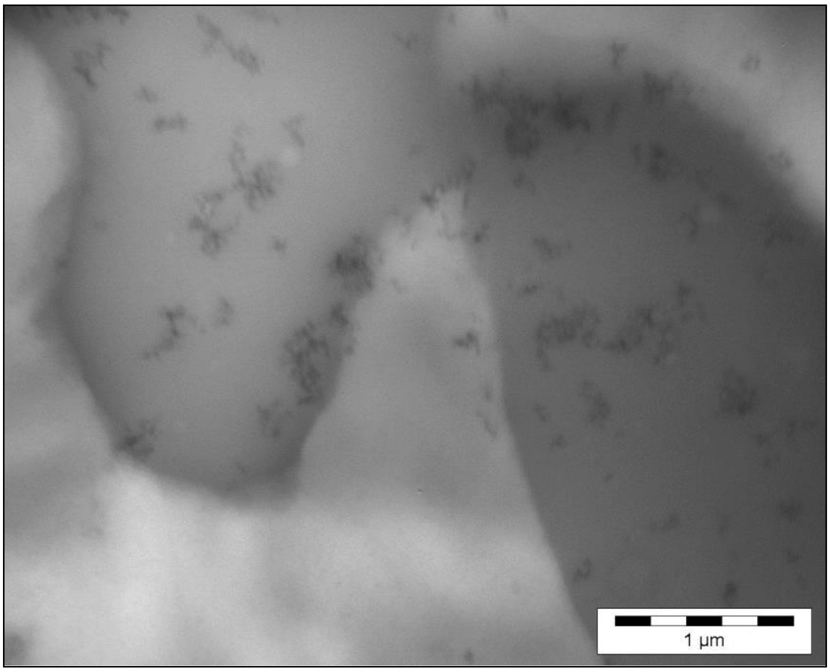
The aim here is not to discuss about interfacial tensions between those two polymers and the silica nanoparticles as it has been widely described, among others, by Elias & al.[35], but to describe and compare the morphologies and behaviours of co-continuous PP/EPDM blends after the incorporation of 1 phr of hydrophilic or hydrophobic silica nanoparticles.

First of all, in such blends, the silica nanoparticles dispersion is ruled by the wettability parameter as described by Cassagnau et al.[35] and, usually, for this kind of polymer blends, the incorporation of silica nanoparticles tends to reduce the size of the dispersed phase[35]. Of course, the incorporation of such particles inevitably modifies the viscosity of the phase in which the particles are dispersed, therefore inducing, in theory, some drastic morphological changes. Nevertheless, as one may see in Figures 9 and 10, the micrographs are fairly interesting as, in both cases, the final co-continuous morphologies have not been altered too much. We can appreciate that, in both cases, the silica particles are only present in the elastomeric phase, and the characteristic size of the two continuous phases has only slightly increased and now ranges from 1 to 3 µm. In both cases, the incorporation of silica particles led to the increase of the viscosity of the EPDM phase, thus of the viscosity ratio between the two continuous phases. This leads to the thickening of the silica-rich elastomeric phase thus inducing, in theory, a significant modification of the overall morphology.

However, as seen in Figure 9, the hydrophobic nanoparticle distribution is homogeneous and apart from small aggregates we can record their presence within the EPDM phase just as well as at the interface.



(a)

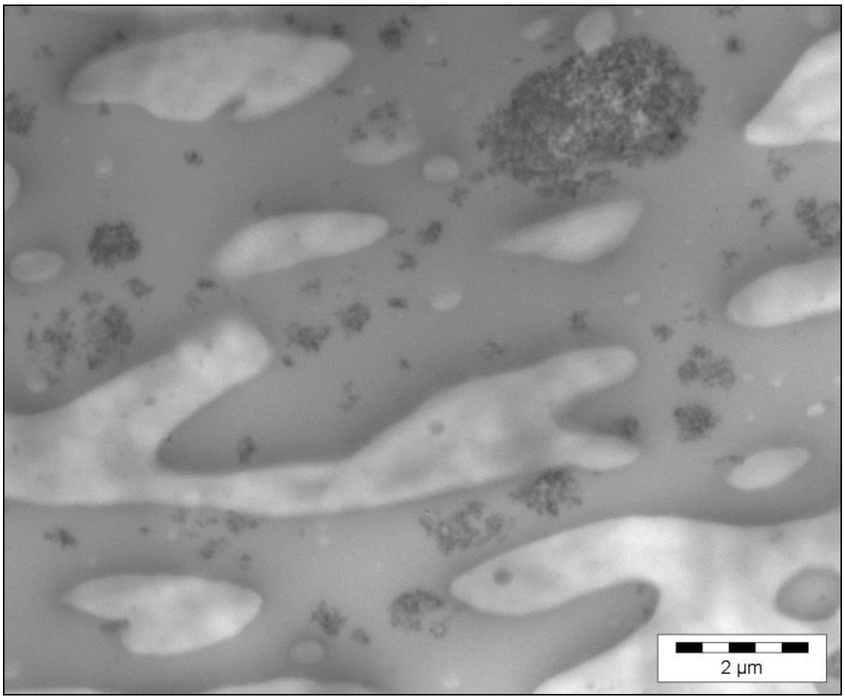


(b)

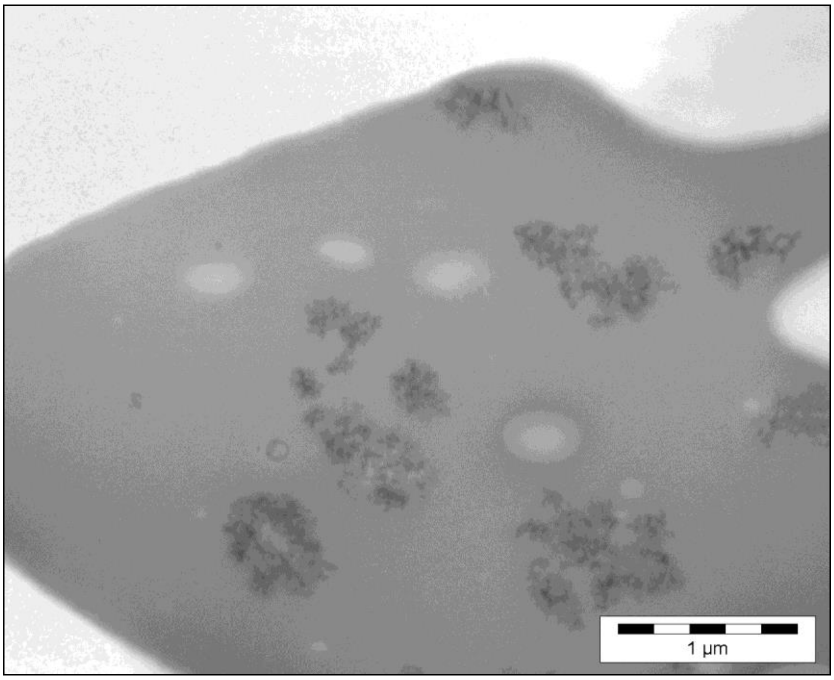
Figure 9 – a, b) TEM micrographs of a co-continuous PP/EPDM blend having 1% of hydrophobic silica nanoparticles.

These nanoparticles, very present at the interface, thus provoke a small but yet very important physical compatibilisation of the phases. In the end the morphology is thus very similar to the one of Blend 3 as the incorporation of hydrophobic silica nanoparticles leads to the physical compatibilisation of the phases which increases the interfacial tension between both phases thus compensating the increase of the viscosity ratio, leading to a very similar co-continuous morphology.

Moreover, as seen in Figure 10, the hydrophilic particles have been segregated within the elastomeric phase in the form of huge aggregates only present inside the EPDM phase and never observed, at any scale, at the interface of the two polymers.



(a)



(b)

Figure 10 - a, b) TEM micrographs of a co-continuous PP/EPDM blend having 1% of hydrophilic silica nanoparticles.

These clusters form local heterogeneities which, very surprisingly, do not perturb the overall morphology. These particles can only be seen as local defects present at large scales inside the elastomeric phase, and do not seem to modify neither the interfacial tension nor the viscosity ratio of both phases.

But, most importantly, these morphological differences actually have surprising impacts on the compression set results. Although the relaxation modulus evolutions during the 10 hours of compression are very similar and do not bring any significant information worth discussing, we can appreciate some strong and reproducible differences concerning their strain recovery behaviours as shown in Figure 11.

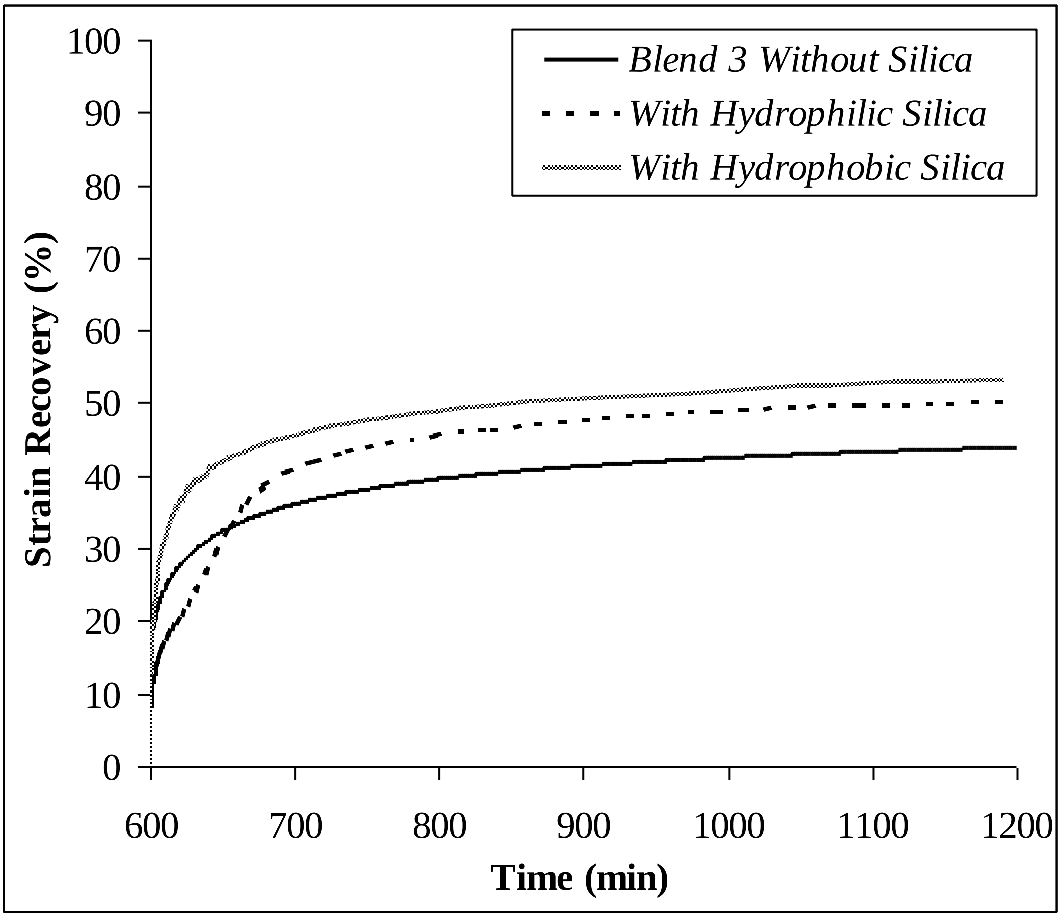


Figure 11 - Strain recovery profiles of both co-continuous blends having 1% of either the hydrophilic or the hydrophobic silica nanoparticles, at 100°C after suppression of the 25% strain.

The presence of silica nanoparticles, either hydrophilic or hydrophobic, definitely improves the final strain recovery 10 hours after having removed the compression strain. This is fairly normal as their presence in the EPDM phase increases its viscosity, thus significantly modifies the morphology, and partially inhibits the relaxation and creep of the elastomeric phase. Nevertheless, the hydrophilic silica radically modified the strain recovery behaviour of the blend showing a very interesting double step recovery profile. Its instant recovery, straight after suppression of the compression, is lower than the one of Blend 3 and of the hydrophobic silica : its recovery is a complex, but yet reproducible, double-step behaviour. This has to be attributed to the presence of large aggregates within the elastomeric phase which somehow perturbs the molecular entropy and the energy restitution mechanism. This profile is particularly interesting as it gives some additional confirmation on the fact that the incorporation of hydrophilic silica particles within such blends usually gives poor industrial processing and elastic properties, as well as poor standardised compression set values commonly measured 30 minutes after suppression of the applied strain.

On the other hand, the addition of hydrophobic silica nanoparticles clearly improves its instantaneous and long term strain recoveries. The overall elasticity of the blend has been improved thanks to the relative inhibition of the elastomer relaxation as well as to the improved interface adhesion between the two present polymer phases. The interface is wider and fading, which shows a partial miscibility due to a very localised interpenetration of the two theoretically immiscible polymers. Even though the viscosity of the elastomer has been greatly increased, the morphology is very similar to the one of Blend 3 : the perturbation of the viscosity ratio has been compensated by the partial compatibilisation of the polymers. This is an important conclusion which allows us to fully appreciate the use and possibilities of such particles within any polymer blend of this type.

Obviously, ongoing studies have to clarify and confirm the enclosed hypotheses, and to quantify the importance of the role of the physical network structure as well as the confinement effect and the residual inner stress. Hence, this will help to better understand the complex nature and correlation of molecular mechanisms ruling, for instance, the TPVs relaxation and strain recovery behaviours.

IV. Conclusion

The main objective of this work was to study the morphology and viscoelastic behaviour of PP/EPDM blends at different proportions, especially at the co-continuity of both phases. In addition, the influence of both hydrophobic and hydrophilic silica particles on the co-continuity morphology was also studied to correlate the morphologies with elastic blend properties. Thus, hydrophilic silica particles tend to migrate within the elastomeric phase and form huge aggregates. On the other hand, hydrophobic particles are dispersed homogeneously and can be found both at the interface and within the EPDM phase. Furthermore, we highlighted the atypical strain recovery profile of the co-continuous and unfilled blend, and investigated the mechanisms which could induce such an elastic behaviour in absence of a chemical network. Therefore, the presence of a physical network assimilated to a “sponge-like” PP structure, combined with a confinement effect of the phases which, additionally, built some residual inner stress along their elaboration and moulding, can explain such an elastic behaviour. As a consequence, the PP phase does not entirely endure an irreversible plastic deformation as it can restore some part of the absorbed stress after suppression of the imposed strain. Nevertheless, the importance of each of these contributions is still to be quantified, and further studies are currently ongoing on that matter. Anyhow, these results highlighted the importance of the morphology on the elasticity of such blends, and proved that the co-continuity of both phases is just as important as the chemical crosslink density of the elastomeric phase. Finally, the impact of hydrophilic and hydrophobic silica nanoparticles on this co-continuous morphology and its viscoelastic behaviours have also been approached. The results confirmed the usefulness of the hydrophobic silica in such systems, especially for the elaboration of thermoplastic vulcanisates. Nevertheless, the inner sources of the elasticity of such blends are still far from being fully understood due to the complexity of the synergy of the various mechanisms involved in their relaxation and elastic behaviours, which can assure some forthcoming and very interesting investigations.

Acknowledgement.

