

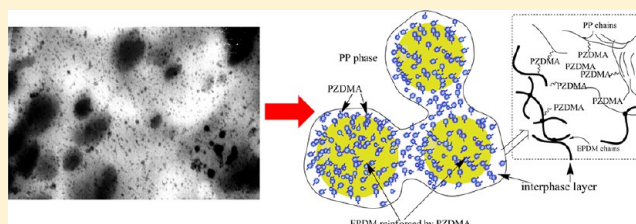
In Situ Reactive Compatibilization of Polypropylene/Ethylene–Propylene–Diene Monomer Thermoplastic Vulcanizate by Zinc Dimethacrylate via Peroxide-Induced Dynamic Vulcanization

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ABSTRACT: This work demonstrates an approach of in situ reactive compatibilization between polypropylene (PP) and ethylene-propylene-diene monomer (EPDM) by using zinc dimethacrylate (ZDMA) as a compatibilizer and, simultaneously, as a very strong reinforcing agent. With the incorporation of 7phr ZDMA in the PP/EPDM (30/70, w/w) thermoplastic vulcanizate (TPV), the tensile strength, tear strength, elongation at break, and hardness of PP/EPDM/ZDMA TPV were increased from 5.3 MPa, 31.3 kN/m, 222%, and 78 up to 11.2 MPa, 64.2 kN/m, 396%, and 83, respectively. This tremendous reinforcing as well as the compatibilization effect of the ZDMA was understood by polymerization of ZDMA and ZDMA reacted with EPDM and PP during peroxide-induced dynamic vulcanization. A peculiar phase structure that rubber particles were surrounded and “bonded” by a thick transition zone that contained numerous of nanoparticles with dimensions of about 20–30 nm was observed from transmission electron microscopy. Scanning electron microscopy results confirmed that incorporation of ZDMA reduced the size of the cross-linked EPDM particles. Moreover, we found that the compatibilized TPV showed a higher $\tan \delta$ peak temperature for EPDM phase and a lower $\tan \delta$ peak temperature for PP phase. The suggested method for in situ reactive compatibilization of PP and EPDM offers routes to the design of new TPV-based technical products for diversified applications.



1. INTRODUCTION

Thermoplastic elastomer (TPE) based on polypropylene (PP) and ethylene–propylene–diene monomer (EPDM) has received considerable success over the years.¹ One of the well-known TPE categories is dynamically cured PP/EPDM blend termed as thermoplastic vulcanizates (TPVs).² It is well known that dynamic vulcanization can achieve fine morphologies consisting of high amounts of cross-linked EPDM particles dispersed in PP continuous phase. During intensive mixing, the EPDM phase is cross-linked under dynamic condition by cross-linking agent. As a result, the viscosity and elasticity of the EPDM increases and the initial morphology consisting of PP domains dispersed in EPDM phase changes to cross-linked rubber particles dispersed in PP phase.^{3,4} TPVs are attractive because they combine the melt processability of the thermoplastics and the elastic and mechanical properties of the thermoset cross-linked rubbers.⁵ Significant improvements in the properties of these materials can be achieved by fully vulcanizing the rubber phase.⁶ Properties of TPVs are generally determined by the compatibility of blend components, extent of cross-linking in rubber phase, degree of dispersion, and morphology.^{7,8}

However, the rubbery-like properties of TPVs are quite difficult to be explained by the rubber-dispersing-in-plastic morphology. It seems that the cross-linked rubber particles physically interact through the finer thermoplastic interlayers,

which appear as a “network” structure.⁹ Oderkerk et al.^{10,11} found that during stretching of a TPV the thermoplastic continuous phase deformed progressively along the stretching direction. The nondeformed thermoplastic layers worked as adhesion points keeping the rubber particles together. Upon TPV relaxation, the elastic forces of the elongated rubber draw back the deformed thermoplastic layer by either buckling or bending. Therefore, controlling the final morphology and improving the compatibility and interfacial adhesion of blend components become crucial to achieving high mechanical performance of TPVs.

