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Plasticization and Morphology Development in Dynamically Vulcanized Thermoplastic Elastomers

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Abstract

Dynamically vulcanized thermoplastic elastomers constitute one of the main categories among various types of thermoplastic elastomers (TPEs). Due to the commercial importance of this particular group of TPEs, tremendous efforts have been dedicated to improve the understanding and control the phase morphology development. The ultimate goal is to obtain materials with improved physical and mechanical properties. As in other polymeric compounds, the parameters during the mixing stage have a significant influence on the final morphology of dynamically vulcanized blends. Furthermore, the phase morphology and, therefore, the distribution of elastomeric domains in the thermoplastic phase are also strongly dependent on the formulation. This chapter discusses the main important processing factors and, more specifically, highlights the effects of plasticization and curing on the morphology development of dynamically vulcanized thermoplastic elastomer blends. The following text provides fundamental information on how one should take into consideration each parameter affecting the morphology of nonreactive and reactive elastomer/thermoplastic blends.

Keywords: Thermoplastic elastomer, dynamic vulcanization, plasticization, morphology, rheological properties

1. Introduction

Thermoplastic elastomers (TPEs) represent a large group of polymeric materials that are melt processable, similar to regular thermoplastics, and they exhibit rubber-like behavior identical to that of cross-linked elastomers. This special characteristic of TPEs is mainly due to the presence of thermoreversible cross-links, which are broken during the melt processing step under high shear and elevated temperature, and formed once again when melt processing is over and the compound reaches ambient temperature. The main concept behind the thermo-

plastic elastomers and, therefore, thermoreversible cross-links is the simultaneous presence of phase-separated hard and soft segments in the compound. Although both phases contribute to the overall physical and mechanical properties of the final product, some specific properties are usually associated with one phase or the other. Below the melting temperature of the hard phase, this phase usually provides the strength, stiffness, and chemical resistance of the material. On the other hand, the soft one acts as an elastomer providing the flexibility and the elastic nature by controlling the hardness, the compression, and the tensile sets. Furthermore, the soft phase dictates the lower service temperature limit of the product.

Commercially available TPEs can be generally classified into the following four groups presented in Table 1.

I	II	III	IV
Block copolymers	Random copolymers	Ionomers	Blends of soft elastomer and hard thermoplastic
<i>Triblock or segmented block copolymers:</i>			<i>Simple (nonreactive) or dynamically vulcanized blends (DV)</i>
SBS			EPDM/PP
SEBS	EPR	Ethylene-methacrylic acid	NBR/PP
TPU	Ethylene- α Olefin	Ethylene-acrylic acid	NBR/PVC
COPE	Propylene- α Olefin	Butadiene-acrylic acid	IIR/PP
COPA	and many more	and many more	and many more
and many more			

SBS: Poly(styrene-butadiene-styrene); SEBS: Poly(styrene-ethylene-butadiene-styrene); TPU: Thermoplastic polyurethane; COPE: Copolyether-ester elastomers; COPA: Copolyamide elastomers; EPR: Ethylene propylene rubber; EPDM: Ethylene propylene terpolymer rubber; PP: Polypropylene; NBR: Nitrile butadiene rubber; PVC: Polyvinyl chloride; IIR: Butyl rubber (isobutylene-isoprene rubber).

Table 1. Classification of thermoplastic elastomers (TPEs) along with few examples.

According to the general categories of TPEs shown in Table 1, the aforementioned properties associated with TPEs could be obtained through numerous paths. In the first three groups, the material mainly consists of blocks or grafted segments of soft and hard constituents through polymerization [1,2]. In addition to these large varieties of TPEs obtained through polymerization, mechanical blending of conventional elastomers with plastics provides another accessible route toward the production of TPEs. In this approach, the polymeric constituents are blended in a conventional melt mixing equipment, such as a twin-screw extruder. The result is often an immiscible blend, particularly due to the fact that the majority of polymeric pairs of large molecular weight and low interactive forces tend to form phase-separated microstructure. Interestingly, the phase-separated nature of these blends is what it is needed to exhibit properties associated with TPEs.

Although some simple nonreactive elastomer/thermoplastic blends, such as ethylene-propylene rubber/polypropylene (EPR/PP), have gained tremendous attention for their use in the automotive industry [3], the nonreactive blends have generally poor elastic recovery and poor hydrocarbon fluid resistance in comparison to their reactive counterparts [4]. Furthermore, the morphology of an immiscible simple blend is prone to change during the reprocessing and downstream operations. These issues may extremely affect the physical and mechanical properties of these types of TPEs. Consequently, simple blending of polymeric constituents is usually not sufficient to guarantee a permanent morphological feature and, therefore, stable mechanical properties regardless of the processing history of the blend. To overcome this issue, chemically cross-linking of polymeric phases is required in order to stabilize the morphology. In this case, the reactive blends of elastomer/thermoplastic blends are generally obtained through dynamic vulcanization (DV) where the elastomer phase is selectively cross-linked in the presence of a curing system. These blends are commonly known as thermoplastic vulcanizates (TPVs). The origin of DV process comes from the work of Gessler and Haslett on polypropylene and chlorobutyl rubber, where the elastomer was cross-linked in the presence of zinc oxide [5]. Fischer [6-9] further pushed the boundaries of our understanding by working on dynamically and statically cross-linked elastomer blends with polyolefins. The work of Fisher on dynamic vulcanization was further extended by complementary investigations done by Monsanto [10-13].

In both simple and dynamically vulcanized blends, the thermoplastic elastomer behavior is usually obtained for high concentration of the elastomer phase, e.g., higher than 50 wt%. This single argument on the concentration of the elastomeric component has a huge consequence on the morphology. The simple blends with high elastomer content tend to form a co-continuous morphology, where both elastomer and thermoplastic constituents are interconnected throughout the whole bulk of the material (Fig. 1a). However, in dynamically vulcanized blends, the elastomer (usually the major and initially part of the co-continuous phase) becomes discontinuous and dispersed during dynamic vulcanization (Fig. 1b). Eventually, the thermoplastic becomes the continuous phase surrounding the cross-linked elastomer particles. This morphology transformation is known as *phase inversion*.

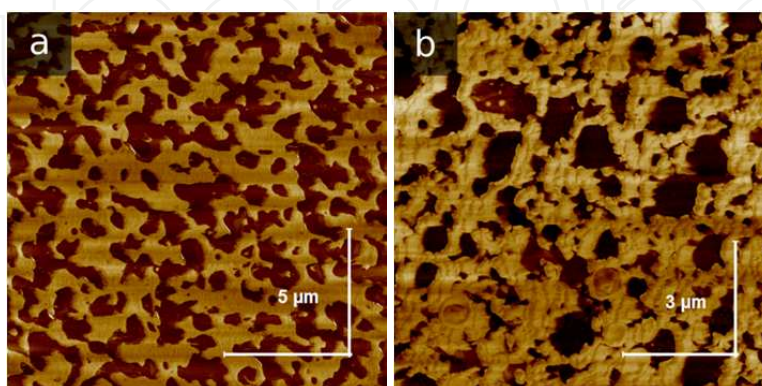


Figure 1. AFM phase micrographs of: (a) nonreactive simple, and (b) dynamically vulcanized EPDM/PP 50/50 (wt/wt %) blends (from [14])

By far, the importance of the phase-separated structure and the role of morphology have been clearly emphasized. For one familiar with polymer blending technology, the fine control of phase morphology even in a simple nonreactive blend composed of merely two components represents a huge challenge. Moreover, the presence of a complex flow field in industrial mixing equipment with simultaneous breakup and coalescence of the dispersed phase creates a far more complicated environment for comprehending the phase morphology development. The level of complexity may even increase when additional components such as processing aids, fillers, plasticizers, and curing system are added. This is commonly the case in the TPV industry where the fine-tuning of the final properties is achieved by combining several different reactive and nonreactive additives.

