

New Understanding of Morphology Evolution of Thermoplastic Vulcanizate (TPV) during Dynamic Vulcanization

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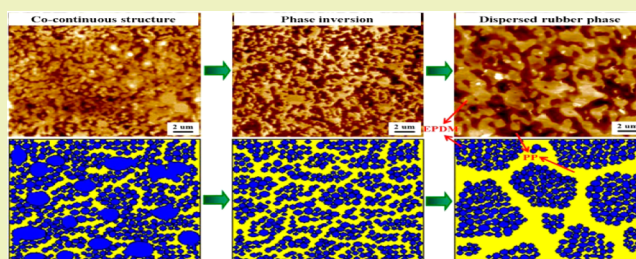
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S Supporting Information

ABSTRACT: Thermoplastic vulcanizates (TPVs) have attracted considerable attention as typical “green” polymers in recent years and have been widely used in industry because they combine the excellent resilience of conventional elastomers and the easy recyclability of thermoplastics. With a new understanding of the formation and agglomeration of the rubber nanoparticles in ethylene propylene diene monomer/polypropylene (EPDM/PP) TPV, we revealed a new mechanism for the morphology evolution of TPV during dynamic vulcanization (DV). The phase inversion in TPV is dominated by the formation and agglomeration of the rubber nanoparticles rather than the elongation and breakup of the cross-linked rubber phase as previously reported. The size of the rubber agglomerates increases with increasing DV time and then remains constant after DV. In addition, we studied the relationship between the cross-linking of the rubber phase, formation and agglomeration of the rubber nanoparticles, and phase inversion and variation of the rubber network during DV. This study provides guidance to control the microstructure of TPV in preparation of high performance TPV products for automobile and electronic applications.

KEYWORDS: Dynamically vulcanized EPDM/PP blends, Atomic force microscopy (AFM), Morphology evolution, Phase inversion, Rubber network, Mechanism



INTRODUCTION

Thermoplastic vulcanizates (TPVs) are a group of high performance thermoplastic elastomers prepared by dynamic vulcanization (DV), which consist of a high content of cross-linked rubber as the dispersed phase and a low content of thermoplastics as the continuous phase.¹ TPVs combine the excellent resilience of conventional vulcanized elastomers and the good processability and easy recyclability of thermoplastics. Therefore, TPVs have attracted considerable attention as typical “green” polymers and have been widely used in industries such as automotive, building, and electronics in recent years. Nowadays, TPVs have become one of the fastest growing elastomers because of the requirements of environmental protection and resource saving.²

To obtain TPV products with excellent softness and elasticity, a high content (60–80 wt %) of rubber phase in TPV is generally required. The microstructure of TPV, including the size and shape of the rubber phase, has a significant effect on the mechanical properties and processability of the TPV.^{3–5} Therefore, the microstructure and

morphology evolution of TPV during DV have attracted much attention.

DV is a complicated reactive blending process consisting of the breakup and cross-linking of the rubber phase and the phase inversion of the rubber phase and thermoplastic phase, which are all keys to the morphology evolution of TPV during DV.^{6–9} Some previous studies reported that the cross-linking of the rubber phase resulted in rapid increases in the viscosity of the rubber phase and the shear stress acting on the rubber phase. Thus, the rubber phase was elongated and broken into rubber microparticles with a diameter of 0.5–3.0 μm dispersed in the PP matrix, leading to phase inversion.^{1,10,11} Goharpey et al. proposed a different mechanism for the morphology evolution of TPV.^{12,13} They reported that the broken rubber droplets formed at the early stage of DV could not coalesce but were transformed into agglomerates of rubber microparticles because of in situ vulcanization, and the agglomerates broke

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down with an increase in DV time because of the shrinkage of the rubber particles at high degrees of cross-linking. Thus, the mechanism for the morphology evolution of TPV during DV is still controversial. Meanwhile, the relationship between the cross-linking and breakup of the rubber phase and the phase inversion in TPV have not been reported yet.

In our previous study, we revealed for the first time that the EPDM phase broke up into nanoparticles at the early stage of DV, and the rubber microparticles in TPVs obtained at the end of DV were actually the agglomerates of rubber nanoparticles with a diameter of 40–60 nm.¹⁴ With the new understanding of the formation and agglomeration of rubber nanoparticles, in the present study, we further studied the morphology evolution of EPDM/PP TPV during DV, which plays an important role in the final properties of the TPV. Then, we studied the relationship between the cross-linking of the rubber phase, formation and agglomeration of the rubber nanoparticles, phase inversion in TPV, and variation of the rubber network during DV. Furthermore, we studied the mechanism for self-agglomeration of the rubber nanoparticles and the change in the size of the rubber agglomerates during DV by using the equations proposed by Wang.¹⁵ We aimed to clarify the mechanism of the morphology evolution of TPV during DV to provide guidance for obtaining high performance TPV products by controlling their microstructure.