Zinc dimethacrylate (ZDMA) is a highly reactive chemical and readily reacts with polymers. In recent years, it is found that different kinds of rubbers can be reinforced by high loading of ZDMA without conventional fillers such as carbon black and silica. In the presence of peroxides, the unsaturated bonds of ZDMA are opened to polymerize, and thus ZDMA can be easily grafted onto rubber chains during the peroxide vulcanization.^{12–16} Incorporation of ZDMA into PP/EPDM blend via peroxide-induced dynamic vulcanization is a feasible method to enhance the interface adhesion between PP and EPDM because of the possible reactions of PP, ZDMA, and

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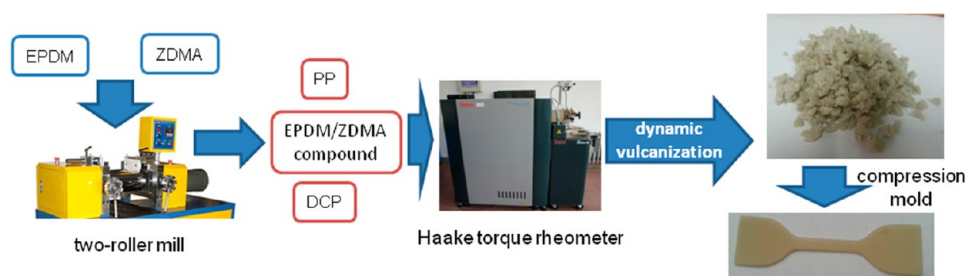


Figure 1. Illustration of the preparation process for PP/EPDM/ZDMA TPV.

EPDM. In situ compatibilizing of ZDMA occurs at the interfacial layer between PP and EPDM through the reaction between the double bonds of ZDMA and the free radicals generated in both EPDM and PP chains, which improves the interface adhesion between PP phase and reinforced EPDM phase. De Risi and Noordermeer¹⁷ evaluated ZDMA with peroxide in PP/EPDM blend and found that more stable free radicals were formed by positioning of the radical on the ZDMA molecule, which limited chain fragmentation of the PP. However, their research focus was the importance of ZDMA in minimizing beta scission of PP during peroxide curing to maintain the mechanical properties of PP phase rather than the potential improvement of interface adhesion between PP and EPDM by ZDMA.

Despite the large number of studies that have been published concerning the production, morphology, rheological, and mechanical properties of PP/EPDM-based TPVs, there are few works about in situ reactive compatibilization of PP/EPDM TPVs.¹⁸ In our previous works,^{19,20} we found that incorporation of ZDMA largely improved the toughness of PP-rich blends due to the in situ reactive compatibilization by ZDMA. The main aim of current work is to prepare a TPV (EPDM-rich blend) based on PP and EPDM with improved interfacial adhesion at 30/70 ratio by peroxide-induced reactive processing in the presence of ZDMA. TPV with ZDMA will be compared with the TPV without ZDMA and the uncured blend to discuss the effect of ZDMA on enhancement of interfacial adhesion between PP and EPDM. The morphology, structural, rheological, and mechanical properties of the resultant TPVs were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), rubber process analyzer (RPA), and mechanical properties test.

2. EXPERIMENTAL SECTION

2.1. Materials. PP (HP500N, MFI = 12 g/10 min (210 °C, 2.16 kg)) was purchased from CNOOC & Shell Petrochemicals. Ethylene-propylene-diene monomer (EPDM4045, density = 0.87 g/cm³, 56% ethylene content, ML(1 + 4, 100 °C) = 40, 7.5% the third monomer: 5-ethylidene-2-norbornene) was purchased from Jilin Chemical (China). ZDMA was purchased from Xian Organic Chemical Technology Plant (Shanxi, People's Republic of China). Dicumyl peroxide (DCP) was purchased from Sinopharm Chemical Reagent (China). The other chemicals were used as received.