2. Plasticization

The use of plasticizers in both rubber and thermoplastic elastomer industries is a well-established technology [15]. Despite the overall processing cost reduction of the final product in the presence of a plasticizer, some technical aspects of a plasticized compound can also be improved. For instance, plasticizers have been used to improve the low temperature mechanical properties to reduce the hardness and acts as a dispersion aid for fillers and additives [16]. It further improves the resistance to oil swell, heat stability, hysteresis, permanent set, elastic recovery, as well as the melt processability and the final appearance of the compound [13].

Several theories such as gel [17,18], lubricity [19-21], and free volume [22] theories have so far been developed and further extended to explain different mechanisms involved during plasticization. In a rather general way, the lubricity theory considers that a plasticizer reduces the intermolecular friction between polymer chains, which is originally considered as its source of rigidity. It acts as lubricant and reduces the resistance to sliding between molecules. In the gel theory, the polymer molecules are considered to form a tridimensional structure held by loose attachments along their chains. According to this theory, the stiffness of the polymer is mainly due to the presence of this tridimensional structure. In such systems, plasticizers act in favor of reducing the number of attachments between polymer molecules and, therefore, enabling the molecules to change their conformation. In the free volume theory, the friction between polymer chains is attributed to the volume between molecules. The free volume in polymers is essentially considered as the required space for chain mobility. By increasing the temperature in a nonplasticized system, the chain mobility increases as a consequence of an increase in free volume. On the other hand, the shrinkage of the free volume with decreasing temperature may reach to critical level where only limited free space is available for polymer chains to have large segmental motion. This critical temperature is known as the glass transition temperature (T_g). Therefore, polymers below T_g behave as solid glassy materials, whereas at temperatures above T_g they possess rubber-like properties. According to this theory, the free volume in a polymer may be increased through different paths [23]: (1) by increasing the temperature (as mentioned earlier), (2) by lowering the molecular weight of the polymer resulting in an increased concentration of end groups, (3) by incorporation and/or increasing the length of side chains in the polymer, (4) by incorporating segments with low

steric hindrance and low intermolecular interaction along the polymer chains, (5) by adding lower molecular weight compounds with lower T_g , which are compatible with the polymer. Consequently, a decrease in the glass transition temperature and an increase in the mobility of polymeric chains as a function of the plasticizer concentration could be readily associated with increases in the free volume.

Once a plasticizer is incorporated and completely dissolved at the molecular level in a desired polymer, the combination of all the aforementioned theories provides an extensive insight into the plasticization mechanisms. However, dissolution of a plasticizer into polymer and the compatibility may largely affect the efficiency of plasticization in both the short and the long term. The compatibility issue is the principal factor in determining the proper plasticizer for a given polymer. Generally, a compatible polymer/plasticizer pair is by nature a homogeneous mixture.

The incorporation of a plasticizer during an industrial compounding process is usually achieved by the expenses of mechanical energy. However, afterward the stability of the compound is directly related to the thermodynamic phase equilibrium between the components. As a result, the widely used compatibility concepts are, therefore, based on the theories of polymer solutions. In a pair of plasticizer/amorphous polymer with an upper critical solution temperature (UCST) phase diagram, the homogeneity of the mixture increases with temperature. At lower temperatures, a mixture containing around 15 to 40 vol% of plasticizer (a typical range in TPVs) may be phase-separated into polymer-rich and plasticizer-rich domains. In certain cases, a lower critical solution temperature (LCST) may also be observed. In contrast to UCST phase diagrams, those systems displaying LCST tend to phase-separate at higher temperature. The complexity of the phase diagram is normally increased when instead of an amorphous polymer; a semicrystalline polymer is to be plasticized. The crystallization process of the polymer tends to be the factor that complicates the formation of a homogeneous polymer/plasticizer mixture. At temperatures high enough to obtain a homogeneous mixture between the amorphous fraction of the polymer and the plasticizer, but low enough that crystallinity still prevails, the presence of local crystal network affects negatively the compatibility and in certain conditions it results in migration of the plasticizer. This reasoning on the effect of crystallinity brings us to a general discussion regarding the flexibility of polymer chains. Flexible chains are known to dissolve more easily in a plasticizer. This mainly is due to lower energy requirement in separating polymer chains, and an easier diffusion of chains in the plasticizer. This process usually increases the mixing entropy and facilitates the mixing. This again demonstrates that the dissolution of crystalline or cross-linked polymer chains in a plasticizer is a laborious task and, therefore, the compatibility between these pairs is much less than the compatibility between flexible amorphous polymer chains and a plasticizer. Beside chain flexibility, crystallinity, and cross-linking, some other criteria have to be as well considered. Some are based on the polarity differences between plasticizer/polymer pairs. Highly polar polymers do not usually dissolve in nonpolar solvents and the other way around. However, some exceptions to this rule have already been observed.

Up to this point, most of the discussion surrounding the compatibility issue was qualitative. However, to choose a proper plasticizer one should estimate the compatibility based on a

measurable value derived from the Flory-Huggins theory [24,25]. The miscibility criterion in this theory is determined by the Gibbs free energy of mixing, which is a combination of the enthalpy and entropy of mixing:

$$\frac{\Delta G^M}{RTV} = \left[\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right] + \left[\frac{\phi_1 \phi_2}{V_1} \chi_1 \right] \tag{1}$$

<i>T</i>	Temperature, [K]
<i>R</i>	Universal gas constant, [J/K.mol]
<i>V</i>	Total volume, [m ³]
<i>V₁, V₂</i>	Molar volumes of plasticizer and polymer, respectively, [m ³ /mol]
<i>ϕ₁, ϕ₂</i>	Volume fractions of plasticizer and polymer, [-]
<i>χ₁</i>	Interaction parameter, [-]

Table 2. Description of parameters of eq. 1

The term in the first bracket represents the entropy change of mixing, whereas the second one represents the enthalpy change. In a polymer/plasticizer mixture, an instantaneous miscibility (or complete compatibility) is achieved when the Gibbs free energy of mixing is negative. This can only be achieved if the enthalpy contribution is small enough in comparison to the entropic one. Therefore, the interaction parameter (*χ₁*), which represents the enthalpic contribution, is an important feature in estimating the compatibility. It characterizes the difference between the interaction energy when a plasticizer molecule is immersed in a neat polymer, versus when it is immersed in a neat plasticizer. The upper limit for *χ₁* to obtain a compatible pair is 0.5. For values greater than 0.5, incompatibility and phase-separation may be observed. Although values for *χ₁* in different polymer/solvent (plasticizer) systems can be found in the literature and in several polymer handbooks [16,26,27], in practice the most useful parameter used to estimate the molecular interactions between two components is the solubility parameter (*δ*). This parameter is the square root of the cohesive energy density. This is the energy that has to be given to a system of pure liquid to extract a molecule from the liquid state. Therefore, it is proportional to the interaction energies between similar molecules. The change in the internal energy of mixing can be related to the solubility parameter based on the following equation [28]:

$$\Delta U^M = \Delta H^M \Big|_{Const. \; Volume} = V \phi_1 \phi_2 \left[\delta_1 - \delta_2 \right]^2 \tag{2}$$

The combination of eqs. 1 and 2 for the enthalpy change of mixing results in an equation relating the Flory-Huggins interaction parameter to the solubility parameters of the polymer and the plasticizer:

$$\chi_1 = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (3)$$

V_1 Molar volume of plasticizer, $[\text{m}^3/\text{mol}]$

A more appropriate relationship documented in the literature for a mixture of polymer/low molecular weight liquid (plasticizer) is the following:

$$\chi_1 = 0.34 + \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (4)$$

Earlier, the limit of compatibility between polymer/plasticizer pairs was determined by a critical value ($\chi_1=0.5$). According to this criterion, compatibility can be approximately estimated by matching the solubility parameters. A typical low molecular weight liquid (plasticizer) may have a molar volume around 100 to 400 cm^3/mol . Accordingly, this translates into a critical difference between the solubility parameters around 0.48 to 0.97 $(\text{cal}/\text{cm}^3)^{0.5}$ (based on eq. 4). As an example, for natural rubber with solubility parameter of 8.30 $(\text{cal}/\text{cm}^3)^{0.5}$ [29], a proper plasticizer shall possess a solubility parameter between 8.3 ± 0.97 $(\text{cal}/\text{cm}^3)^{0.5}$. This simple method is widely used in industry and, although it is considered as a rapid screening technique to identify a proper plasticizer, there might be cases as we will demonstrate shortly that the prediction is not quite exact.