EXPERIMENTAL METHODS

Materials. Table S1 of the Supporting Information lists the characteristic properties of injection-grade PP and EPDM, which were bought from Basell Co., Ltd. (Thailand) and Mitsui Chemicals Co., Ltd. (Japan), respectively. The cross-linking system was composed of resol and SnCl₂ supplied by Xinjiang Karamay Oilfield. A commercially available pentaerythritol tetraakis 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate (1010) was used as an antioxidant.

Sample Preparation. EPDM/PP TPVs were prepared in a Haake internal mixer (HAAKE Rheomix 600 OS; Thermo Fisher Scientific, U.S.A.) equipped with two counter-rotating rotors (Roller Rotors) by using Trigonox 101 (DHBP; Akzo Nobel, Holland) as the initiator. In order to study the mechanism for the morphology evolution of TPV, we selected six samples at six stages during DV. The EPDM/PP premix was prepared by using the same method described in our previous works.¹⁴

Volume Swell Ratio Measurement. The volume swell ratios (Q) of the selected samples measured the degree of cross-linking of the EPDM phase. A rectangular sample (10 mm × 10 mm × 2 mm) was immersed in cyclohexane for 48 h under gentle stirring; the solvent was refreshed after 24 h to remove the extracted components. The swollen sample was weighed, dried, and weighed again. The sample was dried at 80 °C for 12 h to remove the absorbed solvent. The volume swell ratios (ϕ_p) of these samples were calculated by using eq 1¹⁶

$$\phi_p = \frac{V_p}{V} = \frac{1}{1 + \frac{m_s - m_d}{m_d} \times \frac{\rho_p}{\rho_s}} \quad (1)$$

where V_p and V are the volumes of the sample before and after swelling, respectively; m_s and m_d are the masses of the swelled sample before and after drying, respectively; and ρ_p and ρ_s are the densities of the sample before swelling and the solvent, respectively.

Q is defined as the ratio of V to V_p

$$Q = \frac{V}{V_p} = \frac{1}{\phi_p} \quad (2)$$

Morphology Studies. The morphology of the selected samples was examined by using a peak force tapping atomic force microscopy (PF-AFM) (Nanoscope IIIa, Bruker Corporation, Germany) because

of its high resolution.¹⁸ Before the observation, the samples were polished at −130 °C by using a cryo-ultramicrotome (Leica EM UC7, Germany). The distribution of the rubber particle size was determined with the Image-Pro Plus 4.5 software.⁵

Disintegration Tests. The disintegration of the selected samples was studied by immersing approximately 30 mg of each sample with a similar shape in hot xylene (120 °C). As only PP dissolves in the hot xylene, the result of the disintegration test can be used to confirm the development of the EPDM rubber network and further indicate the occurrence of phase inversion in the EPDM/PP blend during DV.

Rubber Process Analyzer (RPA). The cured rubber particles in EPDM/PP TPVs, with a high degree of cross-linking and high modulus, can be approximately regarded as fillers in the PP matrix. Thus, the change in the EPDM rubber network in the PP matrix can be reflected by the “Payne-like effect” of EPDM/PP TPV, which was analyzed by a rubber process analyzer (RPA 2000, Alpha, U.S.A.).¹⁷ The strain scan conditions were 190 °C, 0.2 Hz, and a strain range of 0.7–1300%. Before the analysis, the samples were preheated for 5 min.

RESULTS AND DISCUSSION

Variation of Degree of Cross-linking of Rubber Phase During DV.

The cross-linking of the rubber phase during DV plays a very important role in the phase morphology of TPV. To study the mechanism for the morphology evolution of TPV, we first measured the variation of the degree of cross-linking of the rubber phase during DV. Six samples were selected according to the torque-time curve, and these samples were frozen in liquid nitrogen immediately before morphology observations under PF-AFM. Figure 1 shows the variation of

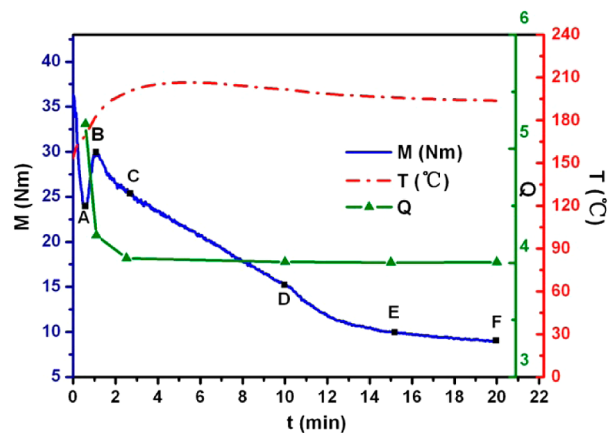


Figure 1. Variations of torque (M), temperature (T), and swell ratio (Q) of EPDM/PP blend in Haake Rheomix.

the torque and temperature as a function of mixing time during DV of the EPDM/PP blend in the Haake Rheomix. At the initial stage, the torque decreases with an increase in mixing time because of the melting of the blend. Sample A is selected at the inflection point A, where the torque reaches a local minimum because the blend has just melted at this point. Thus, sample A represents the EPDM/PP blend at the initial stage of vulcanization. With the rapid vulcanization of the rubber phase, the torque rises dramatically until it reaches a peak. Sample B is selected at the maximum torque point. Then, a linear decrease of the torque is observed upon further vulcanization, and samples C and D are selected in this region. Then, the torque declines very slowly until the end of DV, where samples E and F are selected. During the test, because of the heat generated by the cross-linking of EPDM, the temperature increases from 170 to 210 °C after the feeding of premix.