2.2. Preparation of TPVs. PP/EPDM weight ratio of 30/70 was employed in this study. The weight ratio of DCP was maintained at a constant concentration relative to the amount of EPDM (EPDM/DCP = 100/1 w/w). Samples were prepared in three categories: category1, PP/EPDM (30/70)

blend; category 2, PP/EDPM/DCP (30/70/0.7); and category 3, PP/EDPM/ZDMA/DCP (30/70/7/0.7).

The two-step processing method was employed to prepare the PP/EPDM/ZDMA TPV, in which the EPDM and ZDMA were mixed to get rubber compounds first; then, the rubber compounds were blended with pure PP melt. The preparation of TPVs was done in a Haake torque rheometer by the melt mixing of the components at a temperature that was not higher than 170 °C and at a rotor speed of 80 rpm. In particular, the temperature for adding ZDMA was maintained at 165 °C as possible, avoiding the quick decomposition of DCP at a higher temperature because the half life of DCP at 170 °C was ~1 min. PP was first melted; then, rubber was added. When the torque was stable, DCP was added and the mixing was continued until the final stable torque was reached. Subsequently, the materials were removed from the cavity of rheometer and cooled to room temperature. To prepare test specimens, the room-temperature-cooled blend samples were ground and put into the cavity of hot mold at 190 °C. After 2 min of preheating between the plates of the mold at zero pressure, the sample was compression-molded and then cooled. The sheets with 1 mm thickness were removed and cooled at room temperature. The process is illustrated in Figure 1.

2.3. Characterization Methods. The dynamic mechanical behavior of the samples was determined using a dynamic mechanical analyzer (DMA242C NETZSCH, Germany) with tensile mode at 1 Hz and a heating rate of 3 °C/min in the temperature range from -100 to 100 °C.

Nova Nano SEM 430 (FEI Company) was used to investigate the phase morphology of the sample. Before morphological observation, the surface of samples was coated with a thin layer of gold to prevent electrostatic charging buildup during observation.

For the observation of TEM, the specimens were ultramicrotomed into thin pieces of ~100 nm in thickness with Leica EMUC6 under a liquid nitrogen atmosphere. Then, the observations were carried out on a JEM-100CX II transmission electron microscope (JEOL, Japan) with an accelerating voltage of 100 kV.

Contact angles were measured by the sessile drop technique on the cell lawns previously prepared using an apparatus model OCA 15 PLUS, DATAPHYSICS. PP and EPDM samples for contact-angle measurement were compression-molded between clean polyester films at 190 °C for 4 min and then cooled to 25 °C under pressure for 1 min. ZDMA was compression-molded by using a special smooth mold under a certain pressure. Contact angles results reported were the mean values of 10 replicates.

The FTIR spectrum of TPVs composites film was measured using the attenuated total reflectance (ATR) model in a Tensor 27 spectrometer (Bruker, Germany). Thirty-two consecutive