A more appropriate approach for compatibility studies in terms of solubility parameter is the use of the three-dimensional solubility components proposed by Hansen [30]. In this approach, the individual solubility parameter for each and every phase involved in the system is composed of contributions from van der Waals dispersion forces (δ_d), dipole–dipole interaction between molecules (δ_p), and the contribution from hydrogen bonding (δ_h):

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (5)$$

The advantage of using the three-dimensional components of the solubility parameter is its ability in distinguishing between different chemical interactions, which might be present. For instance, two substances may have exactly the same overall solubility parameter, but with different proportions of $\delta_d/\delta_p/\delta_h$ components. Ethylene carbonate and methanol both possess quite similar overall solubility parameters, around 29.0 $\text{MPa}^{1/2}$ or 14.2 $(\text{cal}/\text{cm}^3)^{0.5}$ [31]. However, comparing their corresponding Hansen solubility components, one could clearly understand their difference. Ethylene carbonate with ($\delta_d=18.0$; $\delta_p=21.7$; $\delta_h=5.1$ $\text{MPa}^{1/2}$) and methanol with ($\delta_d=14.7$; $\delta_p=12.3$; $\delta_h=22.3$ $\text{MPa}^{1/2}$) have a huge difference in terms of hydrogen-bonding interactions [31]. As a result, if these two are to be in contact with a polymer, the difference between their solubility capabilities could be readily predicted through the differ-

ence in their three-dimensional values in the $\delta_d, \delta_p, \delta_h$ coordinates. The three-dimensional distance between two substances is usually calculated based on the following equation:

$$D = (4 \times (\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2)^{1/2} \quad (6)$$

A smaller distance is an indication of similarity and thermodynamic compatibility between two molecules. In the case of the previous example, the distance between ethylene carbonate and methanol molecules is around 20.7 MPa^{1/2}. This shows that these two molecules are not at all similar and they will not behave in a similar manner when subjected to a polymer (regardless of the type of polymer). In a plasticizer/polymer mixture, as the distance increases, the compatibility and the solubility decreases in a way that after a certain distance known as the polymer radius the compatibility is negligible. The simplest and the most practical way to calculate the compatibility between a polymer and a plasticizer is to calculate the three-dimensional distance based on the Hansen solubility components and, then, divide D by the radius of the polymer. This ratio is known as the relative energy difference (RED). A mixture with a RED value smaller than 1 is compatible or even soluble in the best-case scenario; whereas a RED value greater than 1 is a sign of incompatibility and insolubility. This approach provides a more accurate prediction for compatibility; however, care must be taken when dealing with complex mixtures with cross-linked or crystalline polymers. These complexities reduce the radius of a polymer and affect negatively the compatibility with a plasticizer.

In industry, a more complex situation is generally encountered. A plasticizer is usually incorporated into a blend of two or more polymeric constituents. Since the majority of polymer blends are known to be immiscible due to thermodynamic limitations, a question arises regarding the distribution of the plasticizer when mixed in multiphase polymer blends. The answer to this question could simply clarify whether the properties of both phases are affected equally in the presence of a plasticizer, or only one of the phases will be largely affected due to its higher affinity with the plasticizer. To quantify the characteristics of the distribution, a quantity known as distribution or partition coefficient ($K_{A/B}$) has been widely used. This coefficient is the ratio of the weight fraction of the plasticizer in the polymer A over the weight fraction of the plasticizer in the polymer B, i.e., $K_{A/B} = w_{p,A}/w_{p,B}$. A value of $K_{A/B} = 1$ means that the plasticizer is equally distributed in both polymers; whereas, values lower than 1 mean that the plasticizer has a tendency toward polymer B. According to Mishra et al. [32], in those immiscible blends where the distribution of an additional low molecular weight component is entropically driven, the lowest free energy of mixing is usually achieved in the vicinity of $K_{A/B} \sim 1$. This implies that in a system where the plasticizer has a close affinity with both polymers, a uniform distribution is thermodynamically favored. On the other hand, in a blend where only one of the components is compatible with the plasticizer, the plasticizer will obviously migrate to that specific phase. An example of such system is the blend of poly(methyl methacrylate) (PMMA) and acrylonitrile butadiene styrene (ABS) [33]. These two polymers are mutually miscible. However, in the presence of a plasticizer composed of ethylene carbonate and propylene carbonate (1:1), a phase-separated system is obtained. Since the

plasticizer mixture happens to have more affinity with PMMA, a plasticized PMMA phase and an ABS-rich phase are obtained. In this special case, both ABS and PMMA are amorphous polymers. Blends with semicrystalline polymers could behave quite differently. In a conventional compounding process, the semicrystalline polymer crystallizes upon cooling from the molten state. During this stage, the plasticizer even though miscible or compatible with the semicrystalline polymer in the molten state usually migrates to the other phase. As a result, the resulting distribution of the plasticizer in the molten state could be largely different from that of the solid state. In a blend composed of polypropylene (PP) and styrene-ethylene-butadiene-styrene (SEBS), Ohlsson et al. [34] have concluded that the distribution coefficient ($K_{PP/SEBS}$) should vary between 0.33 to 0.47 for blends with 10 to 90 wt% of polypropylene (a semicrystalline polymer). This indicates a preferential distribution of the plasticizer in the SEBS. In dynamically vulcanized blends composed of EPDM/PP in the presence of a paraffinic oil, the distribution of plasticizer has been shown to depend on the concentration and the molecular weight distribution of the polypropylene, as well as on the crystallized or molten state of the material [35]. The $K_{PP/EPDM}$ was lower or close to 1 at room temperature, whereas at an elevated temperature, i.e., 190 °C where polypropylene is molten, the distribution coefficient was larger than 1. Based on a micro-mechanical modeling approach, it has also been shown that the distribution coefficient in a nonreactive PP/SEBS and dynamically vulcanized EPDM/PP blends is in favor of the elastomeric component, but varying with the composition [36]. By considering the rigid nature and difficulty of plasticizing the styrenic blocks in SEBS and crystalline portion of polypropylene, the average corrected $K_{PP/SEBS}$ has been reported to be around 0.51 for the molten state, and 0.76 for the solid state [37]. The same ratio ($K_{PP/EPDM}$) of plasticized dynamically vulcanized PP/EPDM blends was reported to be around 0.89 in the solid state. The scanning electron microscopy (SEM) images of rapidly cooled extruded strands of nonreactive EPDM/PP blends have also provided a significant insight into the distribution of plasticizer [14]. The oriented structure of the EPDM phase in the plasticized extrudate versus the nonoriented structure observed in the nonplasticized blends was associated with the predominant presence of plasticizer in the elastomer phase. The possibility of obtaining an oriented elastomeric structure in the presence of plasticizer was explained in terms of large drop in the rheological properties of the elastomer in the presence of plasticizer to a level at which the polypropylene phase could deform the EPDM phase, which was otherwise a highly viscous and elastic material. Once again, these studies illustrate that even though the chosen plasticizer could have a high affinity with both polymeric components, the preferential distribution of the plasticizer is toward the elastomeric component. In a few studies, however, a separate phase mainly composed of plasticizer was also reported [38,39].