The variation of the degree of cross-linking of the rubber phase in the EPDM/PP blend was characterized by the swell ratio (Q) of these six samples (A–F), and the results are shown in Figure 1. Q of sample A is up to 5, indicating a low degree of cross-linking. The sharp decline of Q from sample A to sample B indicates a rapid increase in the degree of cross-linking of the rubber phase. The increase in the degree of cross-linking enhances the modulus of the rubber phase and thus increases the torque in the Haake Rheomix. The further decrease in Q from sample B to sample C indicates a further increase in the degree of cross-linking. At this stage (from point B to point C), the torque does not increase with a further increase in the degree of cross-linking of the rubber phase, implying that the torque is determined by not only the degree of cross-linking of the rubber phase but also by the microstructure of the blend. The Q of samples C, D, E, and F are the same, indicating that the cross-linking of EPDM is completed at point C. Thus, the decline of the torque from point C to point F is mainly caused by the morphological change of the blend at this stage. Furthermore, the increase in temperature stops at point C, in agreement with the results of Q . The variation of Q and temperature suggests that the cross-linking of the rubber phase occurs at an early stage of DV (about 3 min, Figure 1).

Effect of Degree of Cross-linking on Formation of Rubber Nanoparticles. In our previous studies, we reported that the rubber microparticles in TPV were actually the agglomerates of rubber nanoparticles with a diameter of 40–60 nm.¹⁴ These rubber nanoparticles were formed by the in situ vulcanization of the rubber nanodroplets formed in the EPDM/PP blend at an early stage of DV. We believe that the formation of these rubber nanoparticles and their agglomeration play an important role in the morphology evolution of the EPDM/PP blends during DV. Therefore, the effect of the degree of cross-linking of the rubber phase on the formation of the rubber nanoparticles was studied.

Figure 2 shows the phase images of samples A, B, C, and D observed by using PF-AFM, representing the effect of degree of cross-linking on the formation of the rubber nanoparticles at the early stage of DV. The darker regions represent the EPDM phase, and the lighter ones represent the PP phase. We can observe from Figure 2a that the agglomerates of a great many rubber nanoparticles with a diameter of 25–70 nm are formed at the initial stage of DV (sample A), in good agreement with the calculated minimum size of the broken rubber nanoparticles in the EPDM/PP blend in our previous study.¹⁴ Meanwhile, we can also observe some rubber aggregates with a much larger diameter (about 500 nm) in sample A. The formation of different rubber morphologies is ascribed to the inhomogeneity of the degree of cross-linking of the rubber phase in sample A. Some broken rubber nanodroplets with a high degree of cross-linking transform to rubber nanoparticles at a very early stage of DV. These rubber nanoparticles cannot coalesce, but they do agglomerate with one another. Some other rubber nanodroplets with a lower degree of cross-linkings can still coalesce to form rubber aggregates. With an increase in the degree of cross-linking of the rubber phase, both the agglomerates of rubber nanoparticles and the rubber aggregates can still be observed in sample B, but the number of rubber aggregates decreases, as shown in Figure 2b. With a further increase in the degree of cross-linking of the rubber phase, we can observe only the agglomerates of the rubber nanoparticles in sample C, as shown in Figure 2c. In sample C, the rubber nanodroplets cannot coalesce anymore but transform into rubber nanoparticles and

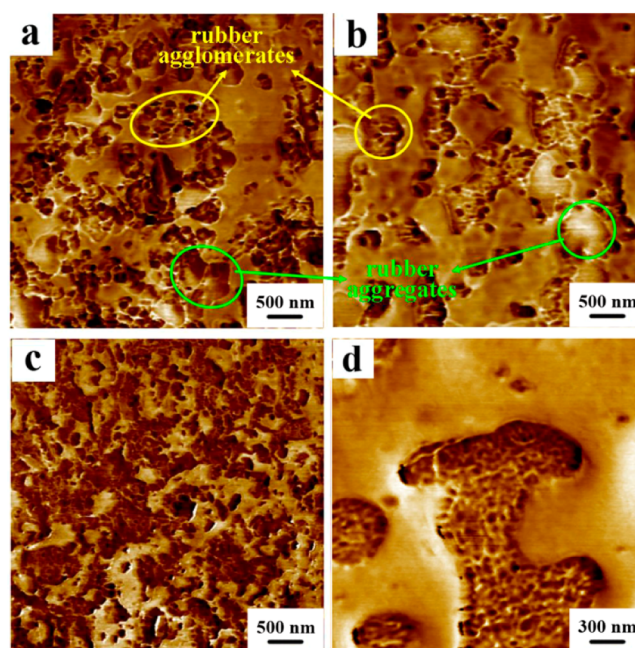


Figure 2. AFM phase images of PP/EPDM (40/60) blend taken at different mixing times (darker regions represent EPDM phase and lighter regions represent PP phase): (a) point A, (b) point B, (c) point C, and (d) point D.