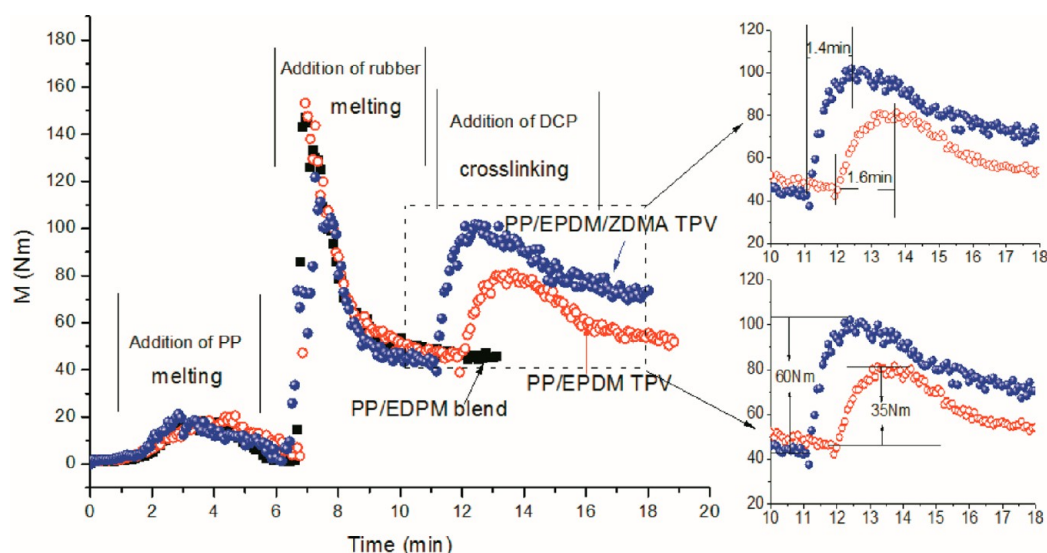


Figure 2. Torque curves of PP/EPDM blend, PP/EPDM TPV, and PP/EPDM/ZDMA TPV as a function of mixing time.

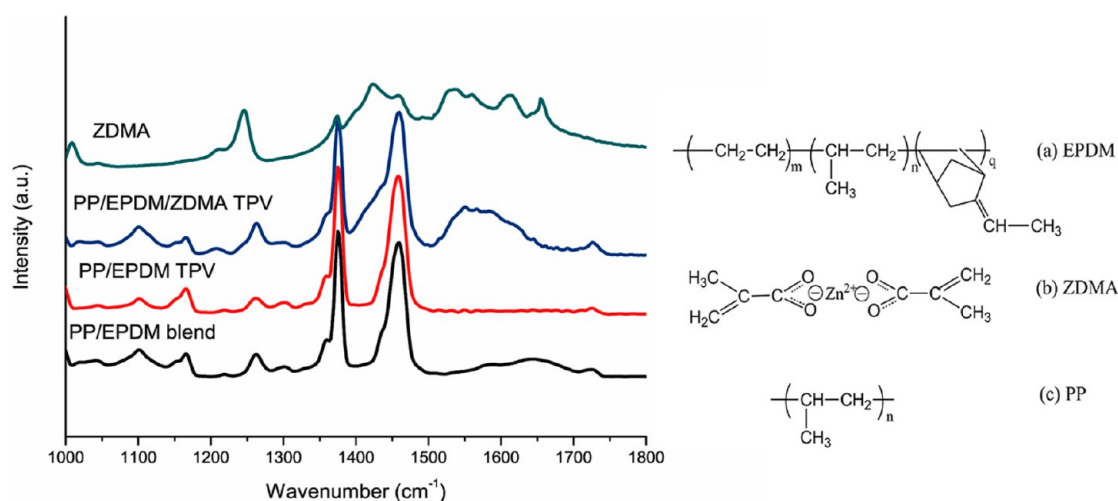


Figure 3. FTIR spectra of PP/EPDM blend, PP/EPDM TPV, PP/EPDM/ZDMA TPV, and ZDMA.

scans were taken, and their average was stored. The resolution of the wavenumber is 4 cm^{-1} .

Melt rheological behaviors of the samples were analyzed using a rubber process analyzer (RPA 2000, Alpha Technologies, USA). The experiments were performed at 190°C . The strain amplitude sweep was performed from 0.05 to 20° at a constant frequency of 1 Hz. The frequency sweep was logarithmically increased from 1 to 1000 Hz at constant strain amplitude of 1° .

The tensile properties and tear strength of the samples were determined using a computerized tensile strength tester (UT-2080, U-CAN Dynatex, Taiwan) with a crosshead speed of 500 mm/min according to ISO 37-2005 and ISO 34-2004, respectively. Shore A hardness was measured according to ISO 868-2003.