3. Morphology development in simple nonreactive thermoplastic/elastomer blends

It was mentioned earlier that the majority of polymer blends form immiscible systems due to thermodynamic limitations. Consequently, blending usually results in a multiphase heterogeneous morphology, which along with other properties of the constituent polymers dictates

the ultimate properties of the resulting compound. Nowadays, compounding is performed in conventional melt-mixing equipment, such as twin-screw extruders, Banbury, or any other internal mixers. The morphology development during the compounding stage strongly depends on the rheological and the interfacial properties of the constituent polymers, their concentrations, the processing conditions and whether or not other additives such as plasticizers, curatives or fillers are present in the system. As a result, for a given immiscible blend composed of only two polymeric components, a wide range of morphologies can be tailored to specifically fulfill the requirements related to the end-use application of the blend. A droplet/matrix type morphology, if well designed, may improve the impact properties and the toughness of materials; the lamellar type will improve the barrier properties; the fibrillar type may improve the tensile properties and the stiffness of the material; and finally the co-continuous morphology may have combinatorial effects due to the simultaneous contributions of both phases at the same time.

Generally, compounding process in conventional melt-mixing equipment begins with the materials in their solid state, e.g., pellets, powders, or bales. These are subjected to intensive mixing conditions such as elevated temperature alongside with shear, which transforms the initial solid state to a molten liquid. As a result, materials are gradually softened, deformed, and finally become molten polymeric components with corresponding viscoelastic properties. The initial transformation of solid pellets to micron-size particles in the early stage of mixing process was shown to be achieved through sheet formation [40]. This mechanism is based on the mutual contact between the solid particles of the dispersed phase with the hot metal surface of the mixing equipment, which alongside with shear results in the formation of sheets/ribbons. The final micron-size particles are finally formed through transformation of these sheets into cylinders, which themselves are broken-up through Rayleigh instabilities. Although this explains the dispersion mechanism of the minor phase, one also needs to take into account the melting behavior of the constituent polymers in the blend. At the early stage of mixing, the melting sequence has a great importance [41,42]. In the case where the minor phase has a lower melting point than the major phase, it rapidly melts and encapsulates the major phase. However, as the temperature of the bulk increases with time during the mixing operation, the major phase begins to melt and becomes the matrix encapsulating the minor phase. As a result, in those blends with component melting characteristics far apart, the melting sequence could be crucial in determining the final morphology.

Once all polymeric components are molten, the mixed medium becomes essentially a mixture of viscoelastic fluids. The morphology refinement at this stage depends on several other parameters, such as shear and elongation rates, mixing time, rheological properties of the constituent polymers, blending composition, interfacial properties, and the presence of other solid or liquid additives (e.g., fillers or plasticizers). In dynamic mixing conditions, the flow and deformation of polymeric components are closely associated to their rheological properties. Among all the rheological properties, the viscosity ratio of the polymeric components at the processing conditions is one of the well-known factors that have been directly related to the morphology of the blend [43,44]. For viscosity ratios greater than 1 ($\eta_A/\eta_B > 1$), the size of the polymeric domains is known to increase monotonically. Furthermore, Favis and Chalifoux

[43] have observed that in contrast to Newtonian dispersions, an immiscible blend with a high viscosity ratio ($\eta_{\text{minor}}/\eta_{\text{major}} \sim 17$) is still deformable. This essentially means that in a complex flow field, where shear and elongational flow coexist, it is still possible to deform a highly viscous dispersed phase. In the other side of viscosity ratio range, a composition dependency has been observed [43]. In the low composition range, the minimum domain size in polypropylene/polycarbonate (PP/PC) blends was reported to be reached around ($\eta_{\text{minor}}/\eta_{\text{major}} \sim 0.15$) and below this value no significant change in the domain size was observed [43]. A similar observation where the polydispersity and the average domain size increased with the viscosity ratio has been reported in EPDM/PP blends with EPDM as the minor phase [45].

The blend composition is another major factor affecting the morphology. When two immiscible polymers are compounded, the morphology in the low composition range mainly consists of droplets of the minor phase in the matrix of the major component. The size and the polydispersity of the emulsion largely depend on the compatibility and, therefore, the interfacial tension and ratio of rheological properties between the polymeric components. As the interfacial tension gets smaller and the viscosity ratio approaches unity, finer droplets of the minor phase are usually observed [46,47]. Further increase in the concentration of the minor phase results in a coarser morphology due to coalescence, where droplets are coalesced with each other and form an emulsion of larger size droplets and increased polydispersity. The increase in the concentration of the minor phase eventually transforms the morphology into a co-continuous type. Each polymeric phase in a co-continuous structure is interconnected throughout the whole bulk of the material and, therefore, both components are expected to contribute simultaneously in the overall properties of the material. Immiscible polymer blends with highly viscous and elastic components generally show a rather wide range of co-continuous composition range. At both extremities of the co-continuity interval, the polymer that constitutes the major phase tends to encapsulate the minor phase. This results in breakdown of the co-continuous structure by transforming it into dispersed-type morphology. The aforementioned co-continuity range and the factors affecting it have major importance in thermoplastic/elastomer blends. As mentioned earlier, most reactive dynamically vulcanized thermoplastic/elastomer blends are produced from their corresponding nonreactive precursor blend at a composition range that coincides with the co-continuity interval [13]. This is mainly due to the fact that in this composition range, there is sufficient amount of elastomeric and thermoplastic components present, which eventually after dynamic vulcanization the elastomer is able to provide the flexibility and rubber-like behavior, whereas the thermoplastic phase guarantees the complete encapsulation of the elastomer phase when it is transformed into dispersed particles.

Several parameters may affect the co-continuity range. Parameters such as the viscosity of the polymeric components, interfacial tension, presence of plasticizer, and mixing time are those which have been carefully studied [48-50]. The early works in understanding the concept of co-continuity were merely concentrated in investigating the effects of concentration and viscosity ratio. Recent studies, however, did not necessarily consider the viscosity ratio as an independent parameter when evaluating the onset of co-continuity [48,51]. Basically for a given viscosity ratio, the onset and therefore the width of the co-continuity range has largely

been attributed to the viscosity of the major phase (η_{major}) regardless of the viscosity of the minor one (η_{minor}); after all, it is the former that is responsible for imposing stresses on the minor phase during processing. Based on some theoretical background on the stability of deformed threadlike emulsions and their packing density, it has been shown that a larger viscosity of the major phase shifted the onset of co-continuity to a lower concentration of the minor phase component [51]. This has also been experimentally observed [49] in a blend composed of EPDM/PP, where the presence of a highly viscous and elastic EPDM in comparison to a less viscous and elastic PP resulted in an asymmetric co-continuity interval, with the onset of co-continuity shifted to a lower concentration of the less viscous PP, and higher concentration of highly viscous EPDM phase as illustrated in Fig. 2.