then agglomerate because of the high degree of cross-linking of the rubber phase. The size and shape of the rubber nanoparticles in sample C are similar to those in sample D (Figure 2c,d), suggesting the completion of the breakup of the rubber phase at point C. This is ascribed to the same degree of cross-linking of the rubber phase in samples C and D, as evidenced by the identical Q of these two samples (Figure 1). Thus, these results demonstrate that the formation of the rubber nanoparticles in the dynamically vulcanized EPDM/PP blend depends on the degree of cross-linking of the rubber phase. The rubber nanodroplets formed by the breakup of the EPDM phase under the shearing stress at the beginning of DV transform to rubber nanoparticles because of an increase in degree of cross-linking. These rubber nanoparticles will not coalesce again, but they will form agglomerates during the further DV.

Morphology Evolution of Blend during DV. To study the morphological evolution of the EPDM/PP blend during DV, the height images of the six selected samples were obtained by using PF-AFM, and the results are shown in Figure 3. The darker regions represent the PP phase, and the lighter regions represent the EPDM rubber phase. A cocontinuous structure is observed in samples A and B, as shown in Figure 3a and b, respectively. This structure is ascribed to the coalescence of some EPDM rubber droplets at these two stages because of the low cross-link degree of the rubber phase, as evidenced in the Effect of Degree of Crosslinking on Formation of Rubber Nanoparticles section. The EPDM continuous phase is transformed into the dispersed phase in the continuous PP matrix in sample C, indicating the occurrence of phase inversion, as shown in Figure 3c. According to Figure 2c, all the rubber nanodroplets have been transformed into rubber nanoparticle agglomerates at point C, facilitating the breakup of the continuous EPDM rubber phase and the formation of the EPDM dispersed phase in the PP matrix. In other words, the

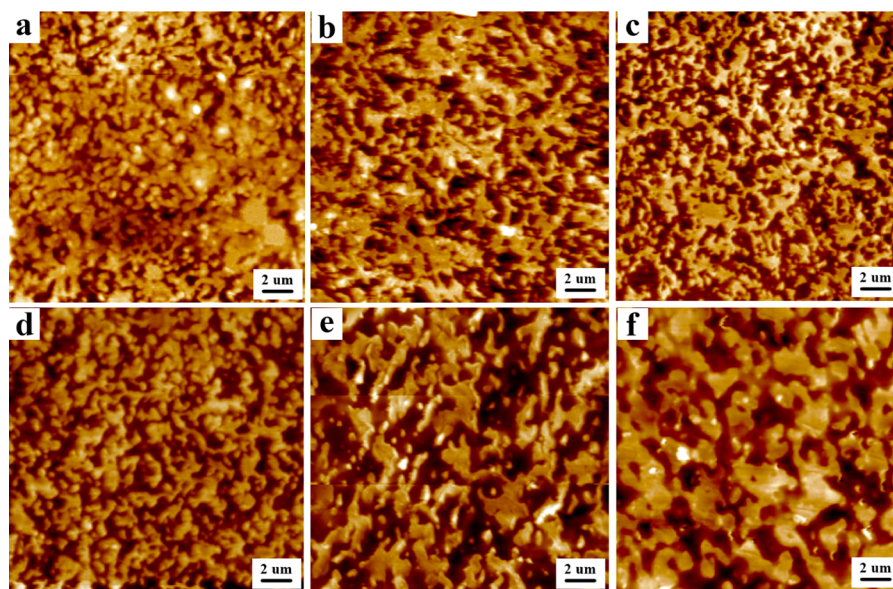


Figure 3. AFM height images of PP/EPDM (40/60) blend taken at different times (darker regions represent PP phase, and lighter regions represent EPDM rubber phase): (a) point A, (b) point B, (c) point C, (d) point D, (e) point E, and (f) point F.