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Chapitre V

Morphology development in thermoplastic vulcanizates : Dispersion mechanisms of pre-crosslinked EPDM phase

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Chapitre V – Dispersion mechanisms of pre-crosslinked EPDM in molten PP

Abstract :

This work aims at studying the fragmentation and dispersion of several pre-crosslinked and plasticized ethylene-propylene-diene terpolymer (EPDM) networks in presence of an isotactic polypropylene (PP) phase under shearing at various proportions. Thus, we first assessed the morphologies and mechanical properties of blends having similar compositions but made from either uncrosslinked, pre-crosslinked or dynamically crosslinked EPDMs. Additionally, kinetic studies of the fragmentation and dispersion of these pre-crosslinked EPDMs brought new results regarding the various mechanisms involved in the morphology stabilization of such thermoplastic / elastomer blends. These results first highlighted the importance of the shearing stress applied by this process, the influence of the gel fraction of the pre-crosslinked EPDMs, as well as the impact of the thermoplastic matrix proportion on the quality of the dispersion of such networks. Therefore, an EPDM having a gel fraction above 0.7 will not be finely and homogeneously fragmented and dispersed in presence of PP, whatever the proportion of the phases, and will only lead to very brittle materials. Nevertheless, contrarily to some theoretical model expectations, a partial fragmentation of the chemical networks was always observed even at very high crosslink density. The influence of the several mechanisms involved in such morphology stabilization were also discussed, such as the parallel break up and the vorticity alignment and break up mechanisms which mostly regulate the dispersion of EPDM into a majoritary PP phase. Additionally, the pure mechanical breaking induced by the process as well as the collision–coalescence–separation type erosion mechanisms appear as the two main mechanisms ruling the stabilization of blends having a majoritary EPDM phase. Finally, the blends crosslinked under shearing showed a clear mechanical property synergy due to their fine and homogeneous morphology coupled with the full crosslinking of the elastomer. In the end, these results brought significant information on TPV morphology stabilization and their related mechanical properties.

Keywords : EPDM / PP blends, crosslink, dispersion

I. Introduction

Ethylene-propylene-diene (EPDM) / polypropylene (PP) blends are surely one of the most currently used elastomer / thermoplastic blends on the market. The study of the inner source of their impressive processing and mechanical properties is a subject of great interest having many relevant consequences on the industrial thermoplastic vulcanisates (TPVs) production[1-4]. Actually, such thermoplastic / elastomer blends present some specific and very interesting properties depending on their morphology, as they can combine the elasticity of the crosslinked elastomeric phase with the processability of the thermoplastic. Over the years, many studies have brought very useful information regarding the highly important correlation between such polymer blend morphology and their final mechanical properties[5-8]. Nevertheless, such a synergy can only be achieved thanks to complex processing steps which obviously induce some strong morphological modifications during the blend elaboration. Thus the key to adjusting and optimising their properties is to exhaustively control their morphology development, which can be quite complex especially regarding the quality of the dispersion of the elastomer in presence of the thermoplastic phase.

Obviously, the final morphology of such blends directly depends on the composition and compounding route which clearly play a primary role on the final properties of TPVs[9-14]. Nevertheless, the initial morphology of such blends prior to the crosslinking step is also a subject of great interest. It has to be set to endure the forthcoming modifications through the crosslinking step which irremediably leads to a drastic increase of viscosity of the elastomeric phase during crosslinking, inducing a complex morphology evolution and stabilization. This induces many consequences especially in the case of two immiscible polymers which show very weak interfacial adhesion.

Additionally, the crosslinking of the elastomeric phase is very important as it modifies the structure, the viscosity and the elasticity of the elastomeric phase, thus the final morphology and properties of such blends[15-19]. The nature and quantity of crosslinker obviously modify the inner structure of the elastomeric network and induce some severe changes on the final blend properties[20-26]. Such crosslinking can also induce a phase inversion which must be taken into consideration during the processing of such blends[27, 28]. Just as well, the interface, ruled by the interfacial tension of the polymers[29], also plays an active role on the final morphology stabilization[30, 31] : a phase compatibilization can drastically modify the morphology and improve the final properties of the blends[32-38]. Furthermore, the influence of additional particles such as silica or carbon black nanoparticles is currently being widely studied for common thermoplastic / elastomer blends[39-46]. Additionally, the effect of the proportion of plasticizer and its diffusion within each phases are just as important[47-50].

In the end, the final morphology relies on the inner structure of the present phases and on the molecular mobility of both polymers at the set temperature which rule the stabilization of the phase morphology involving several mechanisms of morphology development prior and after the crosslinking step[51-55]. The understanding and control of such mechanisms are extremely important in order to achieve the desired properties.

Knowing the foregoing, the fragmentation and dispersion of crosslinked EPDM in presence of PP under shearing is a subject of great importance as the break-up of the partially or highly crosslinked elastomer droplets in presence of the thermoplastic phase happens right after the addition of the crosslinking agent during any TPV elaboration.

Hence, the structure of the EPDM chemical networks had first to be exhaustively studied in order to estimate the influence of the network structure on the fragmentation and dispersion into the PP matrix. The viscoelastic behaviour as well as the inner structure of such networks, especially the insoluble fraction, the chemical crosslink density and the density of elastically active chains, had to be known prior to studying their fragmentation and dispersion in presence of PP in various proportions. This work was actually carried out in one of our previous paper[56].

Secondly, all the typical PP/EPDM blend morphologies had to be reviewed prior to studying such morphology development. This has been done and reported in our latest paper which actually insisted on the characterisation of the co-continuity and its stabilization with the time of blending[45]. We also discussed the use and impact of the co-continuous blend structure on its relaxation and elastic behaviour. This brought forward the presence of a physical network relying on the complex structure of the confined phases. Thus, such a specific blend composition, i.e. PP/EPDM at 30/70 weight percent, appears very important as this co-continuity is the keystone of the combination of the processability and the elasticity for such blends. We will thus study the morphology stabilization of blends having such a composition.

Thus, the main objective of this paper is to study the dispersion of crosslinked and plasticized EPDM networks in presence of a thermoplastic matrix at the most relevant compositions. Also, due to the complexity of the involved mechanisms which are, indeed, tightly linked to the elaboration of any TPV, we intended to separate the effect of blending from the actual chemical crosslinking aspect. We thus focused on the impact of the shearing on both the thermoplastic and the pre-crosslinked EPDM phases. Actually, virtually no study of this type has been reported in the literature, this paper therefore aims at addressing new information on that matter. Henceforth, we will first describe the main morphologies of blends elaborated with PP and pre-crosslinked EPDMs having various crosslink densities, as well as with uncrosslinked and dynamically crosslinked EPDM. We will then examine their morphology stabilization in function of the time of mixing to investigate the mechanisms of morphology development in TPVs. We will finally bring forwards new results concerning the morphology - mechanical properties correlation, to further discuss on the impact of a dynamic crosslinking step during such blend elaboration.

II. Experimental Part

II.1. Materials

PP was supplied by Arkema (PPH 3060) with a melt flow index MFI = 12g/10min. The molecular weights are : $\overline{M_n}$ = 67300 g.mol^{-1} and $\overline{M_w}$ = 273000 g.mol^{-1}.

Experiments were carried out with Vistalon 8800 (ExxonMobil Chemical), a material that comprises a 53.5 wt.% ethylene and 10 wt. % ethylidene norbornene-terpolymer. The following values of molecular weight were measured: $\overline{M_n}$ =160.000 g.mol^{-1} and $\overline{M_w}$ =310.000 g.mol^{-1}. This terpolymer has a specific gravity of 0.86 g.cm^{-3}, and is oil-extended with 13% in weight of paraffinic oil, which yields to a total specific gravity of 0.87 g.cm^{-3} and a Mooney viscosity ML$_{(1+4)}$ of 73 at 125°C. Additional paraffinic oil (Torilis 7200. TotalFinaElf, France) was incorporated into the Vistalon 8800 to mimic industrial compositions. The specific gravity of this oil is 0.90 g.cm^{-3} at 20°C. Its proportion in the PP/EPDM/plasticizer blend was set, according to the industrial standard, to 60 wt.% or phr (grams per hundred grams of Vistalon 8800) for all blends. The corresponding volume fraction of oil (initially present + added) is 0.445. The polymers and chemicals were kindly supplied by Hutchinson (Chalette-sur-Loing, France) and were used as received from the supplier. Radical crosslinking of the EPDM was carried out under shearing by means of an phenol-formaldehyde resin, called resol in the following.

II.2. Compounding routes

II.2.1. Dispersion of pre-crosslinked EPDM networks in PP

First of all, concerning the elaboration of randomly crosslinked and plasticized EPDM networks, such samples were made of the elastomer, the processing oil and the curing system and prepared in an internal batch mixer (Haake Rheomix 600. Thermo Electron) at 100°C. As shown in Figure 1, the following protocol was used: first, the polymer was introduced (at time t=0) into the batch blender and sheared by itself for 2 minutes at 120 rpm in order to ensure the thermal homogenization of the elastomer. The plasticizer was then poured in and the two components were mixed until torque stabilization. Prior to introducing the curing system, the temperature and rotation speed were decreased (80°C and 50 rpm, respectively). As soon as the torque had stabilized, the curing system (resol and catalyst) was introduced and the mixing was allowed to go on until torque started to increase. The blends were then quickly dumped in order to prevent the crosslinking reaction from occurring inside the mixer, then compression molded at 100°C for 2 minutes into 1 mm thick samples, then stored away from light and heat until further testing.

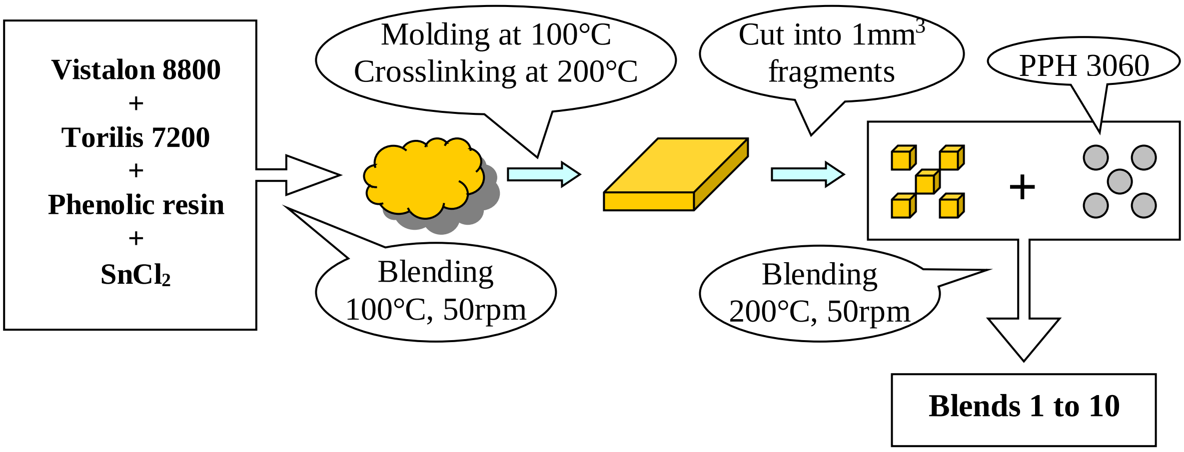


Figure 1 – Schematic representation of the blend preparation

The standard reference amount of resol was 4% w/w (or phr) on the EPDM basis, and 0.6 phr SnCl$_2$ was used as catalyst for all sample preparations i.e. 0.37% weight fraction for all these blends. In order to vary the degree of crosslinking from the standard formulation, the materials were prepared with various amounts of curing resin : 1, 1/4, 1/7, 1/10 and 1/30 of the reference quantity of resol as described in our previous paper[56]. In the following, the EPDM preparation crosslinked with the regular amount of curing additives will be named the "reference" sample (REF), whereas the others will be referred to via the corresponding ratios of crosslinking agent used in their formulation (RES1/4 to RES1/30) as presented in Table 1. The fraction of plasticizer includes both the 60phr of paraffinic oil and the fraction of processing plasticizer originally included in the Vistalon 8800.

These samples sustained viscoelastic measurements for monitoring the crosslinking reaction at 200°C in order to assess the reaction time and material thermal stability. The molded sheets were then crosslinked during subsequent molding in a press at 200°C for adjustable times according to the time length needed to ensure the completion of the crosslinking reaction which were determined by the prior viscoelastic measurements. The insoluble fraction as well as all the network structure parameters were determined on all these plasticized and crosslinked EPDM samples as presented in Table 1 and thoroughly discussed in our previous paper[56].

Prep.	**% w/w of resol**	**% w/w of Plasticizer**	**Gel fraction**	**Tan δ**	**Swelling Ratio**	**μ (mol.m^{-3})**	**Ge (MPa)**	**η^*_{EPDM} (Pa.s)**	**η^*_{EPDM} / η^*_{PP}**	**E (kPa)**	**σ_r (kPa)**	**ε_r (%)**
REF	2.43	36.45	0.998	0.01	4.3	64.27	3.3×10^5	3.4×10^4	17	624	925	136
RES1/4	0.62	37.13	0.989	0.07	8.0	21.21	9.8×10^4	1.6×10^4	8	395	676	486
RES1/7	0.35	37.23	0.962	0.12	11.0	9.64	5.8×10^4	8.5×10^3	4.25	377	623	808
RES1/10	0.25	37.27	0.896	0.18	14.7	3.91	3.4×10^4	5.5×10^3	2.75	173	436	868
RES1/30	0.08	37.33	0.700	0.40	26.7	0.79	2.0×10^3	2.2×10^3	1.1	182	206	952

Table 1 – Linear and non linear properties of Plasticized EPDM crosslinked at different density.

With tan δ = G"/G' the loss tangent, μ the density of chemical crosslinking bridges, Ge the equilibrium elastic modulus, η^*_{EPDM} the absolute complex viscosity of the EPDM crosslinked at 50 rad.s^{-1} samples (η^*_{PP} = 2000 Pa.s at 200°C and 50 rad/s[49]), E Young's modulus, σ_r and ε_r the stress and strain at break respectively[56].

As also presented in Table 1, the tensile properties of the EPDM preparations have also been determined at a constant speed of deplacement (25 mm/min, T=25°C). Furthermore, by applying the Cox-Merz correlation between dynamic and steady flow viscosities we determined the viscosity ratios between these pre-crosslinked EPDM preparations and the isotactic PP at 200°C and 50 s^{-1} for further discussion.

These samples, showing a large panel of crosslink densities, were then cut into 1 mm^3, dimension very similar to the size of the PP granules used for the following blending. Such blends were prepared using isotactic PPH3060 and each of the previous EPDM samples at 200°C without any additional plasticizer. Blends were dumped after stabilization of the torque and left to cool at room temperature. Sampling of the material has been done within the blender at various times in order to assess the variation of the morphology of the blend with the time of mixing.

The first series (Blends 1 to 5) was made using 80% of PPH3060 and 20% of each of the 5 crosslinked and plasticized EPDM samples. The second series (Blends 6 to 10) was prepared using 30% of the same isotactic polypropylene and 70% of each of the 5 EPDM preparations, leading to the 10 blends made of pre-crosslinked EPDM preparations.

II.2.2. Uncrosslinked and dynamically crosslinked PP/EPDM blend elaboration

Additionally to these blends 1 to 10 made of pre-crosslinked EPDMs and either 80 or 30% of polypropylene, we prepared two blends with the reference quantities of reactants (i.e. 4 phr of resol + 0.6 phr of SnCl2) but by crosslinking the EPDM under shearing in presence of either 80 or 20% of PP. These blends were thought to highlight the importance of the dynamic crosslinking route on the final morphology and mechanical properties. Furthermore, two blends were also prepared without any curing agent for comparison purposes.

Blend	% PP	% EPDM	% Plasticizer	% Resol	% Catalyst
DynCross1	80	12.15	7.30	0.48	0.07
DynCross2	30	42.55	25.50	1.70	0.25
Uncross1	80	12.5	7.5	/	/
Uncross2	30	43.8	26.2	/	/

Table 2 - Uncrosslinked and dynamically crosslinked blend compositions (% in weight).

Thus, as presented in Table 2 for these 4 blends, the elastomer was first introduced into the blender and sheared by itself for 2 minutes at 120 rpm and 200°C in order to ensure the fragmentation of the elastomer. The plasticizer was then poured in and the blend was mixed at 50 rpm until torque stabilization. As soon as the torque had stabilized, the polypropylene was introduced and the torque was left to stabilize. For blends 'DynCross1' and 'DynCross2', the curing system (resol and catalyst) was added and the mixing was allowed to go on for 10 minutes to ensure the complete crosslinking of the EPDM. Finally the blends were compression molded at 200°C for 2 minutes into 1 mm thick samples which were stored away from light and heat until testing. Insoluble fraction measurements led to the conclusion that both the samples crosslinked under shearing show a gel fraction of 1, whereas the uncrosslinked samples were confirmed not to have sustained any crosslinking during their elaboration (gel fraction ~ 0).