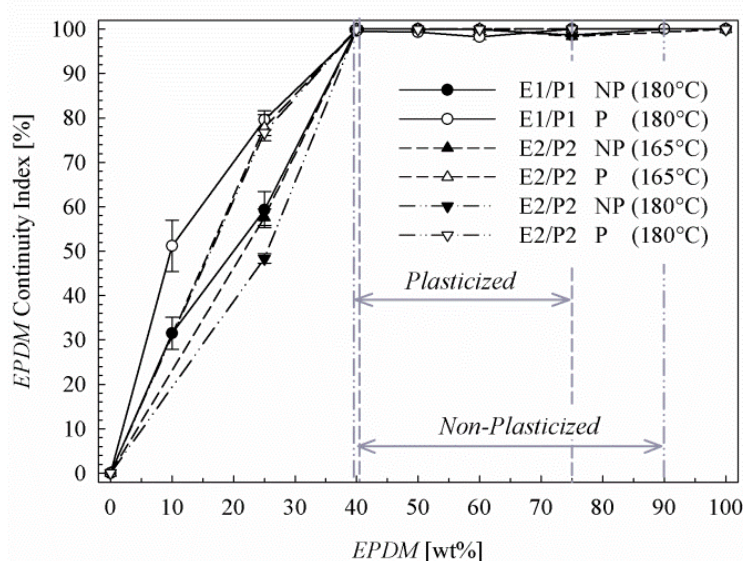


Figure 2. Continuity index of EPDM phase in both plasticized and nonplasticized blends. An asymmetric co-continuity can be clearly observed especially in the case of the nonplasticized system (from [49])

In blends with an identical viscosity ratio, the width of the co-continuity interval could be linked to the interfacial tension. Comparing two distinct immiscible blends with identical viscosity ratio, the one with a higher interfacial tension will have an onset of co-continuity shifted to higher concentrations with a narrow co-continuity interval [48]. Li et al. [52] proposed an interfacial dependent mechanism for the co-continuous morphology development. The authors proposed two distinctive coalescence mechanisms responsible for the co-continuity formation, thread–thread coalescence for low interfacial tension blends, whereas droplet–droplet coalescence mechanism for high interfacial tension blends. Accordingly, the onset and the width of the co-continuity interval is not merely associated with the rheological properties of the constituent polymers, but also to the mobility of interface and the ease of coalescence and percolation of the minor phase.

The use of low molecular weight plasticizers in an immiscible thermoplastic/elastomer blend may simultaneously affect the rheological properties of the components, the interfacial tension, and the volume of the individual phases through swelling. Based on the earlier discussion on

the plasticization of thermoplastic/elastomer blends in the molten state, plasticizers have a slight tendency toward the elastomeric phase. This could clearly indicate that the rheological properties of the elastomer could be largely dropped in highly plasticized systems. Consequently, the ease of deformation and coalescence between elastomeric domains with simultaneous swelling in the presence of plasticizer could result in a coarser morphology, as shown in Fig. 3 [49]. Meanwhile in plasticized blends, a faster percolation and higher continuity index of the elastomeric phase at a lower concentration illustrated in Fig. 2 can be readily understood when the morphologies of nonplasticized and plasticized blends are compared (Fig. 3).

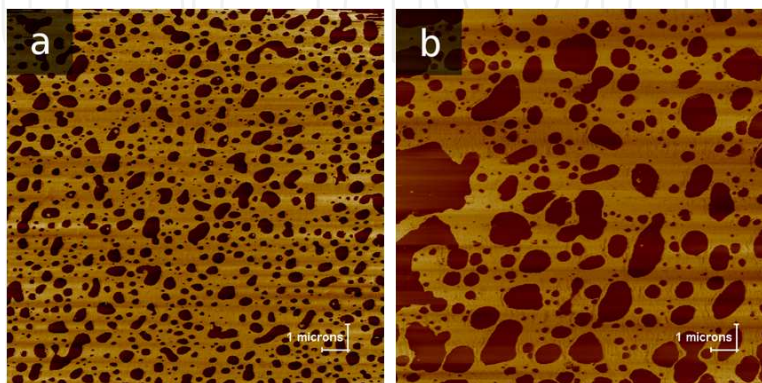


Figure 3. Coarsening effect of a plasticizer in plasticized nonreactive blends of EPDM/PP 25/75 (wt/wt%): (a) nonplasticized (b) plasticized; dark phase: EPDM; bright phase: PP (from [49])

Processing time is another factor that may or may not affect the morphology and it has been investigated by several authors [45,50,53,54]. In few studies performed on blends with high viscosity ratio ($\frac{\eta_{\text{minor phase}}}{\eta_{\text{major phase}}} \geq 1$) and low composition ranges of the dispersed phase, the effect of mixing time was shown to be insignificant regardless of the mixing equipment used, i.e., continuous twin-screw extrusion or internal mixer [53,54]. This is mainly due to the fact that the main deformation and disintegration process is considered to take place within the first few minutes of mixing. A more thorough study covering a wider composition range and blends with viscosity ratios lower or equal to unity demonstrated that the mixing time affected the morphology development, especially in the low viscosity ratio blends [50]. Bu and He [46] work investigated two blends with interfacial tensions of the same order of magnitude, but with different viscosity ratios. The morphology at longer processing times appeared not to be influenced by the viscosity ratio and only by the blend composition. However, at an early stage of mixing, the morphology seemed to depend on the viscosity ratio and whether the low or high viscous component formed the minor phase. For the low viscosity ratio system, when the low viscosity polymer formed the minor phase, the morphology consisted of droplets at low compositions and with further increases in the composition a fibrillar and eventually a co-continuous morphology was formed at a relatively low composition range. On the other hand, when the high viscosity component was the minor phase, it appeared in the form of dispersed droplets and at high concentrations it was transformed into a continuous phase. For blends with viscosity ratio in the vicinity of one, the dispersed phase in either side of the composition range appeared to be in the form of droplets up to a range where a co-continuous morphology was formed. Furthermore, regardless of the blending system and viscosity ratio, the width of

the co-continuity interval was shown to decrease with mixing time. Among other processing parameters, the rotational speed (or indirectly the deformation rate) in an internal mixer has been shown not to have a significant effect on the morphology, especially in the low composition range [53,55].

In both rubber and plastic industries the compounding is usually performed in batch internal mixers or via continuous twin-screw extruders. The twin-screw extrusion process is widely known to be an excellent and versatile technique especially due to its modular design capabilities. The possibility and the advantage of designing different screw configurations generally results in intensive mixing conditions, which provides an efficient distributive and dispersive flow characteristics. Therefore, the comparison between the final morphology and its evolution in an internal mixer and a twin-screw extruder is not as straightforward as it could be imagined. However, although the types of flow fields and their intensities are largely different in those two types of equipment, the overall morphology evolution passes through the same sequences as shown by Sundararaj et al. [54] for polystyrene/polyamide (PS/PA) and polystyrene/polypropylene (PS/PP) blends. The same sequences of sheet formation, transformation into elongated domains, and eventually formation of droplets of the minor phase were observed. Regarding the final domain size of the morphological features, twin-screw extrusion has generally resulted in similar or even finer morphology in the blends [14,56,57]. In both nonplasticized and plasticized thermoplastic/elastomer blends within the co-continuous composition range, Shahbikian et al. [14] have shown that the use of twin-screw extrusion substantially refined the morphology and increased the interfacial area as illustrated in Figs. 4 and 5. The more refined structure especially in the co-continuous composition range provides a more desirable initial morphological state for further reactive and dynamic vulcanization of thermoplastic/elastomer blends.