3. RESULTS AND DISCUSSION

3.1. Torques during Dynamic Vulcanization. Figure 2 shows the evolution of torques during mixing of PP/EPDM blend and PP/EPDM TPVs with and without ZDMA. The first and second peaks observed in each torque curve correspond to the loading and melting of PP and EPDM (or EPDM/ZDMA),

respectively. Afterward, the torque reaches a more or less constant value, indicating complete melting of PP and full homogenization of the blends. Meanwhile, the torque of the PP/EPDM/ZDMA TPV is somewhat lower than that without ZDMA, which may be due to the lubricating effect of ZDMA. Then, the torque of the TPV increases abruptly after the addition of DCP. This is related to drastic changes in the viscosity and elasticity of the EPDM phase due to crosslinking.³ After going through to a maximum, the torque of TPV decreases slowly until it reaches a new constant value at the end of mixing. This implies that the degradation of PP induced by DCP occurs even though it is in the presence of ZDMA.^{17,20} However, it is worth noting that ZDMA leads to a significant increase in the final torque and a more apparent cross-linking reaction for the EPDM phase. It is observed that ZDMA shortens the cross-linking time for reaching max-torque from 1.6 to 1.4 min and increases the Δ torque (difference between max-torque and torque before the addition of DCP) from 35 to 60 N m. The higher final torque may be attributed to the in situ compatibilizing action of ZDMA through the reaction between the double bonds of ZDMA and the free radicals generated in both EPDM and PP chains through the action of the peroxide.

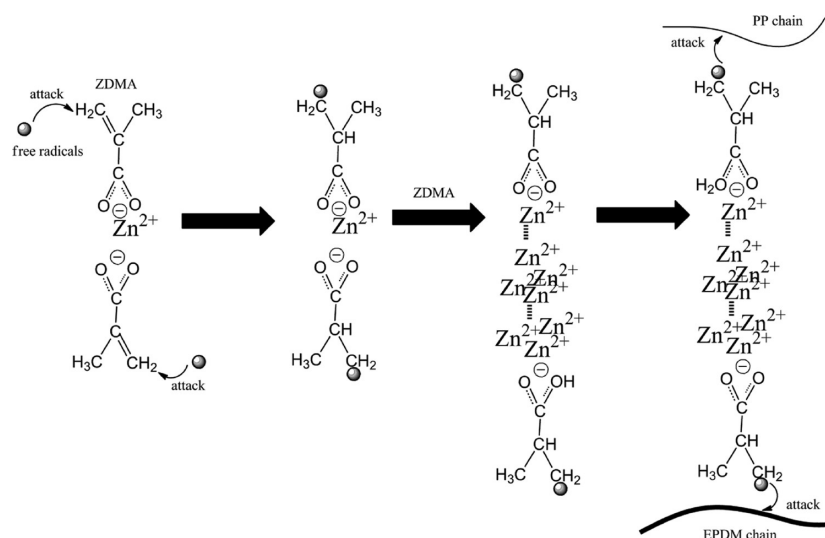


Figure 4. Possible schematic drawing of the possible reactions of PP, ZDMA, and EPDM at the interface between PP and EPDM.

In addition, ZDMA promotes the cross-linking rate of EPDM and graft-polymerizes onto rubber chains to enhance the cross-link density.^{12–16} Considering the fast cross-linking of EPDM phase in the presence of ZDMA, the immobilization of the rubber domains can be breaking down to smaller sizes under the applied shear field,²¹ contributing to the higher final torque. The effect of ZDMA on the cross-linking of rubbers can be found in refs 13 and 15.

3.2. FTIR Analysis. Figure 3 shows the FTIR spectra of PP/EPDM blend, PP/EPDM TPV, PP/EPDM/ZDMA TPV, and ZDMA in the range of 1000–1800 cm^{-1} . The chemical structure of ZDMA shows that the C–O and C=O bonds attached to the same carbon are equalized to the structure shown in Figure 3b. The two coupled carbon-to-oxygen bonds have two characteristic bands with intensities intermediate between C–O and C=O, an asymmetrical stretching vibration band at 1613–1535 cm^{-1} and a symmetrical stretching vibration band at 1450–1400 cm^{-1} .²² Compared with PP/EPDM blend and PP/EPDM TPV, the intensities at 1550–1700 cm^{-1} attributed to the C=C of third monomer (5-ethylidene-2-norbornene) (scheme a) disappear after peroxide dynamic vulcanization, indicating the fully curing of EPDM phase. In the FTIR spectrum of ZDMA, intensity of peak at $\sim 1250 \text{ cm}^{-1}$ is generated from the vibration band of C–(C=O)–O, which conjugated with C=C. The relative intensity of C–(C=O)–O at $\sim 1250 \text{ cm}^{-1}$ obviously becomes weak, which indicates that the C=C double bonds have reacted to a great extent in the process of dynamic vulcanization; namely, the ZDMA have been polymerized. Compared with PP/EPDM TPV and PP/EPDM/ZDMA TPV, the characteristic absorption peaks of ZDMA fuse and broaden, which indicates the complex reactions between EPDM, ZDMA, and PP initiated by DCP during dynamic vulcanization. Here a possible schematic drawing of the possible reactions of PP, ZDMA, and EPDM at the interface between PP and EPDM is given in Figure 4.