Additionally, all these blends sustained tensile experiments at room temperature with an imposed longitudinal deplacement speed of 25 mm/s.

II.3. Morphology characterization

The morphology of these blends was first observed using a Scanning Electron Microscope (SEM) Hitachi S800 instrument. The samples were cryofractured in liquid nitrogen to avoid any morphology alteration. The EPDM phase was selectively extracted as previously described[45]. The fractured surfaces were sputter-coated with gold in order to deposit a 50 nm homogeneous conductive layer. Additionally, Transmission Electron Microscopy (TEM) was another helpful and complementary means of characterization. All blends were observed using a Philips CM120 microscope after preparing the sample surface via an ultra cryo-microtomy process. Samples were ultra-microtomed into 50 nm thin films at -110°C using a crystal blade to ensure that no phase deformation occurred (as these sample preparations were realised below both the PP and EPDM glass transition temperatures). Samples were then marked using a Ruthenium oxide solution which induced an oxidation and fixation of the metal on the diene functions of the EPDM thus showing dark on MET micrographs due to the diffusion of the electrons by the fixed metal[57]. All micrographs and sample preparations were done at the Technological Centre of Microstructures of the University of Lyon 1.

III. Results

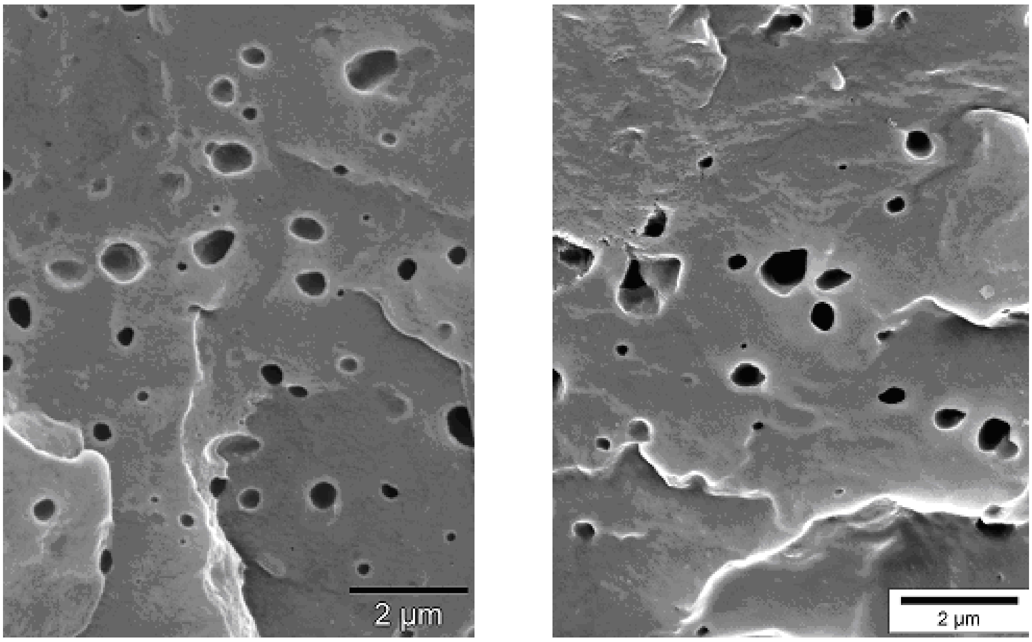
In order to better understand some of the mechanisms involved in a TPV elaboration, we intended to study the dispersion of pre-crosslinked EPDMs having various gel fractions as it would reflect the identical evolution of the EPDM phase right after the crosslinking step during a TPV elaboration. The experiments aimed at estimating the influence of the shearing on both uncompatibilised phases having such a low interfacial tension, and at assessing the possibility of breaking and dispersing such networks in a immiscible thermoplastic phase without any compatibilization. By doing so, we decoupled the mechanisms by focusing only on the contribution of the shearing and the time of blending on the dispersion of pre-crosslinked EPDM samples having preset gel fractions, at various proportions.

III.1. Blend morphologies

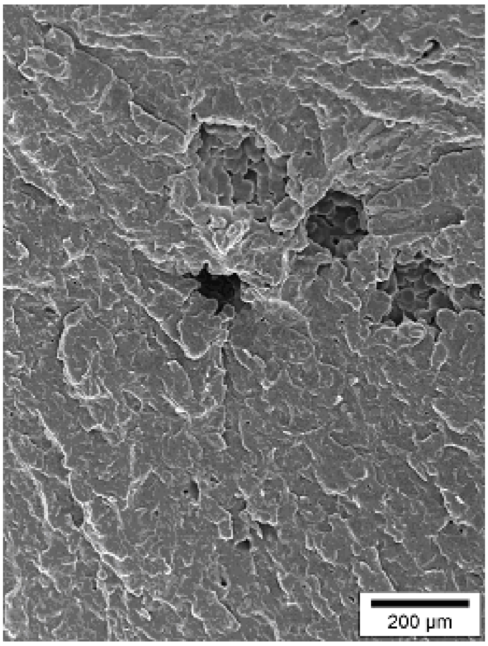
The aim was first to assess the morphologies of both 80/20 and 30/70% PP / pre-crosslinked, uncrosslinked or dynamically crosslinked EPDM blends after 10 minutes of mixing.

III.1.1. PP/EPDM blends at 80/20% ratio

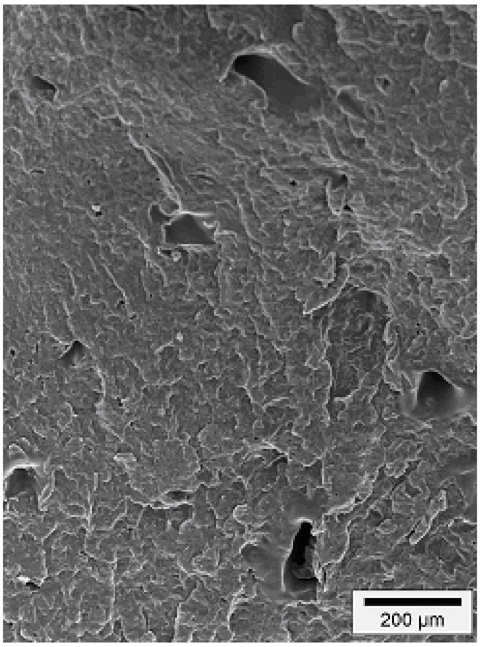
All blend morphologies are present in Figure 2.



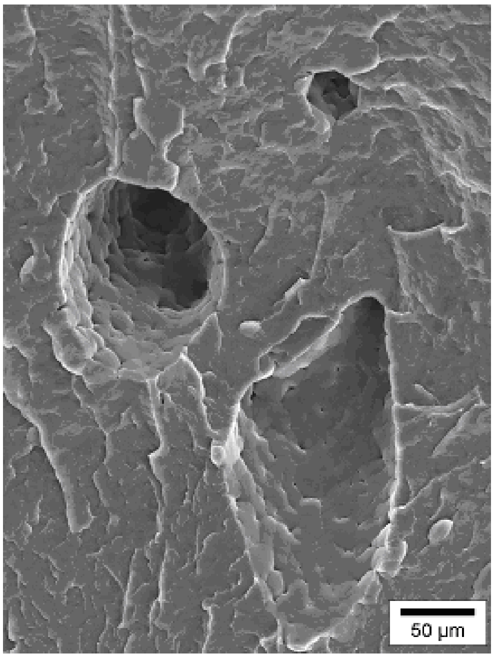
a) b)



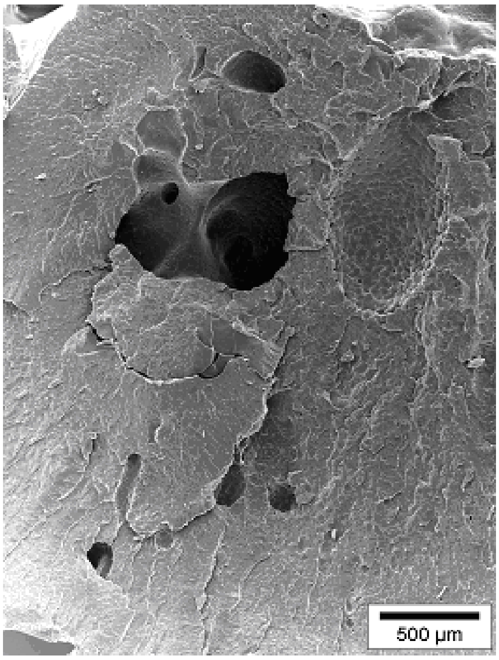
c)



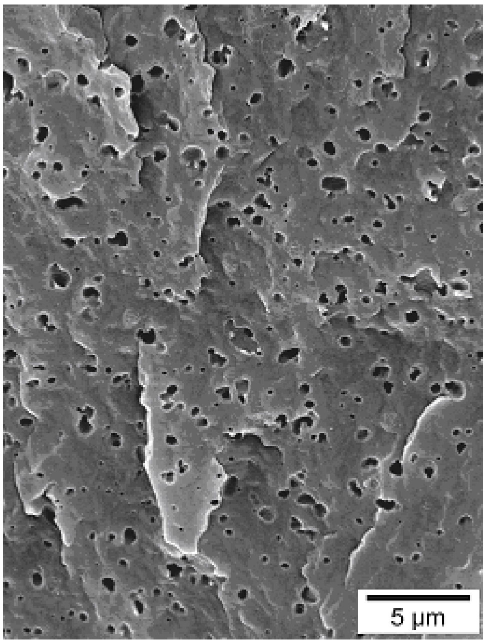
d)



e)



f)



g)

Figure 2 - SEM micrographs (a to g pictures) of PP/EPDM blends in 80/20 (%wt) after 10 minutes of mixing, with :

a) the uncrosslinked blend ‘UnCross1’,

b) Blend 1 made of ‘RES1/30’ – gel fraction in the EPDM phase : $g_{EPDM} = 0.7$

c) Blend 2 made of ‘RES1/10’ – $g_{EPDM} = 0.896$

d) Blend 3 made of ‘RES1/7’ – $g_{EPDM} = 0.962$

e) Blend 4 made of ‘RES1/4’ – $g_{EPDM} = 0.989$

f) Blend 5 made of ‘REF’ – $g_{EPDM} = 0.998$

g) the dynamically crosslinked blend ’DynCross1’ – $g_{EPDM} \sim 1$

As we can see in Figure 2, all blends show a continuous PP matrix with a dispersed EPDM phase. This type of morphology was expected thanks to the various semi empirical models predicting such immiscible blend morphologies at such compositions and viscosity ratios[58].

As any would expect, Blend 1 (made of an EPDM having a 0.7 insoluble fraction) shows a homogeneous morphology made of a continuous PP matrix with micrometric and submicronic EPDM nodules whose size varies from 100 nm to 2 µm. Only rare nodules of a size above 2 µm have been noticed. Blend 1 morphology is thus nearly identical to the blend ‘UnCross1’ made of uncrosslinked EPDM which shows perfectly dispersed EPDM nodules all smaller than 1 µm. Thus, a 0.7 insoluble fraction does not induce any major influence on the dispersion of the EPDM within such a majoritary PP phase. Thus, even above the gel point such a chemical network can be as finely dispersed as uncrosslinked EPDM whereas their rheological behaviours are significantly different.

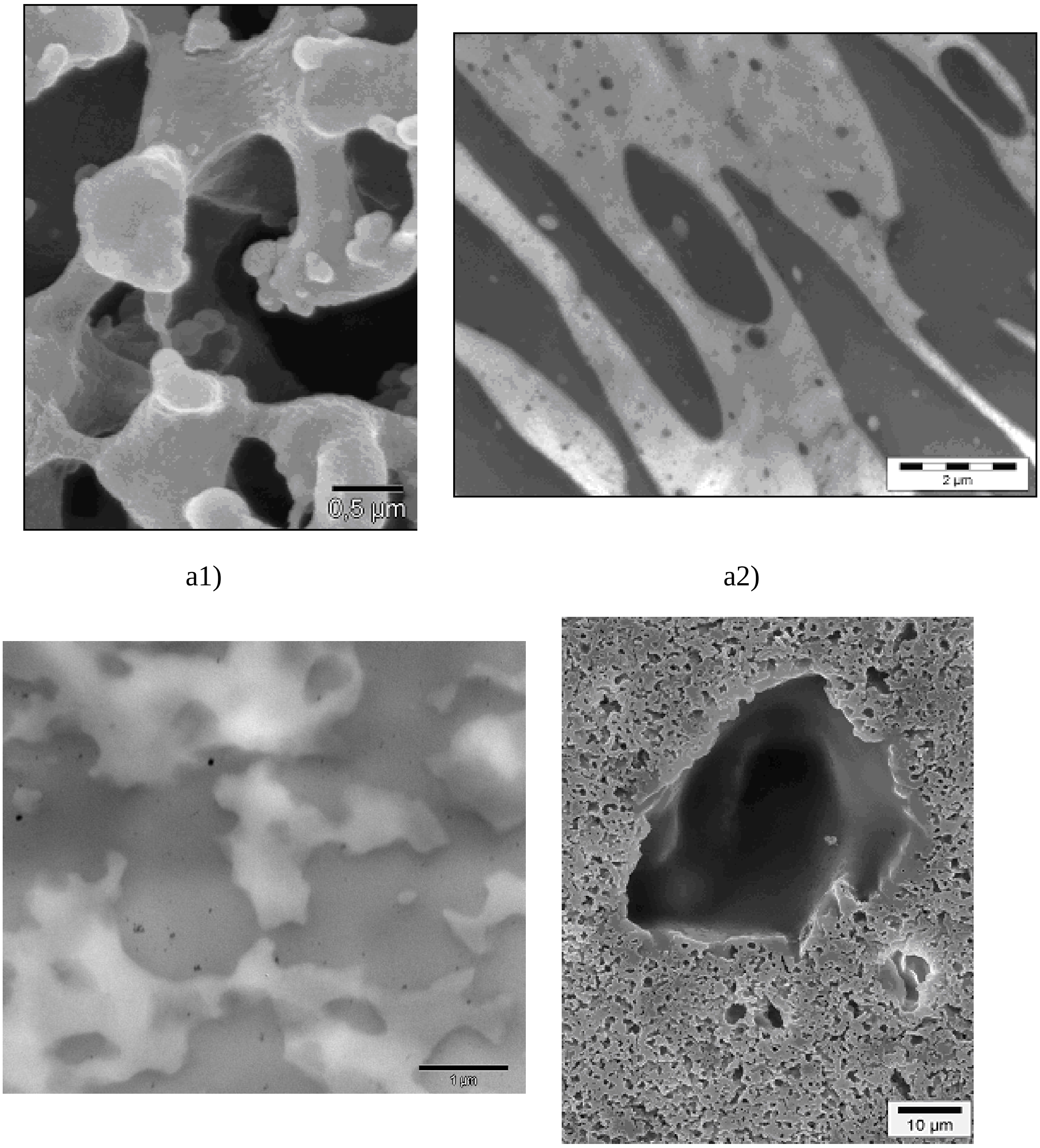
Blend 2, made of an EPDM having a 0.896 insoluble fraction, has shown a morphology very similar to Blend 1 with a continuous PP phase but with clearly thicker dispersed nodules of EPDM with a size varying from 1µm up to 100µm.

Concerning Blends 3 to 5, their morphology is rough and very heterogeneous, and these samples can not be moulded properly because of the presence of EPDM fragments with a size increasing with the crosslink density of the EPDM. Thus the more the EPDM is crosslinked prior to blending the less it gets fragmented and dispersed homogeneously within the PP phase. For EPDM samples having an insoluble fraction under 0.9 the EPDM may get fragmented into micrometric and submicronic nodules whereas only big nodules and fragments of several hundreds of micrometers remain for blends made of pre-crosslinked EPDM having a higher insoluble fraction. Thus, there is a limit behond which a crosslinked EPDM can not be fragmented and finely dispersed within the PP and will remain into rough fragments under these processing conditions. Nevertheless we can appreciate that in every cases the EPDM networks still get fragmented somehow. And the EPDM dispersed phase finally shows, after 10 minutes of blending, a fairly nodular shape. Thus, even for pre-crosslinked EPDM networks having a high chemical crosslink density we can notice that this shearing rate manages to significantly reduce the size of the original EPDM fragments and leads to large nodules. The size and size polydispersity of these nodules increase with the increasing pre-crosslink density of the EPDM.