phase inversion in the EPDM/PP blend during DV depends on the formation and agglomeration of rubber nanoparticles rather than the elongation and breakup of the cross-linked rubber phase as reported in previous studies.^{10,11} This result can also explain the phase inversion in TPV in a wide range of viscosity ratios of EPDM and PP as proposed by Antune et al.¹⁹ Despite the formation of the dispersed phase, these EPDM rubber agglomerates are interconnected with one another and form a strong rubber network, as shown in Figure 3c. These rubber agglomerates are well dispersed in the PP matrix in sample D, but their size and shape are quite irregular, as shown in Figure 3d. Some rubber agglomerates are still interconnected with one another and form a rubber network, but the network is incomplete. Upon further DV, the size of the rubber agglomerates increases significantly to around 2 μm in sample E (Figure 3e), and the PP layers encapsulating the rubber agglomerates are thicker than those in sample D. Thus, the space between the rubber agglomerates significantly increases in sample E, leading to the degradation of the rubber network. With further increases in DV time, the size of the rubber agglomerates in sample F is similar to that in sample E, but the rubber agglomerates in sample F are more regular, as shown in Figure 3f. On the other hand, these results indicate that although a good dispersion of the rubber nanoparticle agglomerates in the PP matrix is obtained and a strong rubber network structure is formed in samples C and D, these agglomerates are metastable and will form much denser rubber nanoparticles agglomerates with a larger diameter at a later DV stage (samples E and F), leading to the weakening of rubber network structure. This motivated us to improve the compatibility between EPDM and PP to obtain a good and stable dispersion of rubber nanoparticles in the PP matrix to prepare TPV products with high performance.

Variation of Rubber Network Structure during DV.

The six selected samples were disintegrated in hot xylene to further study the phase inversion of the EPDM/PP blend and the variation of the rubber network in TPV during DV. As only PP dissolves in hot xylene, the following conclusions can be obtained: (i) If the sample disintegrates, the PP phase is the

matrix. (ii) If the sample does not disintegrate, the cross-linked EPDM phase is the matrix or the blend exhibits a co-continuous structure.

The photographs of the samples immersed in hot xylene at 120 $^{\circ}\text{C}$ for various times are shown in Figure S1 of the Supporting Information. Sample A is not disintegrated even after 20 h of immersion because of a co-continuous structure. Although sample B seems to have a co-continuous structure in Figure 3b, there is some disintegration at the surface of sample B after 11 h of immersion. The partial disintegration of sample B in hot xylene indicates that partial phase inversion has occurred at point B.^{1,19} Samples C, D, E, and F are completely disintegrated into small pieces with a diameter of a few hundred micrometers after immersion in hot xylene for 8, 3.5, 2.5, and 2 h, respectively, indicating the complete phase inversion of the EPDM/PP blend at point C, in good agreement with the AFM results in Figure 3. In addition, the immersion time required for the complete disintegration of the sample decreases continuously from point C to point F indicating the weakening of the rubber network in the dynamically vulcanized EPDM/PP blend with the increase in vulcanization time.

In addition, a RPA was used to further demonstrate the change in the rubber network in the EPDM/PP blend during DV. As previously reported, the storage modulus (G') decreases with increasing strain amplitude (Payne effect) for filled rubbers and eventually reaches a lower bound at sufficiently large strain amplitudes. The difference between the maximum and minimum of G' ($\Delta G'$) is a measurement of the filler network.^{20–22} In this study, the cross-linked rubber phase with a high elastic modulus at the late stage of DV can be regarded as the fillers dispersed in the PP matrix. Thus, a “Payne-like effect” was proposed in this study to indicate the change in the rubber network in the EPDM/PP blend during DV.¹⁷ A larger $\Delta G'$ indicates a stronger rubber network in the blend and a stronger Payne-like effect.^{20,21}

AFM images and the disintegration test indicate that the rubber phase is fully vulcanized, and the phase inversion is complete at point C. Therefore, RPA was performed on samples C, D, E, and F and pure PP to further characterize the

variation of the rubber network in TPV during DV. Figure S2 of the Supporting Information illustrates the strain dependence of G' for these samples. It is shown that the G' of every sample decreases to almost the same value as that of PP as the shear strain approaches 1300%, indicating the complete disruption of the rubber network in every sample. Thus, the G' of a sample at a strain of 1300% can be regarded as the minimum G' , and the difference between the initial G' and the G' at a strain of 1300% is the $\Delta G'$. A very large $\Delta G'$ for sample C indicates a strong rubber network in this sample. $\Delta G'$ is smaller for sample D than for sample C, indicating that the rubber network in sample D is weaker than that in sample C. The almost identical $\Delta G'$ of samples E and F and pure PP indicates that the rubber network in TPV is severely disrupted and then remains stable when DV proceeds to a certain degree, consistent well with the AFM results (Figure 3). In addition, the variation of the initial G' with DV time is in good agreement with the variation of the mixing torque with vulcanization time, indicating that the decline of the mixing torque at the last stage of DV is caused by the disruption of the rubber network rather than the breakdown of the rubber agglomerate structure proposed by Goharpey et al.¹³ A higher initial G' indicates a higher elasticity and stiffness of the blends at the early stage of DV. The initial G' obviously decreases with an increase in DV time, indicating the improved processability of EPDM/PP TPV, well consistent with the torque result that the mixing torque declines with an increase in DV time.

Mechanism of Morphological Evolution during DV.