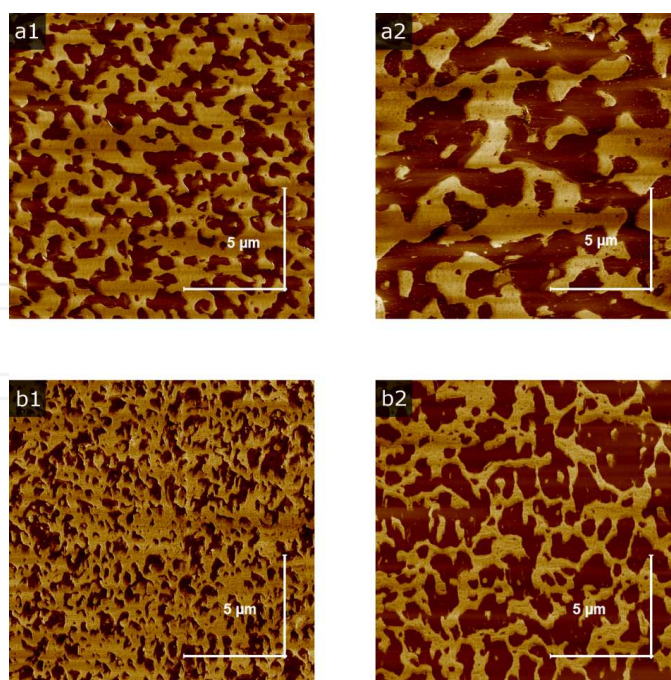


Figure 4. Atomic force microscopy images of EPDM/PP 50/50 (wt/wt%) TPOs: (a) internal mixer, (b) twin-screw extruder. (Column 1: non-plasticized, Column 2: plasticized; Dark phase: EPDM; Bright phase: PP) (from [14])

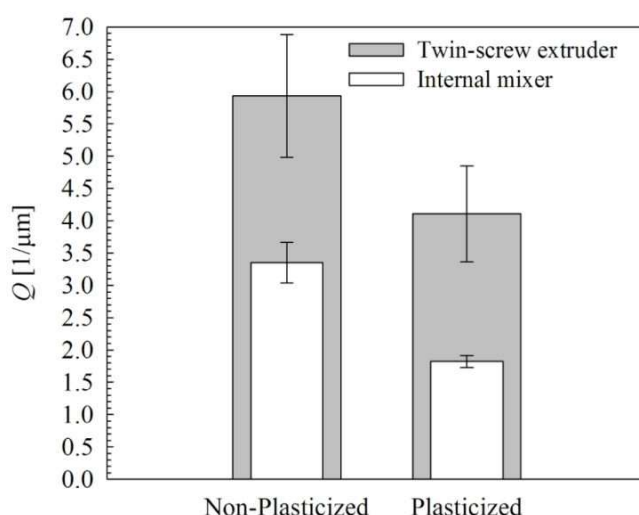


Figure 5. Specific interfacial area (Q) of EPDM/PP 50/50 (wt/wt%) prepared in internal mixer and twin-screw extruder (from [14])

4. Morphology development in dynamically vulcanized nonplasticized and plasticized thermoplastic/elastomer blends

The evolution of phase morphology in reactive blends generally takes place while the rheological, interfacial, and thermodynamic properties of the components are changing due to the chemical reaction. In the case of dynamic vulcanization of thermoplastic/elastomer blends, it is mainly the selective cross-linking reaction of the elastomeric component which influences all the aforementioned properties. The gradual formation of cross-linked elastomer network increases both the viscosity and the elasticity of the elastomer, and affects drastically the morphology development. Throughout this process, the elastomeric major phase, although within a co-continuous structure with its thermoplastic counterpart, is transformed into dispersed particles encapsulated by the thermoplastic polymer. This morphological transformation is widely known as phase inversion. The result is a material most likely with rubber-like properties. Furthermore, dynamically vulcanized blends are melt-processable through existing thermoplastic processing equipments and their final morphology is stable and cannot be altered by any downstream operation. These special advantages of dynamically vulcanized blends have led the interest of both academia and industry toward the improvement of properties through continuously optimizing the parameters affecting their morphology development.

It is known that the elastomer phase in the initial stage of vulcanization is strongly deformed into continuous elastomeric threads and eventually breaks up and forms the final dispersed cross-linked domains [58]. As mentioned earlier, the presence of an initial co-continuous morphology prior to dynamic vulcanization is a prerequisite in obtaining fine dispersed cross-linked elastomer phase at the end of vulcanization [58,59]. From a morphological point of view,

only an initial co-continuous morphology results in an effective and overall transfer of the shear and elongation stresses from one phase to the other and, hence, guarantees the aforementioned breakup of the elastomeric component [58]. The effectiveness of stress transfer and morphology transformation in an initially co-continuous morphology can be visualized by considering the complete opposite hypothetical situation, i.e., an initial dispersed/matrix morphology with the elastomeric component as the droplet phase. In this system, the viscosity and elasticity of the elastomeric component, which already forms the dispersed phase, increase during dynamic vulcanization. As a result, the stress transferred by the low viscosity thermoplastic phase becomes less and less effective in deforming the elastomeric domains and coalescence of the elastomeric domains becomes more and more hindered due to increased viscosity and elasticity of this phase. Consequently, the cross-linking reaction merely stabilizes the already existing, rather coarse dispersed morphology of the elastomeric domains, without any further morphological refinement [60-62]. With this in mind, although the co-continuity is a crucial factor in this process, a stable and unchangeable co-continuous morphology in the intermediate stage of dynamic vulcanization is not a desirable situation. This has been observed in ethylene methyl acrylate and linear low density polyethylene (EMA/LLDPE) blends where phase inversion was hindered due to the presence of a stable co-continuous morphology [63].

To obtain an optimum initial morphology prior to dynamic vulcanization, all the aforementioned parameters discussed in the previous section have to be taken into consideration. For instance, a blend with extremely low viscosity minor thermoplastic phase (low viscosity ratio, $\eta_{\text{thermoplastic}}/\eta_{\text{elastomer}}$) generally forms a dispersed/matrix morphology, where the thermoplastic phase encapsulates coarse elastomeric domains [61]. This is a condition which has to be avoided. On the opposite situation, a highly viscous thermoplastic phase (a high viscosity ratio blend) hinders the dispersion of the cross-linked elastomer particles [62]. The fact that high and low viscosity ratio systems represent completely different initial morphological states prior to dynamic vulcanization means that the torque requirement for mixing could be substantially different from one system to another. Indeed, blends with high initial viscosity ratio with a dispersed thermoplastic phase in an elastomeric matrix have demonstrated a shoulder in the mixing torque during dynamic vulcanization process [61]. This shoulder appears while the blend structure passes through a co-continuous morphology prior to complete vulcanization and dispersion of the elastomeric component in the thermoplastic phase. The shoulder was seen to disappear with less overall mixing torque requirement when the initial morphological state was already a co-continuous type. The appearance of a shoulder in mixing curves has been reported several times and it has been attributed to the onset of phase inversion [60,64]. From an industrial point of view mainly based on the energy consumption during the dynamic vulcanization step, an initial co-continuous structure is desired over the dispersed/matrix one. The co-continuous state guarantees a smoother phase transition with lower energy consumption (lower torque requirement).

In several cases, however, the appearance of a shoulder in the mixing torque could be overshadowed and the phase inversion process could not be easily detected due to the rapid cross-linking reaction [65]. Hence, the kinetics of cross-linking can also play a major role in the phase morphology development during dynamic vulcanization. Generally, the rate of the cross-linking reaction increases with temperature, especially in a blend with a heat reactive curing

system such as phenolic resin [14,64,66]. The higher the temperature, the shorter is the time required to reach a certain level of cross-linking or gel content. The consequence of a faster reaction has been associated with the hindrance in the complete disintegration and dispersion of cross-linked elastomer phase during dynamic vulcanization [60]. At comparatively slower reaction rates, a smoother phase inversion with a better dispersion of elastomeric domains could be usually expected. With similar idea in mind, it has already been observed that the dispersion of a pre-cross-linked elastomer in a thermoplastic phase is a serious challenge especially when the gel content of the elastomer is larger than 70% [67]. Some other reactive systems other than thermoplastic/elastomer blends are as well shown to be affected by the effect of excessive gel content when dispersing one phase into the other. The dispersion of an *in situ* cured epoxy into a polystyrene (PS) is an example, where coalesced and agglomerated structure has been observed for gel content larger than 70% [68].