Finally, comparing Blend 5 and the blend made of dynamically crosslinked EPDM / PP blend (both blends having the same compositions) we can easily notice the radical differences of the morphologies : for blend 5 the pre-crosslinked EPDM could not be dispersed properly, whereas the dynamically crosslinked blend presents a morphology nearly as good as the uncrosslinked blend or Blend 1. Although this ‘DynCross1’presents an insoluble fraction of 100% it is perfectly homogeneous. The dynamically crosslinked EPDM nodules are very thin and round with a narrow size polydispersity. Under these blending conditions the crosslinking kinetics under shearing thus allow a fine dispersion of crosslinked EPDM nodules within the matrix whereas it is impossible to obtain such a homogeneous morphology when trying to disperse pre-crosslinked EPDM preparations having the same gel fraction. This conclusion emphasizes the importance of the processing on the TPV final morphology.

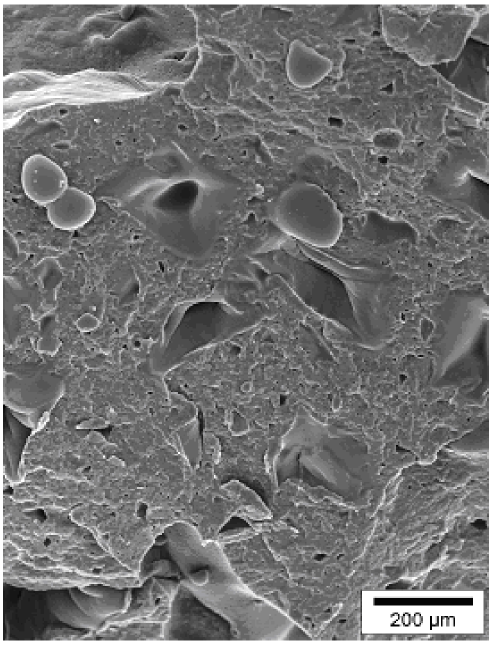
III.1.2. PP/EPDM blends at 30/70% ratio

This blend proportion is surely the most interesting one as 30/70 PP/EPDM blend can lead to co-continuous morphologies which may induce an atypical viscoelastic behaviour as described in our previous paper[45].

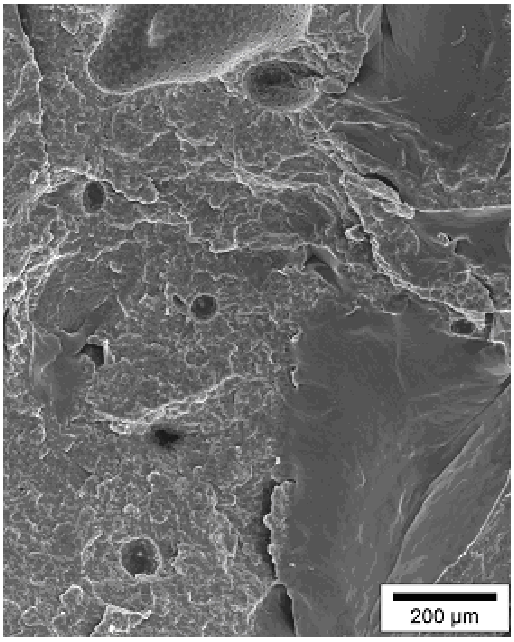


a1) a2)

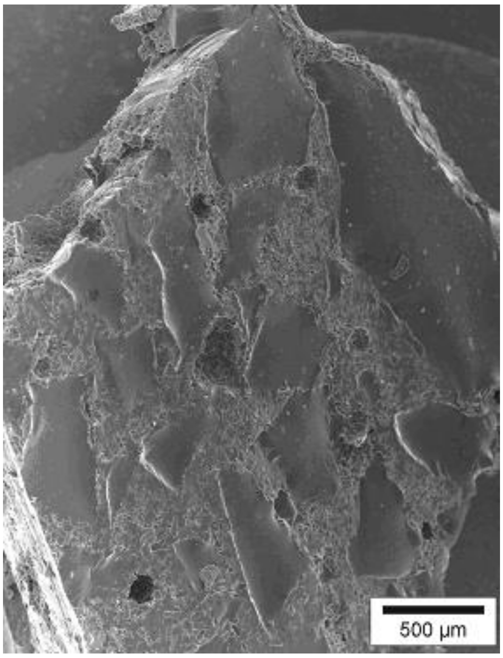
b1) b2)



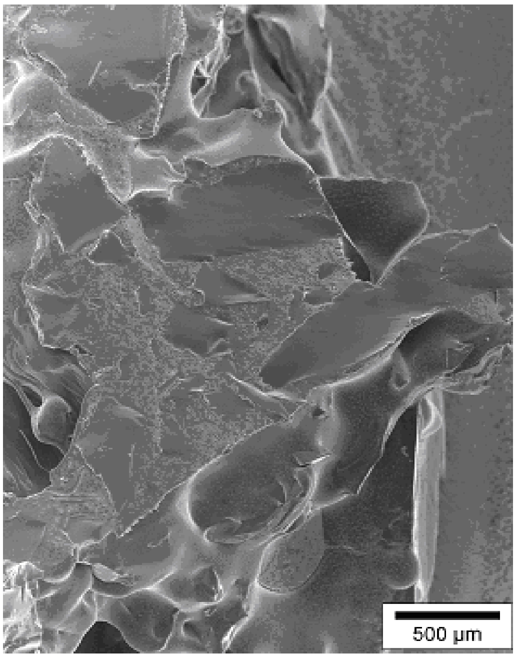
c)



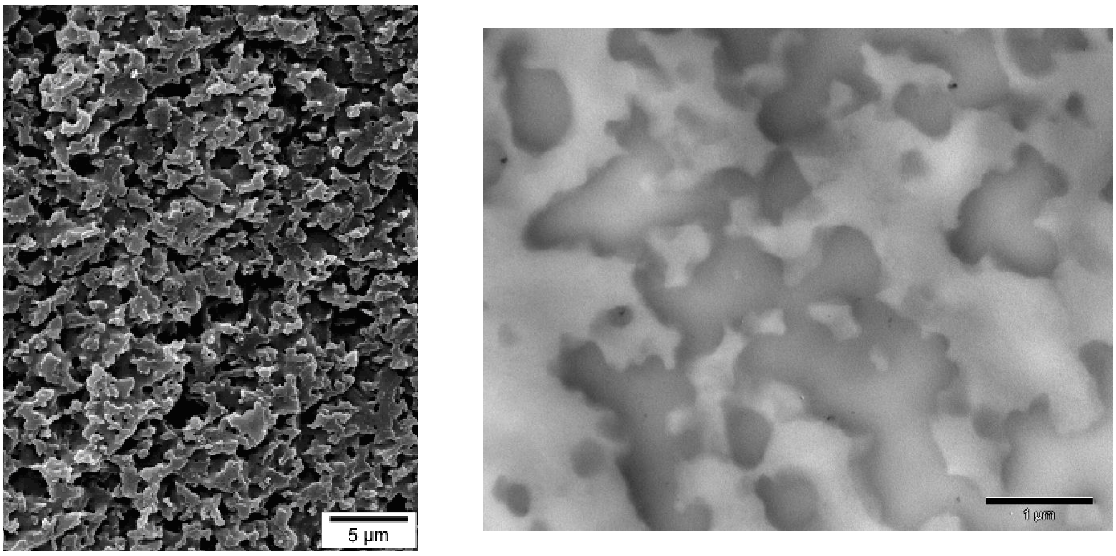
d)



e)



f)



g1) g2)

Figure 3 - SEM and TEM micrographs of PP/EPDM blends (30/70) after 10 minutes of mixing, with :

a1 and a2) the uncrosslinked blend ‘UnCross2’ at different scales,

b1 and b2) Blend 6 made of ‘RES1/30’ – g_{EPDM} = 0.7

c) Blend 7 made of ‘RES1/10’ – g_{EPDM} = 0.896

d) Blend 8 made of ‘RES1/7’ – g_{EPDM} = 0.962

e) Blend 9 made of ‘RES1/4’ – g_{EPDM} = 0.989

f) Blend 10 made of ‘REF’ – g_{EPDM} = 0.998

g1 and g2) the dynamically crosslinked blend ’DynCross2’ – g_{EPDM} ~ 1

As exhaustively discussed in our previous paper[45], the blend made of uncrosslinked EPDM shows a perfectly homogeneous and co-continuous morphology where the size of the two continuous phases ranges from around 1 to 2 µm with nodules of one phase included into the other of dimensions varying from 50 to 500nm (cf. Figures 3 a1 and a2). Upon these results we studied the morphologies of the blends made of pre-crosslinked EPDM at this precise blend composition to assess the impact of the crosslink density of the EPDM on the final blend morphology.

Hence, Figures 3b1 and 3b2 show that Blend 6 (made of the pre-crosslinked EPDM preparation ‘RES1/30’ having the lowest gel fraction i.e. 0.7) is partially made of a clearly continuous PP phase with numerous EPDM nodules of a few micrometers wide perfectly included into it, but also presents some large co-continuous regions. As a matter of fact, as this EPDM has a very low but yet significant pre-crosslink density its viscosity is obviously higher than an uncrosslinked EPDM. Nevertheless, this EPDM preparation has actually been quite well dispersed in the matrix and the morphological changes are not that important since, apart from some residual nodules, Blend 6 is co-continuous in its majority. Some nodules are still present and the morphology is not as thin and homogeneous as the uncrosslinked blend, but the chemical network has actually been efficiently fragmented and dispersed in the thermoplastic leading to a partially co-continuous blend having a crosslinked elastomeric phase.

On the contrary, all other blends (7 to 10 i.e. for $g_{EPDM} > 0.896$) do not present a co-continuous morphology. Blend 7 (made of a pre-crosslinked EPDM preparation having an gel fraction of 0.896%) shows numerous large EPDM fragments and its dispersion within the continuous PP matrix has not been very effective. Looking at the micrographs of Blends 8 to 10 (made of pre-crosslinked EPDM having a gel fraction of 0.896 0.989 and 0.998 respectively) the higher the original EPDM crosslink density, the less it gets fragmented and dispersed.

In this Figure 3, the PP phase can be distinguished (still present) from the removed clusters and fragments of EPDM, nevertheless the extraction of such big EPDM fragments was not fully achieved due to their impressive size and rough shape as we can see for Blends 8 to 10. At this stage of the blending some huge aggregates are fully included in the continuous PP matrix and very few micronic nodules of EPDM are present in the PP phase. As a matter of fact, Blends 8 to 10 could not be moulded properly under a press and turned into powders due to the presence of too numerous and huge heterogeneities. Nevertheless, we can still note that even these EPDM preparations having high crosslink densities still got partially fragmented although they did not lead to homogeneous blends.

Nevertheless, the dispersion of the EPDM is not effective at all: such blends are far from reaching the co-continuity. The highly pre-crosslinked EPDMs can not been fragmented efficiently and large fragments have segregated from the matrix which is only made of a PP continuity. Co-continuity has thus been totally cancelled because the EPDM networks are too dense to be fragmented and dispersed under those relatively soft blending conditions.

Therefore, increasing the gel fraction above 0.7 forbids any proper dispersion of the EPDM and homogeneous morphology under these conditions. The pre-crosslinked EPDM fragments did not sustain a sufficient continuous shearing and then could not be deformed, broken and dispersed properly.

Furthermore, as we can see in Figures 3g1 and 3g2, the dynamically crosslinked blend 'DynCross2' exhibits a co-continuous structure which is very similar to the one observed by Bhadane and al.[59, 60], showing a continuous PP phase combined with the co-continuous and fully crosslinked elastomeric phase. We can thus assess the morphological differences induced by the dynamic crosslinking of the EPDM phase in presence of PP in opposition to the simple blending of the pre-crosslinked EPDMs with PP. Indeed, Blend 10 and the dynamically crosslinked blend 'DynCross2' have identical compositions but their morphology is radically different as observed in Figure 3. The dispersion of a pre-crosslinked EPDM preparation having a very high insoluble fraction is very rough and lead to a very coarse morphology as seen for Blend 10. On the opposite, the dynamic crosslinking of the EPDM under shearing leads to a fine and regular co-continuous morphology under the processing protocol. Actually, above a gel fraction of 0.7 the elastomeric phase cannot properly disperse under these experimental conditions and blend proportion. The impact of the crosslinking route is thus evident. It is clearly impossible to finely disperse an EPDM having a gel fraction close to 1 under these conditions nevertheless the crosslinking under shearing leads to a co-continuous morphology with an EPDM phase having a gel fraction close to 1. Thus, to stabilise a homogeneous morphology it is necessary to disperse the EPDM before its gel fraction reaches 0.7. Such a processing requirement is thus vital in order to combine the thermoplastic with a fully crosslinked EPDM phase into a co-continuous and homogeneous morphology.

III.2. Morphology development

To better understand these morphologies, the following part aims at bringing additional information on the mechanisms involved in the morphology stabilization of such pre-crosslinked EPDM networks in both PP/EPDM proportions used previously. For illustrative purposes, two representative kinetics have been selected : Blend 5 (made of 20% of the pre-crosslinked EPDM preparation 'REF' – $g_{EPDM} = 0.998$) and Blend 7 (made of 70% of pre-crosslinked EPDM preparation 'RES1/10' – $g_{EPDM} = 0.896$). Such a study has been achieved by taking samples at the exact same location within the internal mixer at various times of blending, thus allowing us to follow the blend morphology evolution with the time of mixing.

III.2.1. Blend 5 (80% PP / 20% EPDM prep. 'REF' – g_{EPDM} = 0.998)

These results aimed at studying the viscoelastic deformation, break up and dispersion of highly pre-crosslinked EPDM droplets within a majoritary thermoplastic phase. Hence, the evolution of the morphology of Blend 5 was characterized over 45 minutes of blending.