The above results demonstrate that the formation of the rubber nanoparticles and the development of the rubber nanoparticle agglomerates play a key role in the morphological evolution of EPDM/PP TPV during DV. On the basis of these results, we propose a new mechanism for the morphological evolution of EPDM/PP TPV, as shown in Figure 4, where the yellow regions represent the PP phase and the blue regions represent the EPDM phase. In the unvulcanized EPDM/PP blend, the PP phase (40 wt %) is dispersed in the unvulcanized EPDM continuous phase (60 wt %), as shown in Figure 4a. At the initial stage of DV, the breakup of the EPDM phase under rotational shear leads to the formation of a large number of

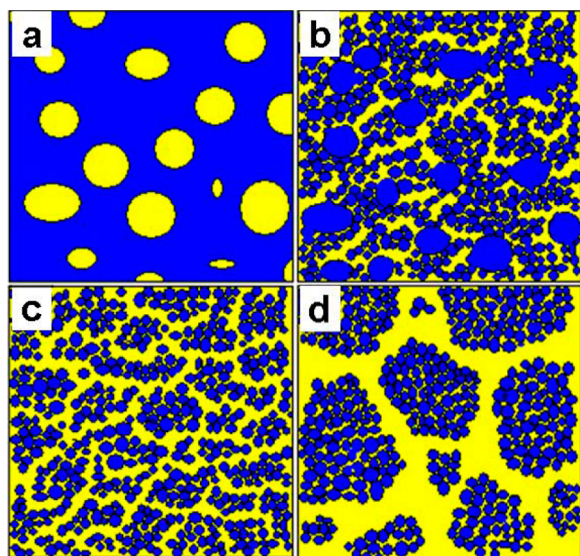


Figure 4. Schematic illustration of morphological evolution of TPV during dynamic vulcanization.

EPDM nanodroplets, according to the calculated results reported in our previous studies.^{13,23} At this stage, the coalescence of EPDM nanodroplets occurs simultaneously with the breakup of the EPDM phase because of the low cross-link degree. With an increase in DV time, some EPDM nanodroplets transform into nanoparticles, which will not coalesce again because of an increase in the cross-link degree, and then these nanoparticles form rubber agglomerates.^{24–31} Because of the inhomogeneous cross-link degree of the rubber phase, some rubber nanodroplets with a lower cross-link degree can still coalesce and breakup. At this stage, the EPDM/PP blend exhibits a co-continuous structure (Figure 4b).

With further increases in vulcanization time, all the broken rubber nanodroplets transform into nanoparticles because of an increase in the cross-link degree. Therefore, the morphological evolution of the EPDM/PP blend at the later stages (points C, D, E, and F) is dominated by the agglomeration of rubber nanoparticles in the PP matrix (Figure 4c,d). The agglomeration of these rubber nanoparticles can be explained by using the equation proposed by Wang¹⁵

$$\Delta W = 2[(\gamma_f^d)^{1/2} - (\gamma_p^d)^{1/2}]^2 + 2[(\gamma_f^p)^{1/2} - (\gamma_p^p)^{1/2}]^2 \quad (3)$$

where ΔW is the change of the adhesion energy upon filler agglomeration; γ_f^d and γ_p^d are the dispersive components of surface energy of the filler and matrix, respectively; and γ_f^p and γ_p^p are the polar components of surface energy of the filler and matrix, respectively. Equation 3 shows that the agglomeration of the cross-linked rubber particles in the PP matrix is an exothermic process ($\Delta W > 0$). Thus, these rubber nanoparticles in the PP matrix agglomerate spontaneously, and they will agglomerate more densely upon further DV, leading to an increase in diameter of rubber agglomerates with the increase in vulcanization time, as shown in Figure 4c and d). The agglomeration of these rubber nanoparticles leads to phase inversion, and the rubber nanoparticle agglomerates become the dispersed phase in the continuous PP matrix, as shown in Figure 4c. In other words, the phase inversion of the EPDM/PP blend during DV depends on the formation and agglomeration of the rubber nanoparticles rather than the elongation and breakup of the cross-linked rubber phase as reported in the literature.^{1,10,11} Furthermore, the dense agglomeration of the rubber nanoparticles and the thickening of the PP layers encapsulating the EPDM agglomerates reduce the interconnection between the agglomerates of rubber nanoparticles, leading to the significant weakening of the rubber network with an increase in DV time and thus the decline of the mixing torque.