3.3. Phase Structure. The phase structure of PP/EPDM/ZDMA TPV was determined by TEM inspection. As can be seen in Figure 5, without ZDMA, the smooth contour of the EPDM droplets (the dark ones) can be clearly distinguished in the PP phase. As shown in Figure 6a, the light phase in the TEM micrograph represents the PP phase, and the dark particles with dimensions of $\sim 0.5 \mu\text{m}$ correspond to the cross-

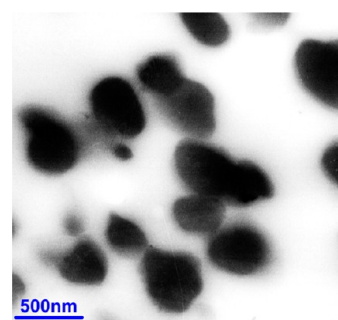


Figure 5. TEM image of PP/EPDM blend without ZDMA.

linked rubber phase. Besides, there is a large gray zone containing numerous nanoparticles with dimensions of about 20–30 nm, occupying more than 80% areas of the observed region. Those gray zones may be the creation of new polymeric structures (PP-polymerized ZDMA-EPDM graft resultants) that should be responsible for the improved rheological and mechanical properties of the resultant TPV, which will be discussed later. The nanoparticles are associated with the polymerized ZDMA,¹⁵ and the rubber particles are the ZDMA-reinforced EPDM phase.¹⁶ The majority of the nanoparticles are preferentially located at the gray zones and rubber phase, which reveals the migration of ZDMA from EPDM to PP phase during mixing, and the gray zones seem to be a thick transition field that “bonds” the rubber particle together. At a larger magnification shown in Figure 6b, it is clearly seen that the interphase boundary between the rubber particles and the PP matrix is blurry. The rubber particles are surrounded by the gray transition layer, indicating the good interphase cohesion between PP and rubber particles. Figure 6c shows the case of rubber particles close to each other. The interface of rubber particles is even more difficult to be distinguished. A possible phase structure of PP/EPDM/ZDMA TPV is postulated in Figure 6d. Although the detailed chemical structures of those gray zones are unclear at present, the peculiar phase structures observed by TEM are undoubtedly resulted from peroxide-induced dynamic vulcanization in the presence of ZDMA. We believe that the observed peculiar phase structures improve the interface adhesion between PP and rubber phase and even the