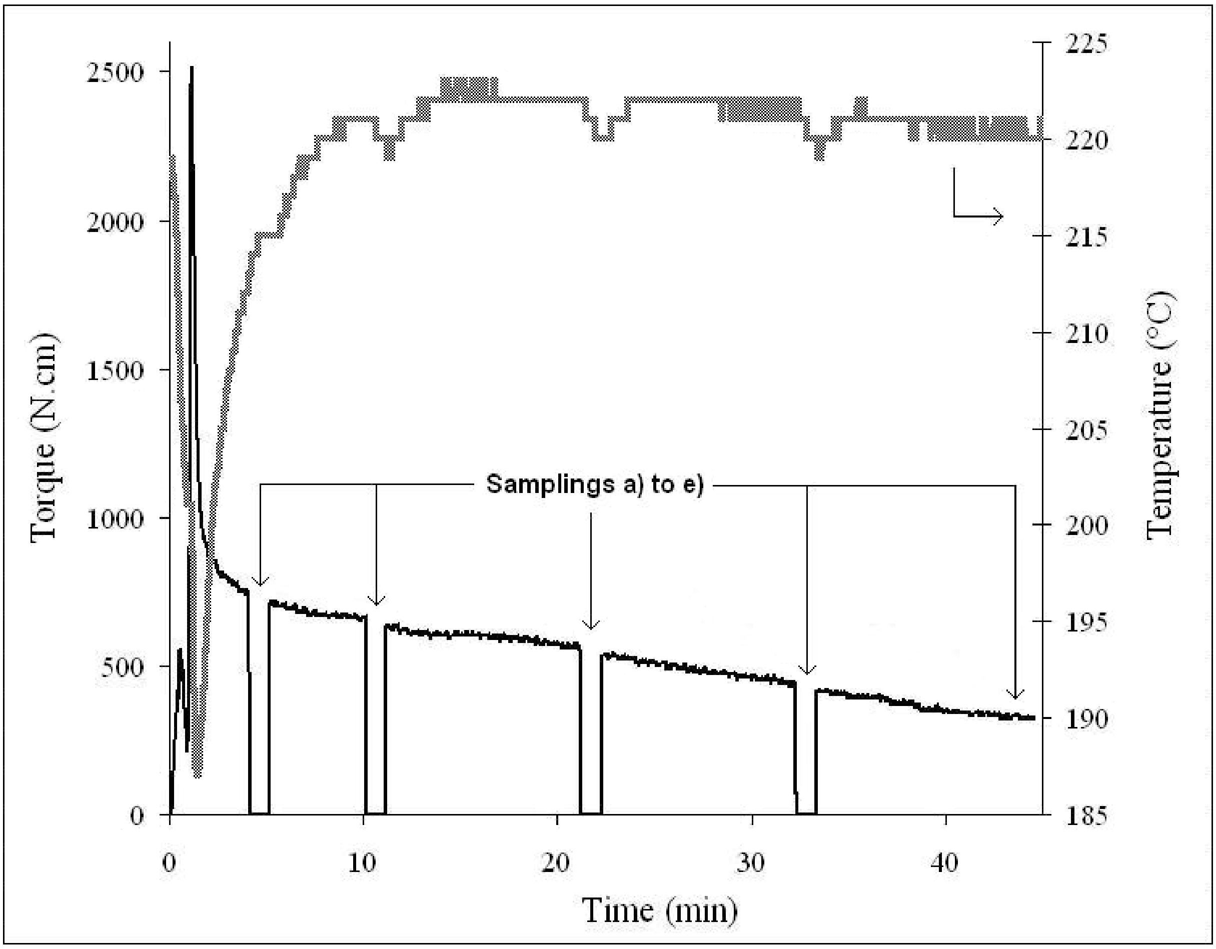
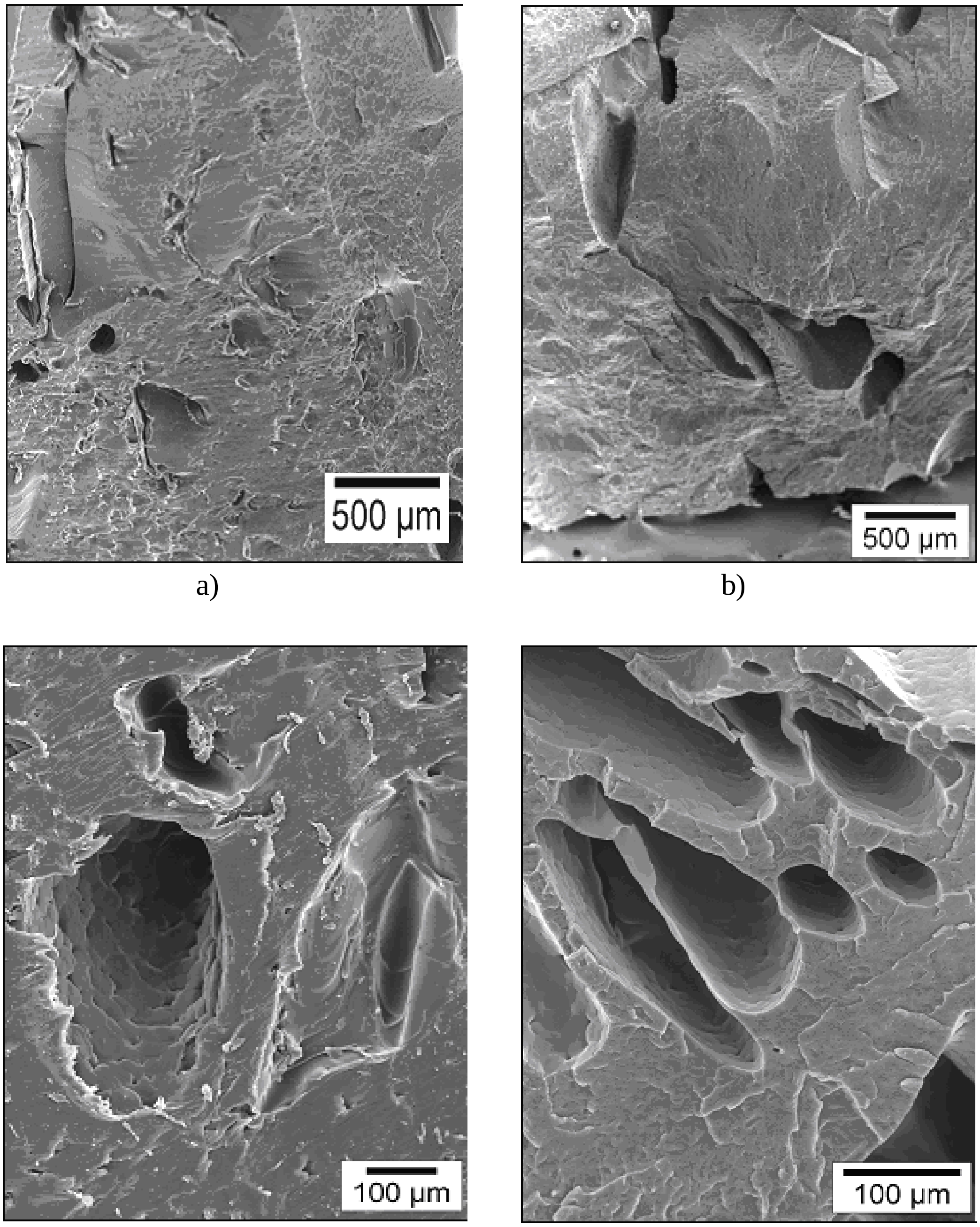


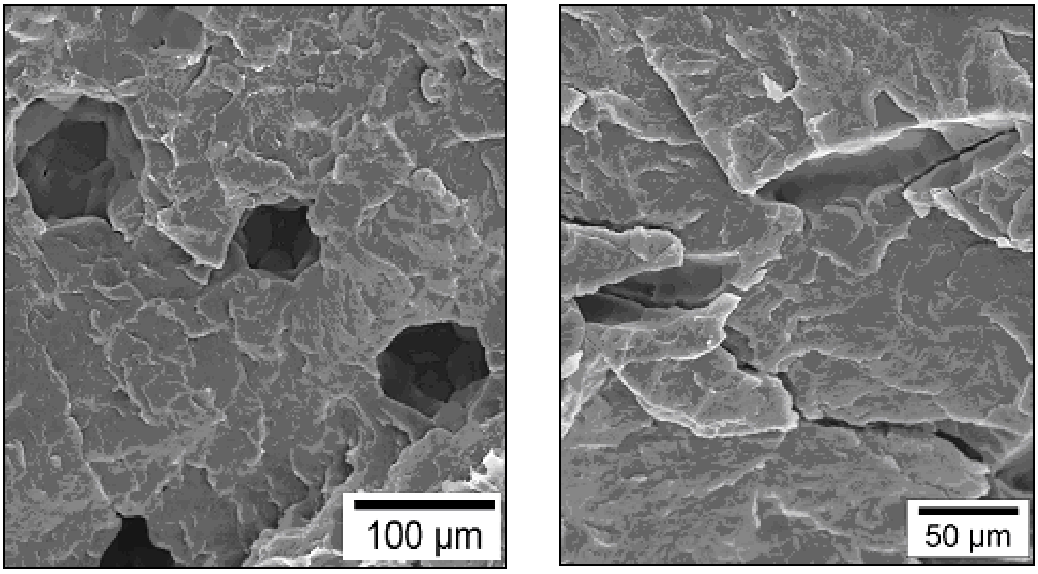
Figure 4 – Torque, temperature and samplings during the processing of Blend 5.

First of all, as shown in Figure 4, the strong decrease of the torque, right after the introduction of the pre-crosslinked EPDM preparation 'REF' (g_{EPDM} = 0.998) and the PP, is due to the melting of the PP and homogenisation of the blend temperature which stabilises within the first 10 minutes. Nevertheless, the torque keeps decreasing regularly over the next 35 minutes of blending whereas the temperature is kept constant. Although this could be induced by the slight and progressive degradation of the PP at this temperature, this torque decrease has to be mostly related to the morphological evolution which is progressively occurring over such a period of time, as demonstrated in Figure 5.



a) b)

c) d)



e1) e2)

Figure 5 - SEM micrographs of Blend 5, made of 80% of PP and 20% of the pre-crosslinked EPDM 'REF' (g_{EPDM} = 0.998) after a) 3, b) 8, c) 18, d) 28, and e1-e2) 45 minutes of blending.

After 3 minutes of blending, the fragments of the pre-crosslinked EPDM preparation 'REF' are virtually intact as shown in Figure 5a: their average size is above 400 µm and some of them are actually still present at their original size and shape. This high crosslink density network may not be broken over such a short period of time with such a shearing and process. After eight minutes of blending, Figure 5b shows that the EPDM is now present as large fragments of around 300 µm wide thus several times smaller than their original size. At this point, the breaking up mechanism induced by the shearing of the phases provokes a modification of the shape of the EPDM fragments as they start to look like huge nodules a few hundreds of micrometers large. Thus, even in presence of a largely continuous molten (thus soft) thermoplastic phase, such shearing can allow some significant erosion and deformation of such a dense chemical network. The mechanical stress induced by the matrix does not forbid the deformation and breaking up of the original EPDM fragments into smaller filaments and nodules.

As the time of blending increases, the size of the EPDM nodules slowly and progressively decreases, and their shape tend to be more fibrilar, highlighting a progressive and ongoing deformation and dispersion of the elastomeric phase as we can observe in Figures 5c and 5d. This finally leads, after 45 minutes of blending, to long EPDM filaments and nodules of around 50 and up to 200 µm as shown in Figure 5 e1 and e2. We could not notice any EPDM nodule of a size below 50 µm at any stage of the blending. Thus such a highly crosslinked chemical network can actually be dispersed over time under this shearing rate. The large EPDM nodules get stretched and deformed by the shearing and broken down into smaller nodules and filaments, but the quality of the dispersion is still quite rough and leads to a heterogeneous material due to the size of the EPDM phase.

III.2.2. Blend 7 (30% PP / 70% EPDM prep. 'RES1/10' – g_{EPDM} = 0.896)

This second kinetic test aims at investigating the morphology development of an EPDM preparation having a relatively low crosslink density in presence of 30% of PP. As discussed previously, blends made of pre-crosslinked EPDM preparations having an insoluble fraction above 0.9 lead to un-cohesive materials after 10 minutes of blending. Therefore, we chose to study the dispersion of the pre-crosslinked EPDM preparation 'RES1/10', having a gel fraction close to 0.9 as it will clearly show the influence of the time of blending.

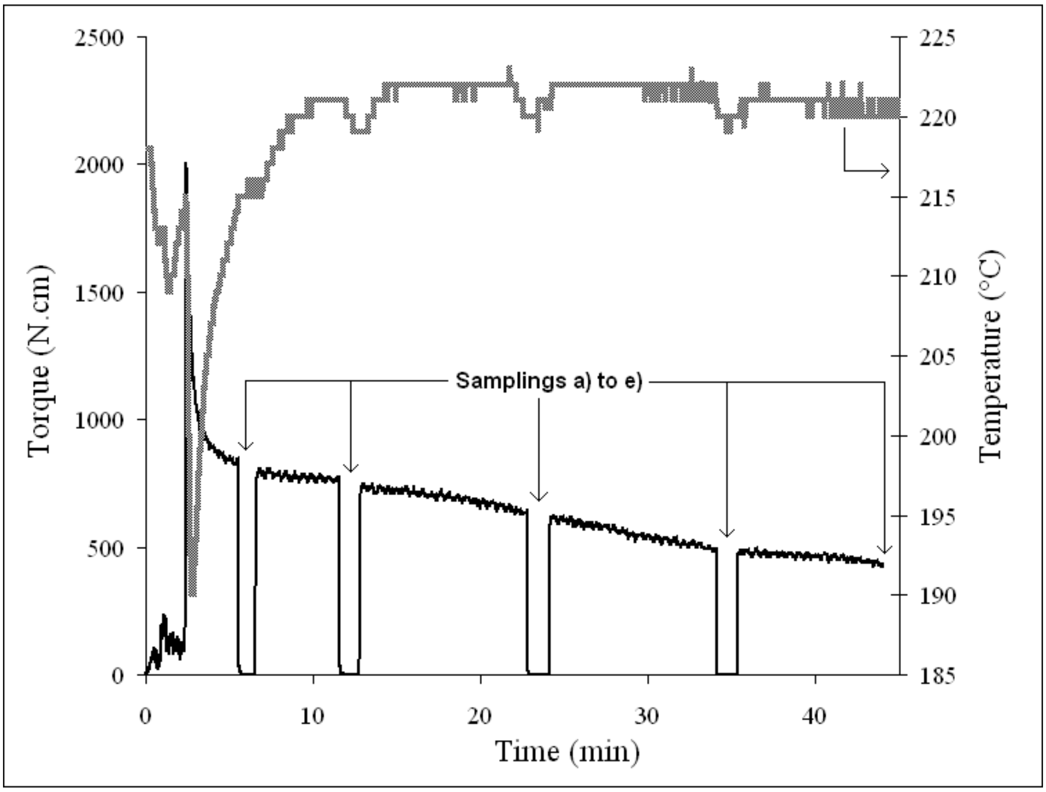
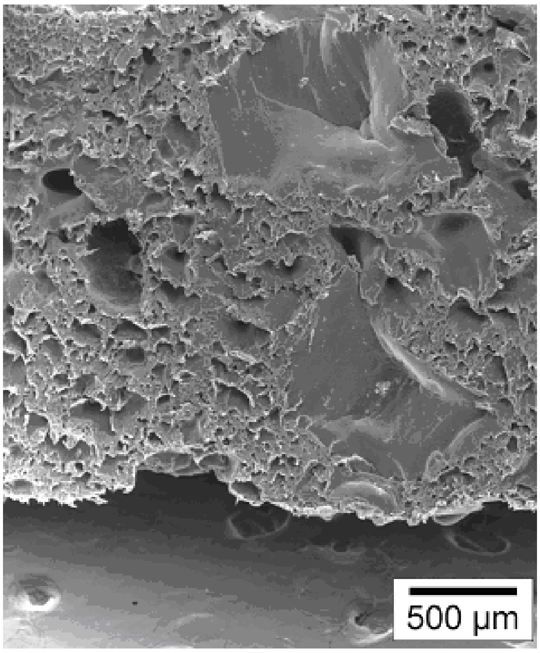
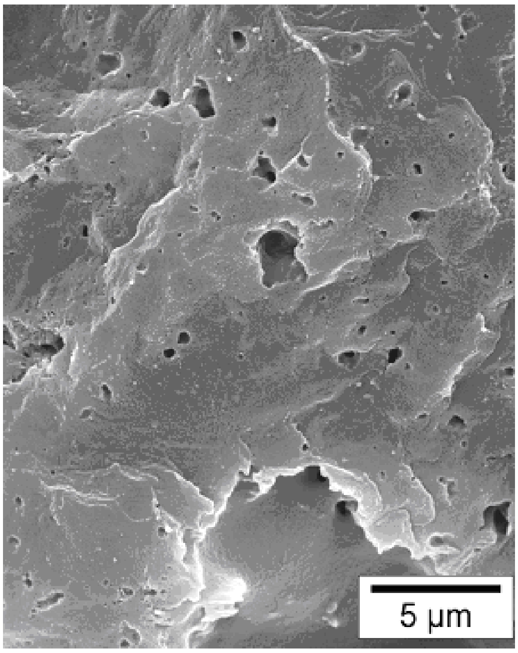


Figure 6 – Torque, temperature and samplings during the processing of Blend 7.

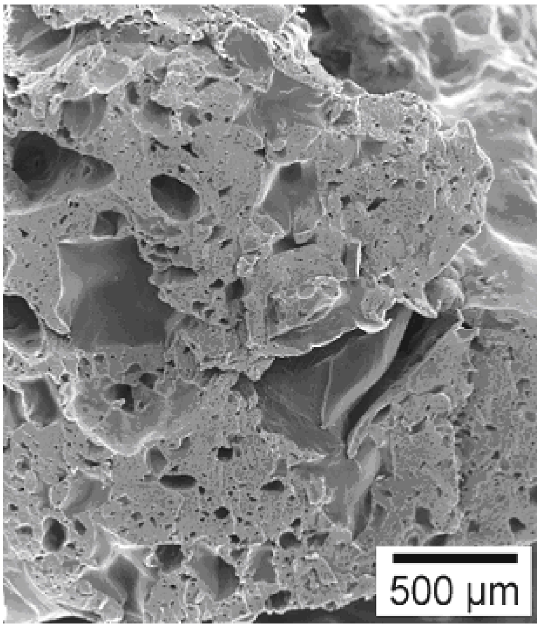
As it can be seen in Figure 6, and similarly to the previous kinetic study, the torque shows a progressive stabilization over the 45 minutes of blending. The following SEM micrographs present the evolution of the blend morphology with the time of mixing.