At the final stage of DV, the agglomeration of the rubber nanoparticles in the PP matrix will be terminated when the hydrodynamic force acting on the EPDM agglomerates and the cohesive force between the rubber nanoparticles are the same.¹⁵ In this case, the size of a rubber nanoparticle agglomerates (R) can be calculated by using the equation proposed by Wang¹⁵

$$R^2 = \frac{H\nu}{\frac{5}{2}\pi\eta\tau\sin^2\varphi} \quad (4)$$

$$\sin\varphi = \frac{r}{R-r} \quad (5)$$

where ν and H are the average connection number of a rubber nanoparticle to the agglomerate and the average force of a

connection, respectively; η and τ are the viscosity of the matrix and the shear rate, respectively; r is the diameter of a single rubber nanoparticle; and φ is the angle that describes the relationship between the size of the rubber nanoparticles and the size of the agglomerate, as shown in Figure S3 of the Supporting Information. η and H are both constant when the temperature and τ are unchanged during the late stage of DV (Figure 1). In addition, ν is also constant because r remains stable at the end of DV. Therefore, according to eqs 4 and 5, we conclude that R remains constant at the end of DV. The weakening of the rubber network is also complete then, leading to a constant mixing torque in the Haake Rheomix. On the other hand, according to the lowest energy principle, the spherical rubber agglomerates dispersed in the matrix are the most stable.³² Thus, the shape and size of the rubber agglomerates become more regular with an increase in DV time (Figure 4d).

CONCLUSIONS

The morphology of the EPDM/PP blends at different stages of DV was observed by using PF-AFM, and the mechanism of morphology evolution based on the formation and agglomeration of the rubber nanoparticles was studied. The results show that the breakup and cross-linking of the rubber phase into nanodroplets occurs mainly at the early stage of DV. The rubber nanodroplets gradually transform into nanoparticles because of the inhomogeneous cross-linking of the rubber phase at the initial stage of vulcanization. Phase inversion occurs when all the rubber nanodroplets have transformed into rubber nanoparticles, which agglomerate spontaneously. Thus, the phase inversion of the EPDM/PP blend during DV is dominated by the formation and agglomeration of rubber nanoparticles rather than the elongation and breakup of the cross-linked rubber phase as previously reported.^{10,11} This result could explain the occurrence of phase inversion in TPV in a wide range of viscosity ratios of PP to EPDM, as proposed by Antune et al.¹⁹ At the later stage of DV, the morphology evolution of the blend is dominated by the further agglomeration of rubber nanoparticles rather than the breakup of the rubber particle agglomerates as proposed by Goharpey et al., leading to thickening of the PP layers encapsulating the rubber agglomerates and significant weakening of the rubber network. The shape and size of the rubber agglomerates remain constant when the temperature and shear rate both remain constant at the end of DV, consistent with the equations proposed by Wang.¹⁵ Because the morphology evolution of EPDM/PP TPV during DV plays an important role in the final properties of the TPV, this work provides guidance to control the microstructure of the EPDM/PP TPV in the manufacture of high performance TPV products for a wide range of industrial applications.

ASSOCIATED CONTENT

Supporting Information

Characteristics of the used materials (Table S1), photographs of the disintegrated samples in hot xylene for various times (Figure S1), result of RPA testing for samples C–F (Figure S2), and schematic representation of a rubber nanoparticle and rubber nanoparticles agglomerate (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Antunes, C. F.; Machado, A. V.; Martin, V. D. Morphology development and phase inversion during dynamic vulcanisation of EPDM/PP blends. *Eur. Polym. J.* **2011**, *47* (7), 1447–1459.
- (2) Duin, M. V. Recent developments for EPDM-based thermoplastic vulcanisates. *Macromol. Symp.* **2006**, *233*, 11–16.
- (3) George, S.; Ramamurthy, K.; Anand, J. S.; Thomas, S. Rheological behaviour of thermoplastic elastomers from polypropylene/acrylonitrile-butadiene rubber blends: Effect of blend ratio, reactive compatibilization and DV. *Polymer* **1999**, *40*, 4325–4344.
- (4) Naderi, G.; Lafleur, P. G.; Dubois, C. Microstructure-properties correlations in dynamically vulcanized nanocomposite thermoplastic elastomers based on PP/EPDM. *Polym. Eng. Sci.* **2007**, *47* (3), 207–217.
- (5) l'Abée, R. M. A.; Duin, M. V.; Spoelstra, A. B.; Goossens, J. G. P. The rubber particle size to control the properties-processing balance of thermoplastic/cross-linked elastomer blends. *Soft Matter* **2010**, *6* (8), 1758.
- (6) Nicolini, A.; Rocha, T.; Jacobi, M. Dynamically vulcanized PP/EPDM blends: Influence of curing agents on the morphology evolution. *J. Appl. Polym. Sci.* **2008**, *109* (5), 3093–3100.
- (7) Mousa, A. The effect of DV on the mechanical properties of EPDM/PP thermoplastic elastomers. *Int. J. Polymer. Mater.* **2005**, *54* (7), 619–631.
- (8) Bhadane, P. A.; Virgilio, N.; Favis, B. D. Effect of DV on continuous morphology. *AIChE J.* **2006**, *52* (10), 3411–3420.
- (9) Ellul, M. D.; Tsou, A. H.; Hu, W. Crosslink densities and phase morphologies in thermoplastic vulcanizates. *Polymer* **2004**, *45* (10), 3351–3358.
- (10) Coran, A. Y.; Patel, R. Rubber-thermoplastic compositions. Part I. EPDM-polypropylene thermoplastic vulcanizates. *Rubber Chem. Technol.* **1980**, *53* (1), 141–150.
- (11) Abdou-Sabet, S.; Datta, S. *Polymer Blends*; Wiley Interscience: Hoboken, NJ, 2000; Vol. 2.
- (12) Goharpey, F. Formation of rubber particle agglomerates during morphology development in dynamically crosslinked EPDM/PP thermoplastic elastomers. *Rubber Chem. Technol.* **2003**, *76*, 239–252.
- (13) Katbab, A. A.; Goharpey, F.; Nazockdast, H. Mechanism of morphology development in dynamically cured EPDM/PP TPEs. I. Effects of state of cure. *J. Appl. Polym. Sci.* **2001**, *81*, 2531–2544.
- (14) Wu, H.; Ning, N.; Tian, M.; Zhang, L. New understanding of microstructure formation of the rubber phase in thermoplastic vulcanizates (TPV). *Soft Matter* **2014**, *10*, 1816–1822.
- (15) Wang, M. The role of filler networking in dynamic properties of filled rubber. *Rubber Chem. Technol.* **1999**, *72* (2), 430–448.
- (16) Vennemann, N.; Bökamp, K.; Bröker, D. Crosslink density of peroxide cured TPV. *Macromol. Symp.* **2006**, *245–246* (1), 641–650.
- (17) Shibulal, G. S.; Naskar, K. Scrutinizing the influence of strain-induced fiber orientation on the melt rheological behavior of short aramid fiber/thermoplastic elastomer composite using rubber process analyzer. *J. Appl. Polym. Sci.* **2013**, *128* (6), 4151–4163.