Beside the kinetics of the curing reaction, the mixing intensity is also a crucial factor which clearly affects the morphology of reactive blends. By mixing intensity, we mainly consider the apparent shear rate of the mixing system. Although this is an important mixing parameter, it cannot be easily dissociated from the effect of temperature through viscous dissipation. In a simple argument, one may observe an increase in the mixing temperature by increasing the rotational speed of the mixing equipment, i.e., by increasing the intensity of mixing. This additional increase in temperature could readily affect the morphology development through its influence on the rate of the cross-linking reaction. In a situation like that, the morphology development is said to be mainly controlled by the fragmentation of the cross-linked elastomer rather than by the transient equilibrium between coalescence and breakup of particles [61]. It has been pointed out that the significant effect of mixing intensity on the final morphology is through its effect on the rate of the cross-linking reaction [60,63].

Mixing intensity can be otherwise investigated by the use of different types of mixing equipment, e.g., internal batch mixers or twin-screw extruders. Regardless of the mixing equipment, the transition between co-continuous to dispersed-type morphologies with well-dispersed cross-linked elastomer domains has merely been attributed to the state of gel content in the blend [64]. This basically means that for a phase transition to happen the gel content of the mixture has to reach a certain level and, if an appropriate blend formulation with well-designed mixing conditions is set in advance, the transition will eventually happen at a similar point in the reaction regardless of the mixing equipment. In most cases with rapid reactive curing systems, the phase transformation occurs quite fast within the first one minute upon the addition of the curing system [58]. Despite this rapid onset, the final morphology of dynamically vulcanized blends depends on both the rate of the curing reaction and the total amount of shear exerted on the blend [69]. Large and to some extent coarse and interconnected vulcanized elastomeric domains have been reported for those dynamically cross-linked blends obtained in a twin-screw extruder in comparison to the ones from an internal mixer [14,69]. The observed morphological features have been mainly attributed to the fast curing reaction (due to larger viscous dissipation) and a shorter residence time in an extrusion process. A morphology comparison for dynamically vulcanized EPDM/PP blends is shown in Fig. 6. The mixture blended in an internal mixer resulted in distinct EPDM domains. On the other hand, in a twin-screw extrusion process, coarse, ruptured, and to some extent large and interconnected domains of EPDM appeared at the end of process.

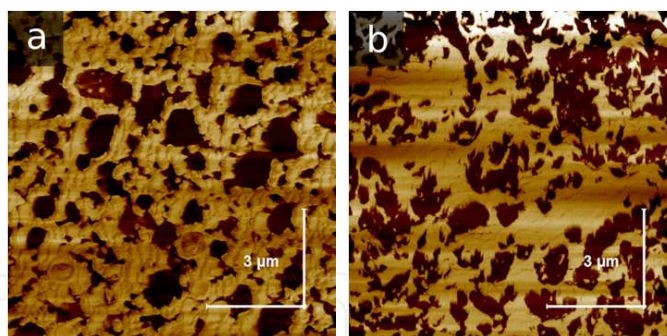


Figure 6. Atomic force microscopy images of reactive nonplasticized EPDM/PP 50/50 (wt/wt%): (a) internal mixer, (b) twin-screw extruder (Dark phase: EPDM; Bright phase: PP) (from [14])

The fast curing reaction in a twin-screw extrusion process in comparison to the reaction rate in an internal mixer has readily been quantified by the gel content of the final blend [14]. In blends with especially low elastomer content, the distinguishable effect of the mixing equipment on the reaction rate can be observed in Fig. 7. One may notice that at 25 and 40 wt% of EPDM, the final gel content of the elastomeric phase is significantly lower when dynamic vulcanization is performed in an internal mixer.

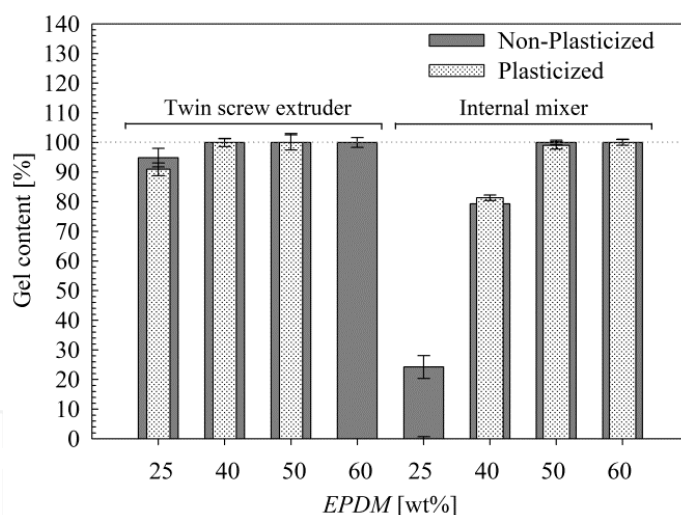


Figure 7. Gel content of the EPDM phase in both nonplasticized and plasticized dynamically vulcanized EPDM/PP blends (from [14])

In several reactive blends, other than the main polymeric components and the curing system, a plasticizer may also be incorporated. Already, the presence of a plasticizer is known to affect the morphological state prior to the dynamic vulcanization step. As it is discussed in the previous section, it is expected to observe phase morphology with larger and percolated elastomeric domains in plasticized blends prior to the addition of a curing system (Figs. 4 and 5). Meanwhile, whether a plasticizer could affect the rate of the cross-linking reaction may actually provide further information regarding the morphology evolution during dynamic

vulcanization. Several characterization techniques such as gel content measurements and thermal analyses by differential scanning calorimetry are usually employed to evaluate a curing reaction. However, the rheological characterization of an elastomer compound by means of an oscillating disc rheometer (ODR) or a conventional rheometer is the most common technique to follow the curing behavior of an elastomer. In a conventional rheometer, one may measure the dynamic rheological properties such as the storage and loss moduli, i.e., G' and G'' , and obtain the crossover point between these two quantities. The aforementioned crossover is the point where the elastic properties of the material overcome the viscous ones. An easy and convenient explanation is that after the crossover point during the curing reaction, the elastomer becomes more and more capable of storing the mechanical energy rather than dissipating it by means of internal friction. As a result, this rheological point has a special importance and it is attributed to the onset of network like behavior in polymeric systems. By returning to the subject of plasticization and its effect on the cross-linking reaction, the crossover point in plasticized elastomer has been clearly shown to be reached at longer times when compared to an identical nonplasticized elastomer [66]. As an example, the effects of both temperature and plasticization on the crossover point of an EPDM containing phenolic curing system are shown in Fig. 8.