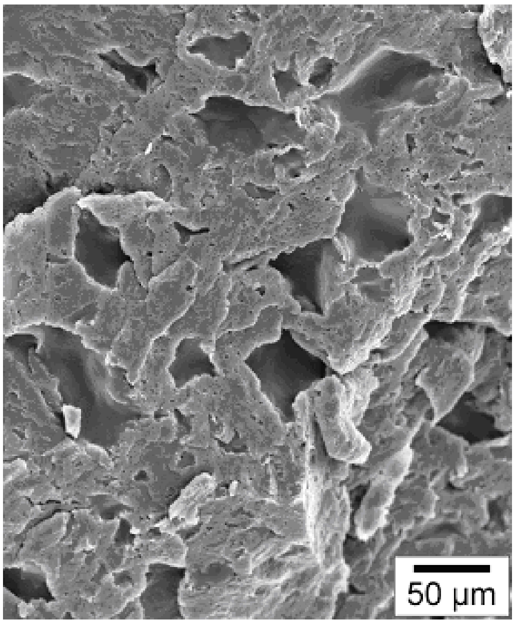
a1)



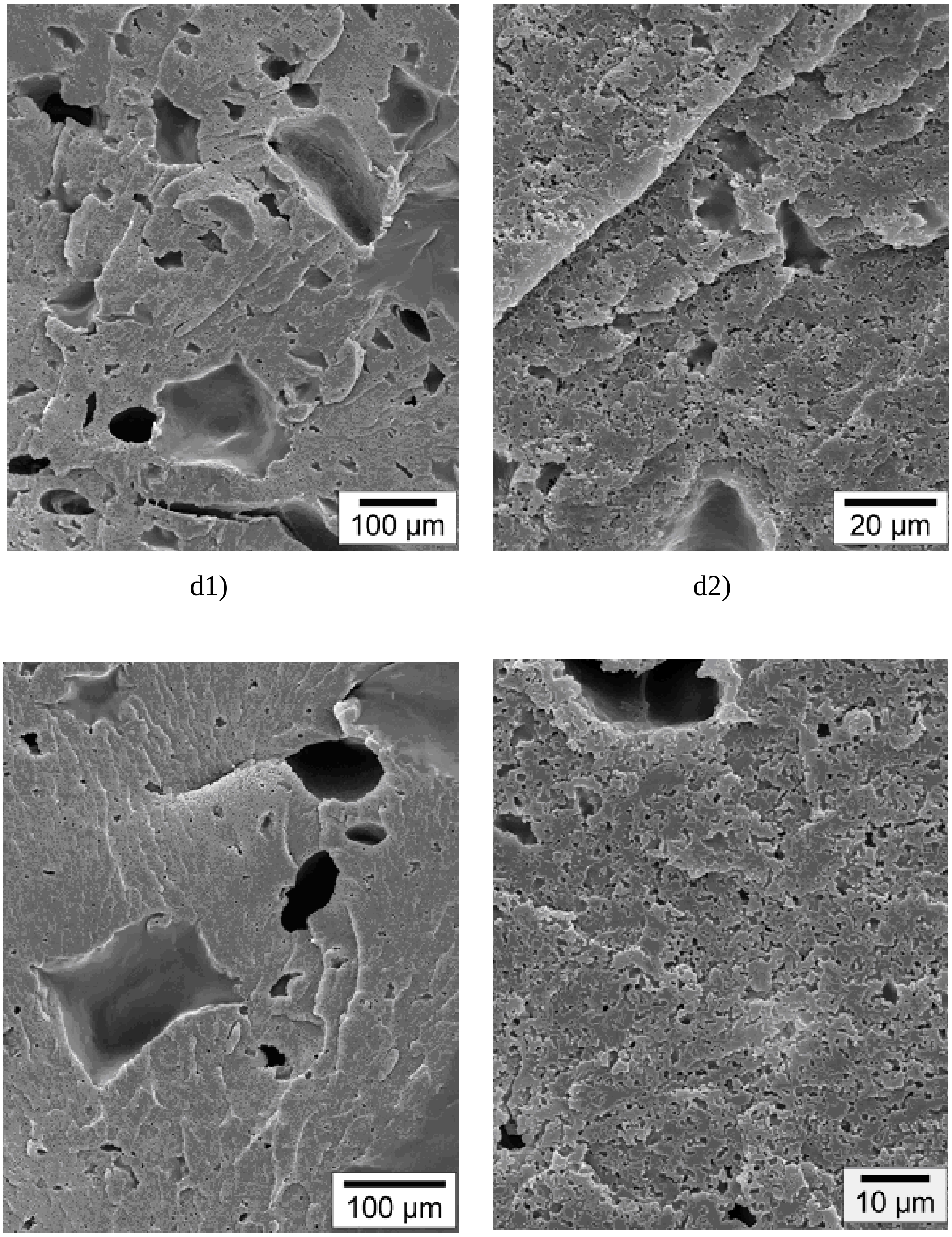
a2)



b)



c)



d1) d2)

e1) e2)

Figure 7 – SEM micrographs of Blend 7, made of 30% of PP and 70% of the pre-crosslinked EPDM ‘RES1/10’ (g_{EPDM} = 0.896) after a1-a2) 3, b) 8, c) 18, d1-d2) 28, e1-e2) 45 minutes of blending.

Figures 7a1 and 7a2 show that, after only three minutes of blending, the pre-crosslinked EPDM is present as fragments of around 500µm but also as sharps nodules of 2 µm dispersed in the PP continuous phase. The size polydispersity is very broad and the shape of the EPDM fragments is always sharp. The large majority of the pre-crosslinked EPDM preparation ‘RES1/10’ (having a gel fraction of 0.896) has been fragmented into 100 µm-large fragments dispersed into the PP matrix. The EPDM network is clearly under fragmentation and the morphology has not stabilised yet. After eight minutes of blending, the PP phase is still continuous but gets richer in EPDM nodules and the size of the EPDM fragments is clearly decreasing, as we can observe in Figure 7b. The fragmentation thus affects the entire fraction of the EPDM which can potentially, under these conditions, be partially broken down and dispersed within such a thermoplastic phase. Ten minutes of blending later, we can notice in Figure 7c very few fragments more than 100 µm wide, some of them having a nodular shape which confirms the role of the shearing on their deformation and stabilization. With the increase of the time of blending, the micrometric EPDM nodules get more and more numerous, the PP continuous phase gets richer in EPDM nodules and the number of huge fragments of a few hundreds micrometers decreases. Finally, the more time passes, the more the EPDM fragments get finely and homogeneously dispersed as small nodules. Nevertheless there are still important sharp fragments which have not been properly broken down even after 45 minutes of shearing. Anyhow the PP phase is always clearly continuous and only very rare regions present a slight co-continuity, indicating that such processing does not lead to the expected morphology. Furthermore, the fragmentation of the EPDM after 45 minutes of blending is still ongoing. Under these conditions it is thus not possible to achieve a homogeneous morphology even over such a long period of blending. Even though most of the EPDM gets fragmented into nodules, the morphology has not stabilized yet and the blend still appears very lumpy due to some remaining sharp EPDM fragments having a broad size polydispersity.

III.3. Mechanical Properties

III.3.1. PP/EPDM (80/20) blends

The mechanical testing of the different samples allowed us to assess the importance of the morphology on such blend properties.

Blend	E (MPa)	σ_s (MPa)	ε_r (%)
PP neat	660	28.7	640
UnCross1	470	20.7	520
1	380	18.5	20
2	310	14.8	12
3 to 5	< 280	< 13	< 10
DynCross1	510	19.8	530

Table 3 – Tensile properties (25°C, 25 mm/min) of all blends made of 80% of PP, with : E Young's modulus, σ_s the yield stress and ε_r the strain at break.

As expected, Table 3 shows that the properties of the blends made of pre-crosslinked EPDMs are drastically affected by their compounding route. Whatever the pre-crosslink density of the EPDM, the final properties are extremely poor especially regarding their elongation at break ε_r and yield stress σ_s. All properties are even more atrophied as the pre-crosslinked EPDM gel fraction increases. These blends actually show poor mechanical properties and appear uncohesive. The heterogeneity of the morphology of Blends 3 to 5 is such that it is extremely difficult to mould them into testing specimens under a press. The EPDM nodules, roughly broken down and dispersed within the PP phase, represent uncohesive defects which literally ruin the material macroscopic properties: the continuous thermoplastic phase sustains most of the elongational stress during testing and the presence of pre-crosslinked EPDM nodules strongly alters the yield threshold of the thermoplastic. The EPDM nodules thus act like inclusions which significantly disturb the deformation and yield behaviour of the PP phase under traction.

Comparatively, a blend made with 20% of uncrosslinked EPDM has a very similar traction profile to neat PP. Nevertheless, looking at Blend 1 it can be pointed out that its elongation at break is 32 times lower than that of a neat PP, and 26 times lower than that of the PP / uncrosslinked EPDM blend, whereas these two blends have very similar morphologies. Finally, the presence of a 0.7 gel fraction in the pre-crosslinked EPDM nodules, as for Blend 1, leads to a similar morphology but yet to very different mechanical properties even though the morphologies seem very similar. This definitely shows the impact of the presence of a low density chemical network phase into the PP matrix: even if its morphology seems pretty regular, the presence of the pre-crosslinked EPDM nodules dispersed in the PP matrix strongly alters the PP phase elongational deformation behaviour. And the higher the EPDM pre-crosslink density is, the less it gets finely fragmented, the less homogeneous the dispersion is, and the worse the mechanical properties of the blends get.

Nevertheless, looking at the dynamically crosslinked 'DynCross1' blend properties, very satisfactory tensile properties can be observed similarly to those of the blend made of uncrosslinked EPDM, or only PP. The crosslinking under shearing did not induce any significant weakening contrarily to all blends made of pre-crosslinked EPDMs. The dynamically crosslinked blend behaves as a cohesive material due to its homogeneous morphology and regular dispersion of the EPDM nodules, and its high insoluble fraction does not penalize its mechanical properties. Therefore, such a dynamic crosslinking of the EPDM under shearing in presence of the thermoplastic phase leads to an apparently improved cohesion of the blend phases which can not be achieved by simply blending pre-crosslinked EPDM into PP. Nevertheless, the explanation of such radical differences of the tensile behaviours of these blends having a nearly identical morphology is not trivial. Anyway, such results actually confirm the usefulness of the dynamic crosslinking step on the tight combination of the phase properties.

III.3.2. PP/EPDM (30/70) blends

Obviously, all blends having a majoritary EPDM proportion also sustained the exact same tensile testing in order to correlate their morphology to their mechanical properties.

Blend	E (MPa)	σ_r (MPa)	ε_r (%)
UnCross2	44	3.93	210
6	30	3.44	200
7	24	0.5	120
8 to 10	< 20	< 0.5	< 20
DynCross2	27	4,7	260

Table 4 – Tensile properties (25°C, 25 mm/min) of blends made of 30% of PP, with : E Young's modulus, and σ_r and ε_r the stress and the strain at break respectively.

First of all, as shown in Table 4, Blends 8 to 10, similarly to Blends 3 to 5 (made of the most highly pre-crosslinked EPDMs) show extremely poor tensile behaviours. These three blends did not present any co-continuity and clearly show large EPDM fragments of over 100 µm roughly included within the PP matrix. The presence of EPDM fragments bigger than 100 µm act like weak links which totally ruin the blend tensile properties. These blends are not cohesive at all and their poor mechanical properties are due to their very coarse morphology.

On the other hand, Blend 6 seems to have an inner structural cohesion as its tensile profile is very similar to the one relative to the blend made of un-crosslinked EPDM which presents a perfectly homogeneous co-continuity. And actually, among all blends made of pre-crosslinked EPDM, only Blend 6 has shown a partial co-continuity which has a significant impact on its traction profile. As a matter of fact, this Blend 6 also presented some regions with a continuous PP phase with dispersed 20µm large EPDM fragments and nodules which apparently represent only minor imperfections on a macroscopic scale. Although its morphology did not seem to be that homogeneous, the actual properties of this blend are not too much altered by the presence of the pre-crosslinked EPDM having an original gel fraction of 0.7.

In comparison, the tensile properties of the dynamically crosslinked blend are much better than the ones of the blends made of pre-crosslinked EPDMs. As seen previously, this blend shows a co-continuous morphology with a fully crosslinked EPDM phase: its traction properties are clearly better than all other pre-crosslinked blends proving once again the strong impact of the dynamic crosslinking on the cohesion of the material. Thus, despite the poor interfacial tension between such phases, the crosslinking under shearing lead to a very cohesive material made of a continuous PP matrix coupled with a continuous and fully crosslinked EPDM phase. In the end, apart from this dynamically crosslinked blend, the final mechanical properties of all these blends are always worse than the properties of the blend made of uncrosslinked EPDM, which emphasizes, once again, the very poor cohesion induced by the dispersion of pre-crosslinked EPDM, and the strong influence of the coarseness of the morphology on the final mechanical properties.

IV. Discussion

First of all and from a qualitative point of view, we can conclude from the blend morphologies that the higher the pre-crosslink density of the EPDM, the less effective its dispersion in presence of PP. The size polydispersity of the residual EPDM fragments and nodules increases with the pre-crosslink density, leading to very coarse and weak materials, whatever the proportions of the polymers. In the end, only EPDMs having an gel fraction below 0.7 will be significantly fragmented and dispersed homogeneously in presence of PP under such shearing.

Additionally, although the EPDM may not always be dispersed properly it always gets somehow broken and fragmented whatever its crosslink density and its proportion in the blend. Even in the case of the EPDM preparation having the highest pre-crosslink density, after 10 minutes of blending the average size of the EPDM fragments have been divided several times, from an original macroscopic scale to a microscopic scale. And this conclusion is valid for both 80/20 and 30/70 blend proportions. But under these experimental conditions, a pre-crosslinked EPDM having an insoluble fraction above 0.7 leave tremendous imperfections which will literally eradicate any proper mechanical behaviour and will lead to uncohesive materials. This first highlights the fact that the homogeneity of the morphology and the size of the EPDM inclusions have a drastic impact on such blend behaviours in tensile properties.

Nevertheless several considerations, based upon literature, are required in order to understand these observations, especially regarding the importance of the 0.7 gel fraction and the influence of the proportion of PP on the quality of the dispersion of the elastomer.

To begin, it must be taken into account the fact that the proportion of PP plays a significant role: the dispersion of the pre-crosslinked EPDM leads to fibrilar and nodular particles of EPDM mostly when the PP phase is majoritary, whereas such fragmentation and dispersion leads to rougher and sharper fragments with a broader polydispersity of size in the case of blends having a majoritary EPDM phase. This brings forwards the fact that the influence of the various mechanisms is different in function of the proportion of the polymers.

Increasing the proportion of the thermoplastic phase up to 0.7 obviously decreases the shearing stress within the blend due to the very low viscosity of the thermoplastic matrix at this temperature. This should, in theory, lead to a far worse fragmentation and dispersion of the elastomer when the PP phase is majoritary. Nevertheless, under such experimental and processing conditions, our results lead to the opposite conclusion: even though the residual nodules of EPDM are bigger in the case of blends having a clearly majoritary PP phase, the polydispersity of size and shape of the residual EPDM phase is much worse in the case of the blends having a higher EPDM proportion. Therefore, either the mechanisms involved in such morphology stabilization are different, or the contribution of the possible mechanisms is strongly affected by the proportion of the phases.