- (18) Trtik, P.; Kaufmann, J.; Volz, U. On the use of peak-force tapping atomic force microscopy for quantification of the local elastic modulus in hardened cement paste. *Cem. Concr. Res.* **2012**, *42* (1), 215–221.
- (19) Antunes, C. F.; Duin, M. V.; Machado, A. V. Effect of crosslinking on morphology and phase inversion of EPDM/PP blends. *Mater. Chem. Phys.* **2012**, *133* (1), 410–418.
- (20) Payne, A. R. The dynamic properties of carbon black-loaded natural rubber vulcanizates. Part I. *J. Appl. Polym. Sci.* **1962**, *6* (19), 57–63.
- (21) Wang, L.; Ning, N.; Tian, M.; Zhang, L. Filler dispersion evolution of acrylonitrile–butadiene rubber/graphite nanocomposites during processing. *Composites, Part A* **2013**, *47*, 135–142.
- (22) Fröhlich, J.; Niedermeier, W.; Luginsland, H. D. The effect of filler–filler and filler–elastomer interaction on rubber reinforcement. *Composites, Part A* **2005**, *36* (4), 449–460.
- (23) Wu, S. Formation of dispersed phase in incompatible polymer blends: Interfacial and rheological effects. *Polym. Eng. Sci.* **1987**, *27* (5), 335–343.
- (24) Puyvelde, P. V.; Yang, H.; Mewis, J.; Moldenaers, P. Breakup of filaments in blends during simple shear flow. *J. Rheol.* **2000**, *44*, 1401.
- (25) Leal, L. G.; Cent, J. Droplet coalescence and breakup with application to polymer blending. *J. Cent. South Univ.* **2007**, *14* (1), 1–5.
- (26) Utracki, L. A.; Shi, Z. H. Development of polymer blend morphology during compounding in a twin-screw extruder. Part I: Droplet dispersion and coalescence—A review. *Polym. Eng. Sci.* **1992**, *32* (24), 1824–1833.
- (27) Fortelný, I.; Živný, A. Theory of competition between breakup and coalescence of droplets in flowing polymer blends. *Polym. Eng. Sci.* **1995**, *35* (23), 1872–1877.
- (28) Janssen, J. M. H.; Meijer, H. E. H. Droplet breakup mechanisms: Stepwise equilibrium versus transient dispersion. *J. Rheol.* **1993**, *37*, 597.
- (29) Dressler, M.; Edwards, B. J.; Windhab, E. J. An examination of droplet deformation and break-up between concentrically rotating cylinders. *J. Non-Newton Fluid* **2008**, *152* (1), 86–100.
- (30) Tsakalos, V. T.; Navard, P.; Peuvrel-Disdier, E. Deformation and breakup mechanisms of single drops during shear. *J. Rheol.* **1998**, *42*, 1403.
- (31) Grizzuti, N.; Bifulco, O. Effects of coalescence and breakup on the steady-state morphology of an immiscible polymer blend in shear flow. *Rheol. Acta* **1997**, *36* (4), 406–415.
- (32) Garzón, I. L.; Michaelian, K.; Beltrán, M. R. Lowest energy structures of gold nanoclusters. *Phys. Rev. Lett.* **1998**, *81* (8), 1600.