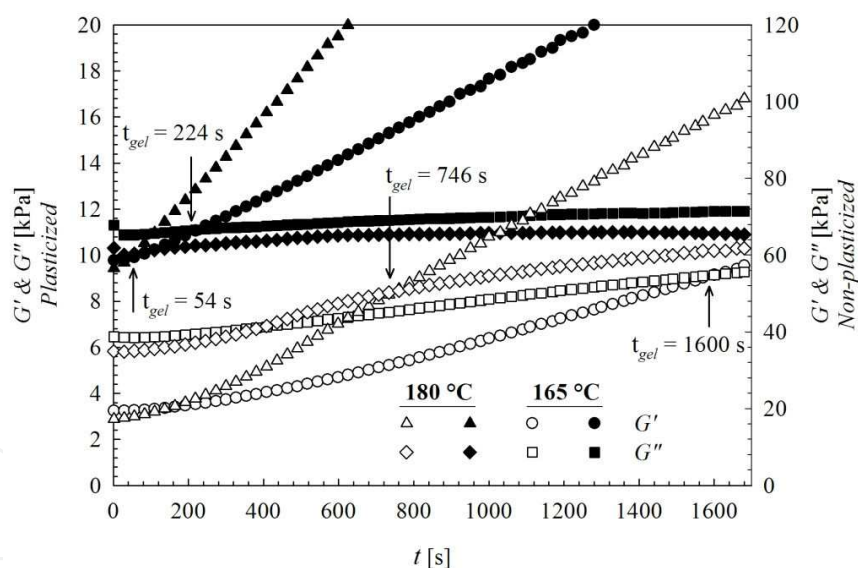


Figure 8. Effects of plasticization and temperature on the curing behavior of EPDM (filled symbols: nonplasticized; open symbols: plasticized; the crossovers are indicated by arrows) (from [66])

Performing such measurement is sometimes impossible for a reactive blend with a complete set of ingredients, i.e., both elastomer and thermoplastic phases in the presence of a curing system and plasticizer. The difficulty lies in the fact that in most cases it is impossible to inhibit the curing reaction while mixing with high-melting-point thermoplastic phase. If one needs to understand the effect of certain ingredients, such as plasticizer, on the curing behavior of complete formulation, two logical paths could be envisaged. The first one is to design a special

formulation with no interference between the mixing conditions, e.g., temperature, and those which may initiate the curing process [66]. In a specially designed reactive EPDM/PP blend, the presence of a plasticizer was shown to induce an initial delayed reaction with a subsequent rapid curing behavior [66]. The second approach toward characterizing the effect of a plasticizer on the curing behavior is based on the gel content analysis of dynamically vulcanized blends [14]. A low level of gel content in the presence of a plasticizer at the end of dynamic vulcanization, especially for the low elastomer content reactive blends is already reported in Fig. 7. These observations, both on the neat elastomer and dynamically vulcanized formulations, indicate that the presence of a plasticizer induces a delayed reaction. How could this affect the morphology development in plasticized dynamically vulcanized blends? According to the previous discussion in this section, a slightly slower but gradually cross-linking reaction could actually result in smooth and good dispersion of the elastomer without its excessive rupture. However, a delayed reaction, especially in a flow field of low extensional and/or shear deformations, may actually result in large coalesced elastomer domains, which is an undesired morphological state in the case of dynamically vulcanized blends [66]. The formation of such coalesced structure in the presence of plasticizer can be observed in Fig. 9, where a plasticized reactive EPDM/PP was subjected to an *in situ* curing and shearing at 0.1 s^{-1} in a rheometer. One may see that the initial co-continuous morphology was gradually transformed into elongated elastomeric domains, where afterward at later stage and longer times (Fig. 9d), large domains of EPDM were formed mainly due to coalescence of elastomeric domains.

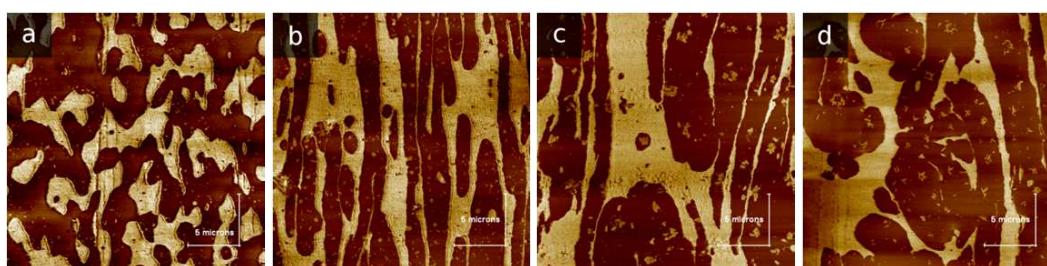


Figure 9. Atomic force microscopy images of a plasticized EPDM/PP 50/50 (wt/wt%) reactive blend at different shearing stages in a rheometer at $165\text{ }^{\circ}\text{C}$ and 0.1 s^{-1} : (a) initial morphology prior shearing and curing, (b) after 450 s, (c) after 2700 s, (d) after 7200 s (Dark phase: EPDM; Bright phase: PP) (from [66])

In a similar nonplasticized reactive blend that was subjected to an identical flowing condition, a complete different morphology evolution could be observed (Fig. 10). First of all, the initial morphology is comparably finer. Furthermore, the gradual shearing with the no delayed curing reaction transforms the co-continuous morphology into a structure where less coalescence could be observed. More interestingly, at longer times (Fig. 10d) the thermoplastic phase shows the tendency of encapsulating the elastomeric domains. This morphological transformation is basically what is wished for when dynamic vulcanization process is in mind.

To conclude, the ideal morphological state at the end of the dynamic vulcanization process with finely dispersed elastomeric particles could only be achieved with the finest initial morphology and with a well-designed formulation and processing parameters. All these together, in a perfectly fine-tuned mixing procedure based on a correct blending sequence with

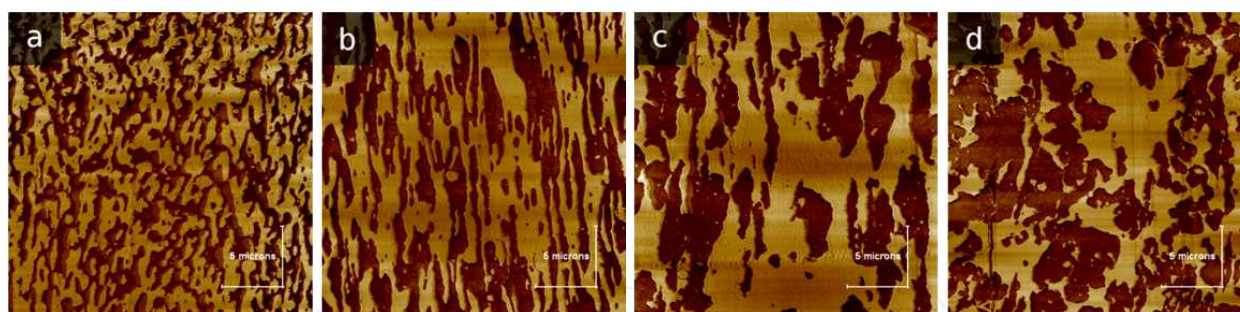


Figure 10. Atomic force microscopy images of a nonplasticized EPDM/PP 50/50 (wt/wt%) reactive blend at different shearing stages in a rheometer at 165 °C and 0.1 s⁻¹: (a) initial morphology prior shearing and curing, (b) after 450 s, (c) after 2700 s, (d) after 7200 s (Dark phase: EPDM; Bright phase: PP) (from [66])

respect to all ingredients and their corresponding effects on the phase morphology evolution, will guarantee the success of the dynamic vulcanization process.

5. Concluding remarks

The morphology evolution and the state of the final phase structure have crucial effects on the physical and mechanical properties of a reactive thermoplastic/elastomer system. A successful approach toward product development of such materials usually begins by identifying the essential requirements of the final product. Accordingly, the ingredients should be carefully chosen as each fulfills a special role in the overall formulation. Thermoplastic elastomers may contain several different chemicals such as polymeric components, curing system, fillers, additives, and plasticizer. Product development could only be successful if the role and the effect of each ingredient on the phase morphology are thoroughly investigated in advance. Throughout this procedure, the rheological, interfacial, and thermal properties of complete formulations with the curing behavior have to be all considered. Only based on this information, an effective mixing and blending strategy can be established, which at the end will guarantee the desired target properties.

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