So first, in the case of the blends having a large proportion of PP (i.e. 80%), there has to be a continuous stress throughout the material thanks to the clearly majoritary and continuous PP matrix which includes the dispersed EPDM phase. This actually assures the continuity of the shearing stress applied to the dispersed phase throughout the blend. Whereas it is not the case when the EPDM phase is originally majoritary say for instance for Blends 6 to 10: here the presence of large fragments imbedded in the minoritary but still continuous PP matrix can not ensure a homogeneous stress continuity throughout the blend, thus perturbing the shearing of the phases. And under these conditions no phase inversion can happen. The large and hardly fragmented EPDM clusters reduce the impact of the shearing and lead to some inevitable mechanical breaking of the networks, which could explain the instantaneous reduction of the size of the fragments in the first couple of minutes for every blends.

Nevertheless, we have to look at the possible mechanisms and their importance in order to better understand the influence of the proportion of the thermoplastic phase on such polymer blend morphology stabilization.

First of all, we can affirm that our results agree with the conclusions of Deyrail and Cassagnau[53] saying that the elastomer droplet deformation decreases with the increase of the crosslink density. They observed a severe decrease of droplet deformation for elastomer droplets having a tan δ below 0.7. And we can see that our pre-crosslinked EPDM preparations 'RES1/4' and 'REF' actually present a tan δ below or equal to this value, and they both lead, in any proportion, to very coarse blends with residual and hardly broken down EPDM fragments.

Secondly, Fenouillot and Perrier-Camby[61] observed that, for a thermoplastic/thermoset with a gel fraction between 0.4 and 0.7, it was possible to make long and thin elastomeric fibers, which can potentially break up into droplets, within a thermoplastic matrix. Looking at our results it agrees with the same order of magnitude as we observe fibers under breaking and stretched droplets for blends made of pre-crosslinked EPDM having a gel fraction of up to 0.7.

Furthermore, the viscosity ratios between each of the pre-crosslinked EPDM preparation and the isotactic PP were determined, as presented in Table 1. We can notice the wide panel of viscosity ratios for these blends made of pre-crosslinked EPDM. In theory, there can hardly be any deformation and break up of dispersed viscoelastic droplets into a Newtonian matrix above a viscosity ratio of 4[53]. And this actually fits our observations well, as all blends made of either 'RES1/7', 'RES1/4' and 'REF' definitely show coarse morphologies and weakened mechanical properties. Nevertheless this conclusion is supposed to be valid only for uncrosslinked polymer droplets and Newtonian polymers.

Concerning the involved fragmentation mechanism, we can first consider the Rayleigh-Taylor instabilities in the case of immiscible fluids having significantly different viscosities[62, 63]. The interpenetration and interdiffusion of materials may occur due to the dynamic process by which the two fluids seek to reduce their combined potential energy. In that case the ensuing turbulence and mixing can lead to the appearance of heterogeneities and contribute to the phase dispersion of one phase into another.

Additionally, for blends having a clearly continuous PP phase, the stress induced by the shearing is continuous throughout the blend and the pre-crosslinked EPDM may get deformed according to the deformation mechanisms which have been originally studied by Grace[64] and Leal[65], but more recently detailed by Huneault and Sundararaj[66-70].

As a matter of fact, for all blends made of pre-crosslinked EPDMs, the elastomeric phase has to sustain a deformation due to the shearing stress imposed by such a blender along its inside walls and along the roller rotors, leading to long filaments which will eventually break up into nodules. This elastomer break up may be induced by a parallel droplet break up mechanism under simple flow[68], and by the vorticity alignment and break up mechanism described by Lin and al.[69]. Although we have to take into account the complexity of the flow within such a Haake blender as it is not a simple flow as used for all these models. We also have to take into consideration the fact that the crosslink density of the chemical network can actually induce some important consequences on these mechanisms, as discussed in the following.

The stress imposed by viscous shear was first estimated to validate these hypotheses and to further discuss on these mechanisms. As a matter of fact, we can qualitatively compare the stress imposed by the shearing to the PP phase and the stress at break of the EPDM preparations. Actually, this process was chosen as it allows, in theory, to study the influence of pure shearing on the fragmentation and dispersion of such chemical networks in presence of a purely viscous thermoplastic phase at a constant temperature, as it is made to ensure shearing with negligible mechanical breaking. In the hypothesis of a homogeneous blend having a continuous PP matrix and submitted to a shear rate $\dot{\gamma}$ the applied stress can be simply expressed by $\tau = \eta \ \dot{\gamma}$:

According to the mixing condition, $\dot{\gamma}$ can be approximated by [9]: $\dot{\gamma}$ = 0.82 x N with N the number of rotations per minute. Consequently with: $\eta^{*}_{50PP} \square 2000 \ Pa.s$ [49], the imposed shearing stress is approximately 80 kPa.

We can then qualitatively compare this value to the tensile properties of the EPDM preparations (as presented in Table 1). First of all, the higher the number of crosslinks, the higher the Young’s modulus. And the higher the crosslink density, the higher the stress at break but the lower the strain at break. Thus, the less the EPDM is crosslinked the better its strain at break is, the larger its strain at break is, thus the more the network can be deformed before it breaks. Therefore, lowly crosslinked EPDM preparations may be deformed more easily under shearing than the EPDM preparations having a gel fraction above 0.9. The higher their degree of crosslinking, the less they will deform before breaking, thus the more they will break up into big fragments instead of being deformed into filaments.

Thus, comparing qualitatively the mechanical properties of such EPDMs to the stress imposed by such process, we can affirm that the shearing stress is of the same order of magnitude as the stress at break of the lowly pre-crosslinked EPDM samples, although it is not high enough to break such fragments. But it is high enough to induce a significant deformation, highlighting the potential influence of the parallel break up mechanism as well as of the vorticity alignment and break up mechanism which is applicable to this kind of process.

Nevertheless, when the PP phase is hardly continuous, as for Blends 7 to 10 having very rough and coarse morphologies, there can not be any continuity of the stress throughout the blend. Thus there must be some additional strong contribution of the mechanical breaking up of the fragments by this process especially at the first moment of bending. There can not be any continuity of the stress through such blends due to the abundance of large and highly elastic fragments which acts like strong defects : they act like clusters and the blend is absolutely not cohesive, therefore the shearing applied can not be continuous throughout the blend. The EPDM fragments can only be broken down by pure breaking between the rotors prior to sustaining the stress imposed by the shearing process once they get embedded in the PP continuous phase. Note that a pure crosslinked EPDM with gel fraction higher than 0.7 turns into powder under shearing in a batch mixer.

Thus, the lowly crosslinked EPDMs may get deformed and dispersed by the shearing but, still, we have to consider another contribution to this parallel break up and pure mechanical breaking mechanisms in order to explain the presence of micrometric nodules in blends made of highly pre-crosslinked EPDM preparations.

Henceforth, in polymer blends having a high viscosity ratio, the erosion of elastomer droplets can induce the formation of sheets which can deform and break up into smaller daughter droplets[67]. Lin and Sundararaj[67, 68] concluded that the break up mode of polymer drops for systems having very high viscosity ratio, thus especially for blends made of pre-crosslinked EPDM having a gel fraction above 0.9, can not only be described by the viscosity ratio and the capillary number as it involves an erosion break up of the bigger droplets which decreases in size and lead to smaller droplets.

Added to this, we can also make the hypothesis of the coalescence of the EPDM fragments due to the elastomer chain interdiffusion followed by the elongation and break up of the filaments according to the mechanism detailed by Bhadane and al.[60]. This can lead to the formation of long interconnecting filaments which can induce the formation of micrometric nodules once those filaments gets broken up by the extensive shearing, as observed for all blends made of a majoritary pre-crosslinked EPDM phase. These daughter droplets may then, once dispersed and imbedded in the PP continuous phase, eventually sustain a second break up mechanism by elongation and break up of the fiber leading to even thinner ‘daughter’ droplets, even for systems having a viscosity ratio above 3.5. It may be noted that such drop breakup up is possible up to a viscosity ratio of 60.

Although such an erosion was mainly reported in blends having a clearly majoritary thermoplastic matrix[60], the rate of erosion can be expected to dramatically increase with the composition of the elastomer as more droplets leads to more collisions[60], thus more coalescence and dispersion of the EPDM as thin micrometric nodules.

Looking at our previous results, such an erosion mechanism appears to be mainly affecting the blends made of highly pre-crosslinked EPDM, contrarily to the parallel break up mechanism which affects all the more the blends made of lowly pre-crosslinked EPDM.

Thus, to sum up these conclusions, we must consider the competition of these mechanisms involved in such morphology stabilization in order to explain all morphologies, the principal mechanisms being : the pure mechanical breaking of the large fragments, the parallel break up of stretched fibers into daughter elastomeric droplets, the vorticity alignment and break up of droplets, and the erosion of the large fragments due to the coalescence of the elastomer by chain interdiffusion. When the PP phase is clearly majoritary, the original EPDM fragments first gets mechanically broken very quickly and dispersed as large fragments. Then the shearing stress continuity makes them sustain a significant deformation which allows a deformation-break up mechanism to occur if the gel fraction does not exceed 0.9. In that case, the pre-crosslinked EPDM may get deformed into filaments, broken up and dispersed as smaller nodules with a fairly small size polydispersity. Whereas for blends having a major EPDM phase proportion, the original lack of continuity of the stress induces a stronger mechanical breaking contribution during the first minutes of blending. Then the large fragments mostly get eroded as smaller daughter nodules according to a collision–coalescence–separation type erosion mechanism, which leads to large residual eroded EPDM fragments plus micrometric nodules born from the erosion. Nevertheless, any pre-crosslinked EPDM having a gel fraction close to 1 will not sustain much erosion nor deformation and will only be broken down into rough fragments due to the pure mechanical breaking contribution which is always somehow present for any kind of process (shearing in the gap between the rotor and chamber surface of the mixer).

Nevertheless, comparing our results with the literature, we have to specify that, in the present case, our elastomeric phase is pre-crosslinked, thus has a chemical network structure which can be assimilated to a viscoelastic solid. Whereas all those mechanisms do not take into consideration such a structure, they still fit our observations very well.

Moreover, concerning the structure of the EPDM, Bhadane et al.[60] showed that uncrosslinked EPDM blended with PP tends to form an interconnected dispersed phase made of nodules linked by nanofibers. Involving the collision-coalescence-separation type erosion mechanism as explained before. And actually, dynamically crosslinked blends can present a gradient of crosslink density due to the specific processing condition during which the crosslinking kinetic is in direct competition with the dispersion of the under-crosslinking

EPDM. This leads to co-continuous morphologies having specific and atypical EPDM structure as explained by Bhadane et al.[1]. But a blend made of pre-crosslinked EPDM, thus made from the fragmentation and dispersion of a perfectly homogeneous chemical network, may not lead to such a structure, which explains the extremely poor mechanical properties of virtually all blends made of pre-crosslinked EPDMs. In their case, the EPDM networks sustain an erosion mechanism thanks to a partial inter-diffusion/agglomeration, of EPDM domains although it may not be efficient enough to lead to the stabilization of an interconnected EPDM dispersed phase : the high viscosity and elasticity of the elastomer coupled with the very low interfacial tension prevent the complete coalescence of the droplets[60]. Thus not the only the blend morphology but also the physical and chemical structures of the EPDM phase highly matters on the final blend properties.

All these conclusions lead to the fact that only the crosslinking under shearing of the elastomeric phase, in presence of PP, can lead to a cohesive material with a very thin and uniform morphology with a fully crosslinked EPDM phase complex structure, either dispersed or co-continuous, inducing a good synergy of the mechanical properties.

To this point we can add that such a dynamic crosslinking of the elastomer might also induce a slight compatibilization of the phases which is not the case for blends made of pre-crosslinked EPDM. The incorporation of a radical promoter catalyst such as $SnCl_2$ during blending can lead to the formation of a small fraction of PP-g-EPDM copolymer which would migrate at the interface thus inducing a small compatibilization of the phases[71, 72]. On the opposite, when blending pre-crosslinked EPDM with PP, the catalyst is trapped within the EPDM network and such a possible compatibilization is thus forbidden. But unfortunately it appears difficult to avoid such contribution and to estimate its influence on the final blend properties, although we can assess that such a compatibilization may not be significant on such systems.

To conclude, in spite of their raising importance on industrial matters, such dispersion mechanisms have a relevant and concrete impact on the processing of TPVs : their elaboration relies on the crosslinking of an elastomeric phase in presence of a thermoplastic under shearing thus involving the competition of several complex mechanisms of erosion, coalescence, deformation, break up and dispersion of the elastomeric phase.

Therefore, during any TPV elaboration, attention must be given to the combination of all these contributions as they can induce radically different morphology developments. An initial pure mechanical breaking can first lead to a rough but cohesive and continuous blend as there is a need to break down large fragments which can not be done by another mean under such a shearing stress. Whereas the continuity of the stress throughout the material during blending can induce a more homogeneous deformation and dispersion of even high density networks thanks to the previously described mechanisms.

These conclusions emphasize the complex contributions of both the shearing and the mechanical breaking on the fragmentation and dispersion of such chemical networks and, indirectly, the utility and complexity of a dynamic crosslinking. As a matter of fact, during such TPV elaboration, the dispersion of the under-crosslinking elastomer has to be done before reaching a 0.9 gel fraction as it will not be dispersed homogeneously above this value.

There is thus a competition between the morphology stabilization and the kinetic of crosslinking, because a proper dispersion of such an elastomer into a PP phase must be done during the crosslinking step as it will be efficient only until its insoluble fraction reaches 0.7. This conclusion definitely justifies the utility of crosslinking the elastomeric phase under shearing in order to achieve a homogeneous dispersion and cohesive morphology.

Thus, the need of controlling and setting a very homogeneous initial blend by compatibilizing both phases takes all his sense. The thinner and the more homogeneous the morphology prior to the dynamic crosslinking step, the better the final dispersion of the EPDM after crosslinking. Thus the more cohesive the material will be as this will prevent the creation of large crosslinked EPDM fragments which will not be dispersed correctly once present in the blend after the crosslinking step. This leads to the conclusion that, during the elaboration of any TPV, it seems more logical and effective to blend both the thermoplastic and the uncrosslinked elastomer first in order to obtain a fine and homogeneous morphology prior to dynamically crosslinking the elastomeric phase under high shearing, as it will minimise the consequences of the drastically increasing viscosity ratio which can perturb the morphology stabilization. This could induce the formation of massive heterogeneities which would not be further fragmented within the blend. Thus, if the crosslinking kinetics and process are not well set and controlled, a roughly dispersed EPDM phase could crosslink very quickly and high density networks would not get fragmented and dispersed into the thermoplastic matrix, and this could significantly weaken the blend macroscopic properties.

In any case, these results surely highlight the complexity and usefulness of a dynamic crosslinking step in order to avoid, as much as possible, a bad dispersion of any crosslinked

EPDM into the thermoplastic phase right after the crosslinking step. Only a dynamic crosslinking of the elastomer can allow a proper synergy of the properties by ensuring a homogeneous morphology and structure whatever the blend proportion, although it requires a perfect timing of each steps during the TPV elaboration. Thus these results brought some new information on how to better control such a complex process in order to stabilize the desired blend morphology and structure.

V. Conclusion

The main objective of this work was to study the dispersion mechanisms under shearing of pre-crosslinked and plasticized EPDM networks in presence of polypropylene in various proportions, and to compare these blend properties and morphologies to uncrosslinked and dynamically crosslinked blends made in the same proportions. Consequently, this paper aims at better understanding the various mechanisms of fragmentation and dispersion involved in the morphology stabilization of thermoplastic vulcanisates. As far as we know, no such work has been quantitatively reported in the literature yet.

First of all, under our experimental conditions of shearing, it appeared possible to fragment and homogeneously disperse elastomeric networks having a gel fraction as high as 0.7 into a thermoplastic matrix, whatever the proportion of the phases. Above this value, the pre-crosslinked EPDM networks are not dispersed efficiently into fine particles, leading to coarse morphologies with quite large remaining fragments (size of 200 μm of order of magnitude with a broad distribution) which act as strong imperfections literally ruining the macroscopic properties of the blends which thus appear extremely brittle.

Furthermore, whatever the gel fraction of the pre-crosslinked EPDM, and whatever the proportions of the phases, such process always induces some fragmentation and dispersion of the pre-crosslinked elastomer. Although the Rayleigh-Taylor instabilities can be involved in such immiscible blend morphology development, other dominant mechanisms have to be taken into account depending on the EPDM crosslink density and concentration in PP/EPDM blends, such as :

- Parallel break-up: The mechanism of parallel break-up of pre-crosslinked EPDM is the dominant one for gel fraction lower than 0.7 and whatever the PP concentration. However, in the case of blends with a clearly continuous thermoplastic phase, pre-crosslinked EPDM networks will mainly be deformed as long filaments later fragmented and dispersed as micrometric nodules thanks to the continuity of the imposed shearing stress throughout the material during blending. In that case, the parallel break up (with a possible vorticity alignment contribution) is the first order mechanism. On the other hand, in the case of blends having a majoritary elastomeric phase, the fragmentation and dispersion of pre-crosslinked EPDMs lead to more heterogeneous morphologies with EPDM fragments and nodules having a broad size polydispersity due to the lack of the stress continuity throughout the material which inhibits the contribution of such a mechanism.

- Erosion: The mechanism of erosion is mainly observed for EPDM gel fraction higher than 0.7. Furthermore, this mechanism was observed to be time dependent. For instance, even in this case of very dense chemical networks, the inter-diffusion/agglomeration of the EPDM domains allows a partial coalescence then elongation and break up of the pre-crosslinked EPDM fragments which get slowly fragmented according to this erosion mechanism. This contribution is actually especially important during the first instant of blending, and is followed by a collision–coalescence–separation type erosion mechanism which mainly rules these blend morphology evolutions. On the other hand, blends having a majorarity EPDM proportion sustain a significant contribution of pure mechanical breaking (grinding process) which induces a rough but effective breaking up of the elastomeric fragments.

Finally, the crosslinking under shearing of the elastomer in presence of PP (i.e. reactive crosslinking) leads, in every proportions, to a very fine and homogeneous morphology with a complex and cohesive elastomer structure, leading to improved mechanical properties. The advantage of the crosslinking under shearing, compared to the fragmentation and dispersion of pre-crosslinked EPDM in presence of a thermoplastic phase, appears clearly vital to elaborate cohesive TPVs. Our results thus brought new information on the mechanisms involved in such morphology development, and highlighted the utility of crosslinking the elastomer under shearing in order to obtain the desired synergy of mechanical properties.

Therefore, from a TPV elaboration point of view, during the crosslinking of the elastomer, the EPDM must be dispersed homogeneously within the thermoplastic phase before its gel fraction reaches 0.7. After that, the crosslinked EPDM phase will not be fragmented and dispersed properly and the blend properties will be seriously altered.

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Conclusion générale

Conclusion générale

Cette thèse a porté sur l'étude de mécanismes fondamentaux impliqués dans l'élaboration des thermoplastiques vulcanisés (TPV) du type PP/EPDM.

L'étude bibliographique a tout d'abord mis en avant la complexité de ces matériaux, tant sur le plan des formulations que du procédé d'élaboration et des processus conduisant à la morphologie finale du mélange. Cette dernière est le résultat de la concomitance et de la compétition entre les mécanismes de « dispersion », au sens large, d'une phase viscoélastique dans une autre (fractionnement de gouttes, coalescence, co-continuité, …) et l'augmentation de viscosité de la phase EPDM en cours de réticulation. La maîtrise de cette morphologie, en particulier via l'inversion de phase qui permet au polypropylène, minoritaire, de devenir la phase continue, est l'élément-clé de l'obtention des propriétés spécifiques des TPV (élasticité de type caoutchoutique et mise en œuvre analogue aux thermoplastiques). Toutefois, la compréhension des processus et la corrélation entre les caractéristiques de la morphologie et les propriétés finales est encore incomplète, et les progrès résulteront de la synthèse des connaissances développées dans divers domaines et par de nombreuses équipes. En effet, l'élaboration d'un TPV repose sur plusieurs domaines scientifiques : les mélanges de polymères, la physicochimie des interfaces, la rhéologie, la chimie de la réticulation… Toutefois, pour analyser tous ces aspects, dans le cas de systèmes tels que les mélanges PP/EPDM réticulés dynamiquement, il est nécessaire d'individualiser autant que possible les paramètres et mécanismes impliqués dans leur élaboration. La stratégie de nos travaux de recherche a donc consisté à étudier des systèmes simplifiés dans le but de s'affranchir de l'interdépendance des mécanismes en question.

Nous avons tout d'abord étudié la structure et le comportement viscoélastique d'une gamme d'EPDM plastifié (60 parts) présentant des densités de réticulation variables, le but étant de corréler la structure chimique et physique de tels réseaux à leur comportement viscoélastique de relaxation et de recouvrance élastique. Ces premiers travaux ont permis de modéliser la structure exacte de ces réseaux d'élastomère plastifié et réticulé par des quantités variables de résine phénolique en présence de $SnCl_2$. La densité de nœuds de réticulation chimiques, d'enchevêtrements physiques, de chaînes élastiques actives ou pendantes ainsi que la masse molaire moyenne entre ponts de ces différents réseaux ont pu être déterminées à partir des modèles classiques de dynamique moléculaire. De plus, ces calculs ont permis de déduire que la résine phénolique affiche une réactivité constante quelle que soit la proportion utilisée. Lors du test viscoélastique de DRC, le temps de relaxation et la valeur du module de relaxation au plateau augmentent avec la densité de réticulation de l'EPDM : plus le réseau est réticulé plus la masse molaire moyenne des chaînes pendantes est faible et plus la relaxation, et donc la recouvrance, aux temps courts est importante. L'ajustement des profils de relaxation de ces réseaux aux temps longs et le couplage de plusieurs modèles de dynamique moléculaire nous ont permis de prédire les profils de recouvrance élastique de nos échantillons, en bonne concordance avec l'expérience. Un tel modèle pourra en théorie être appliqué à tous types de réseaux similaires à partir de la simple connaissance de la structure des réactifs et des mesures des taux d'insoluble et de gonflement. En d'autres termes, la prédiction de la recouvrance de ce type de réseaux peut être faite uniquement à partir de leur profil de relaxation.

Ensuite, une fois la structure et le comportement viscoélastique de ces réseaux déterminés, nous avons orienté nos recherches vers l'étude morphologique des mélanges PP/EPDM. En particulier, l'étude exhaustive de la co-continuité d'un mélange non réticulé nous a permis de conclure quant à la présence d'un réseau physique induit par la structure même des phases. Ce mélange, pourtant dépourvu d'un réseau chimique, présente toutefois des profils de relaxation de contrainte et de recouvrance élastique tout à fait surprenants. En effet, cette morphologie, particulièrement fine et homogène aux premiers instants de mélange, induit une structuration du matériau qui présente alors un réseau physique pouvant recouvrer 40% d'une déformation de 25% appliquée pendant 10 heures à 100°C. Cette morphologie atypique constitue ainsi une source essentielle du caractère élastique de ce type de mélanges. Ces résultats indiquent ainsi que les propriétés élastiques de mélange PP/EPDM réticulé sous cisaillement dépendent du couplage de la présence d'un réseau chimique dû à l'élastomère réticulé, et physique induit par la morphologie co-continue. De plus, la finesse de cette morphologie est intimement liée au temps de mélange : cette morphologie est établie en moins de deux minutes et la présence de nodules nanométriques au sein des phases co-continues s'atténue avec le temps de mélange. La dispersion de nanoparticules de silice hydrophobe améliore quant à elle les propriétés élastiques de ce type de réseau physique.

Ainsi, un TPV du type PP/EPDM co-continu à base de silice hydrophobe affichera donc en théorie une élasticité particulièrement intéressante à court et à long terme.

La complexité de l'étude des TPV repose sur le fait que les mécanismes de développement morphologique sont intimement couplés à la cinétique chimique de réticulation de la phase élastomère. Pour découpler ces mécanismes, nous avons ainsi étudié la dispersion d'une phase élastomère préalablement réticulée et présentant des densités de réticulation variables. Cette étude approfondie des mécanismes de fragmentation et de dispersion de gouttelettes d'élastomères pré-réticulés en présence d'une phase thermoplastique semblait judicieuse car l'inversion de phase et la stabilisation de la morphologie sont les paramètres clé de l'élaboration des TPV. Ces cinétiques de développement morphologique nous ont ainsi permis d'estimer les mécanismes impliqués dans la dispersion de l'élastomère présentant une densité de réticulation variable, comme c'est le cas au cours d'une étape de réticulation sous cisaillement. Ces résultats ont apporté des informations fondamentales quant aux mécanismes de dispersion de réseaux chimiques en présence d'une phase thermoplastique. Cette étude a tout d'abord mis en avant la possibilité de disperser, au sein d'un mélangeur interne, des préparations d'élastomère possédant un taux d'insoluble allant jusqu'à 70% de façon homogène dans le polypropylène, quelle que soit la proportion des phases. Toutefois, même pour des taux d'insoluble proches de 100%, ce type de procédé induit toujours une fragmentation et dispersion significative mais conduit dans ces cas là à des défauts supérieurs à 10µm, provoquant ainsi une dégradation importante des propriétés du matériau. De plus, l'importance de la proportion de thermoplastique sur la qualité de dispersion de l'élastomère a été clairement mise en avant. En effet, plus la proportion d'EPDM est importante, et plus sa densité de réticulation est élevée, plus le mécanisme d'érosion par collision-coalescence-séparation joue un rôle important, et moins la dispersion par déformation et rupture des gouttelettes est prépondérante. Du point de vue de l' élaboration des TPV, ces résultats conduisent à la conclusion que, pendant une étape de réticulation dynamique, il faut assurer une dispersion très rapide de l'EPDM avant que son taux d'insoluble dépasse 70% ; au delà de cette valeur la phase élastomère réticulée ne sera plus dispersée de façon homogène et conduira à des défauts micrométriques qui altèreront les propriétés finales du mélange.

En conclusion, cette étude a permis d'éclaircir plusieurs points primordiaux à l'élaboration des TPV. D'un point de vue chimique, la structure du réseau de la phase élastomère, en particulier les chaînes pendantes et les enchevêtrements physiques, jouent un rôle essentiel sur les propriétés de relaxation de contrainte et de recouvrance élastique. Ce réseau chimique à l'échelle moléculaire peut en théorie être formé en simultané avec un réseau physique, à l'échelle micrométrique, induit par une co-continuité des phases élastomère et thermoplastique, et conduire ainsi à une structuration « multi-échelle » et à une synergie de propriétés élastiques de ces réseaux. Enfin, un tel mélange nécessite de débuter la réticulation de l'élastomère sous cisaillement dès les premiers instants où la co-continuité des phases apparaît. Ensuite, pour compenser le phénomène d'agglomération et les problèmes de stabilisation morphologique dûs à l'augmentation de viscosité liée à la réticulation de la phase élastomère, il faut ensuite assurer la dispersion de l'élastomère avant que celui-ci ne présente un taux de gel supérieur à 70%. Dans ce cas, il sera possible de stabiliser une morphologie co-continue avec une phase élastomère entièrement réticulée sous forme de micro-gels interconnectés, particulièrement adéquate du point de vue des applications à caractère élastique.

Toutefois, de nombreuses zones d'ombre restent encore à élucider et les perspectives sont nombreuses. Admettre la stabilisation d'une phase d'EPDM réticulée sous forme de micro-gels implique la présence d'un gradient de densités de réticulation au sein de cette phase créé durant l'étape de réticulation sous cisaillement. Quel serait alors le gradient de densité de réticulation optimal et comment pourrions-nous le contrôler ? De plus, l'influence de la cristallisation du PP au sein d'une morphologie co-continue mériterait d'être étudiée et corrélée à son comportement dynamique en compression. En particulier, le rôle d'agent nucléant des nodules d'EPDM dispersés et la caractérisation précise des zones amorphes et cristallines dans la continuité de PP seraient un sujet d'étude particulièrement intéressant. La stabilisation morphologique de mélanges co-continus réticulés de façon variable sous cisaillement et à base de silice hydrophobe, ou d'un autre type de charges de façon générale, pourrait aussi faire l'objet d'une étude prometteuse afin de corréler leur morphologie à leur profils de relaxation de contrainte et de recouvrance élastique. Il serait aussi utile de différencier l'influence des réseaux physique et chimique sur la recouvrance, instantanée et aux temps longs, de ce type de mélanges. Enfin, le rôle des charges n'a été abordé que très succinctement dans ces travaux. A priori les charges nanostructurées jouent également un rôle clé dans l'élaboration et les propriétés des TPV, et une étude plus ciblée sur cet aspect serait des plus pertinentes dans la continuité de ces travaux.

Résumé en français :

Le travail présenté dans ce mémoire de thèse porte sur l'étude des aspects fondamentaux liés à l'élaboration d'un thermoplastique vulcanisé (TPV) commercialisé par la société Hutchinson. Les propriétés mécaniques spécifiques des TPV, en particulier dans le cas des mélanges PP/EPDM, sont directement liées à la structure et à la morphologie du mélange, corrélées elles mêmes à la compétition entre la réaction de réticulation et l'action de mélange. Cette corrélation complexe donne lieu à une synergie des propriétés de mise en œuvre du thermoplastique combinées à l'élasticité de l'élastomère réticulé. Dans un premier temps, nous avons modélisé les réseaux moléculaires d'EPDM plastifiés et réticulés afin de déterminer avec précision leur structure exacte en fonction de la concentration d'agent réticulant utilisé. Nous avons ensuite étudié le mécanisme de relaxation aux temps longs à l'origine du mécanisme de recouvrance élastique. Une étude morphologique exhaustive a ensuite été menée sur des mélanges à base d'EPDM non réticulé, montrant qu'ils peuvent, dans certaines conditions, présenter une recouvrance élastique surprenante due la présence d'un réseau physique induit par une morphologie co-continue très particulière. La présence de silice conduit de plus à une amélioration de cette recouvrance. Enfin, nous avons étudié les mécanismes de dispersion d'échantillons d'EPDM (préalablement réticulés) dans une phase fondue de PP, ce qui a permis de conclure quant à l'importance de la proportion des phases et à l'influence du taux d'insolubles sur la qualité de la dispersion de la phase élastomère. *In fine*, au-delà d'un taux d'insoluble de 70% dans la phase élastomère, seule une morphologie grossière et non homogène peut être obtenue, atrophiant de ce fait les propriétés mécaniques des dits mélanges.

Titre en anglais :

Study of the fundamental aspects involved in the elaboration of PP/EPDM thermoplastic vulcanizates such as the Végaprène®.

Résumé en anglais :

This work focuses on the study of the fundamental aspects involved in the elaboration of a thermoplastic vulcanizate (TPV) commercialized by the Hutchinson company. The specific mechanical properties of a TPV, especially in the case of PP/EPDM blends, are directly linked to its structure and morphology, which are both correlated to the competition between the crosslinking reaction and the blending action. This complex correlation leads to a synergy of the processing properties of the thermoplastic, combined with the elasticity of the crosslinked elastomer. Thus, first, we modeled the molecular networks of various crosslinked and plasticized EPDM in order to determine with precision their exact structure in fonction of the concentration of crosslinking agent used. We then studied the mechanism of long-time relaxation which is the source of the elastic strain recovery mechanism. An exhaustive morphological study was then undertaken on blends made of uncrosslinked EPDM, showing that they can, under some precise conditions, present a surprising elastic strain recovery due the presence of a physical network induced by a very particular co-continuous morphology. Moreover, the presence of silica nanoparticles leads to the improvement of this recovery. Finally, we studied the mechanisms of dispersion of pre-crosslinked EPDM samples in a molten PP phase, which allowed us to conclude on the importance of the proportion of both phases and on the influence of the gel fraction on the quality of the dispersion of the elastomeric phase. *In fine*, beyond a gel fraction of 0.7, the dispersion of the elastomer is rough and leads to a coarse and heterogeneous morphology, literally ruining such blend mechanical properties.

Discipline :

Matériaux polymère et composite

Mots-clés :

Thermoplastiques vulcanisés, PP/EPDM, réticulation, morphologie, recouvrance élastique

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