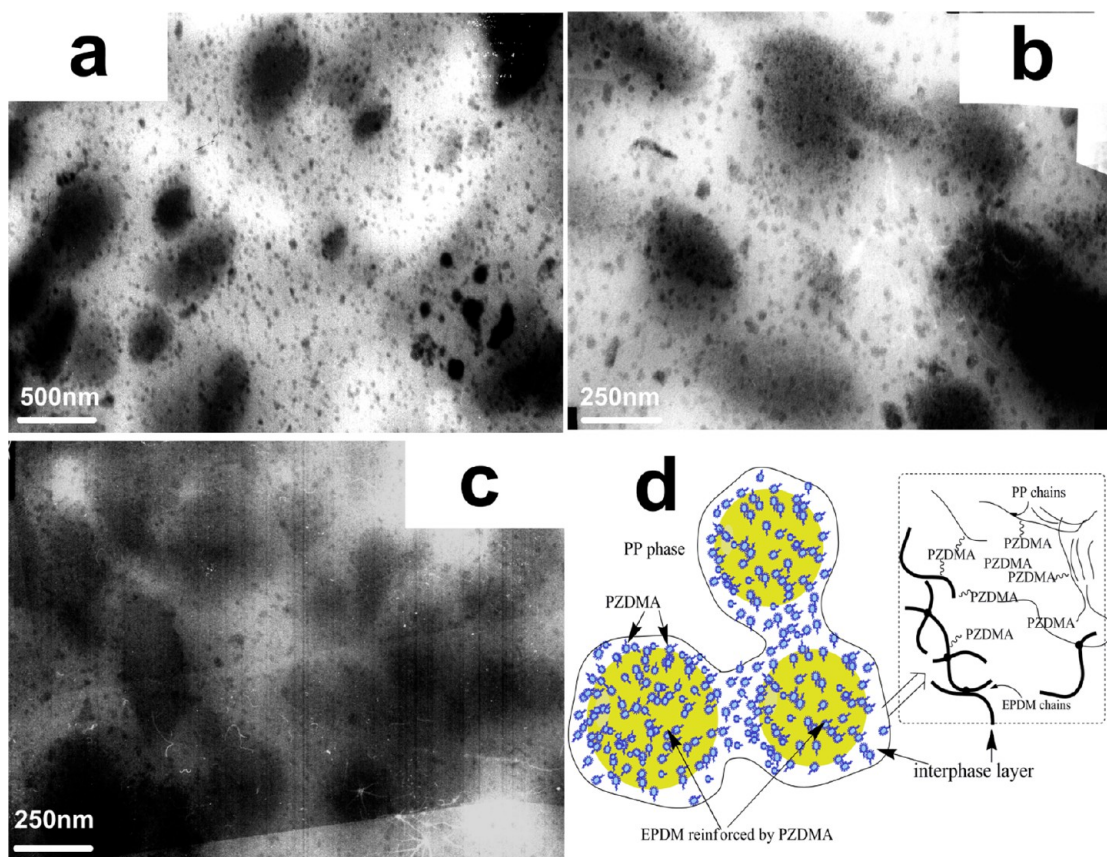


Figure 6. Representative images showing the structure of the PP/EPDM/ZDMA TPV: (a) TEM image for case of rubber particles away from each other, X20000; (b) TEM image for case of rubber particles away from each other, X40000; (c) TEM image for case of rubber particles close to each other, X40000; and (d) possible schematic representation of phase structure.

interaction between rubber particles, contributing to the enhanced performance of PP/EPDM/ZDMA TPV

3.4. Migration of ZDMA from EPDM to PP Phase. The migration of ZDMA from EPDM to PP phase can be well explained as a wetting/dewetting process between polymers and ZDMA. Hereby, the driving force is the difference of the interfacial tensions among the PP, EPDM, and ZDMA. The contact angles with water and diiodomethane are listed in Table 1. The surface tension, dispersion, and polar components of the

Table 1. Contact-Angle and Surface Tension Results of PP, EPDM, ZDMA, and PZDMA

sample	contact angle (deg)		surface tension (mN/m)		
	water	diiodomethane	dispersion component (γ^d)	polar component (γ^p)	total (γ)
PP	96.3	37.2	41.36	1.86	43.22
EPDM	101.2	57.8	36.7	1.97	38.67
ZDMA	20.4	31.2	35.64	37.66	73.3

materials are estimated from the contact-angle data by using the following two equations (eq 1 for water and eq 2 for diiodomethane):

$$(1 + \cos \theta_{\text{H}_2\text{O}}) \gamma_{\text{H}_2\text{O}} = 4 \left(\frac{\gamma_{\text{H}_2\text{O}}^d \gamma^d}{\gamma_{\text{H}_2\text{O}}^d + \gamma^d} + \frac{\gamma_{\text{H}_2\text{O}}^p \gamma^p}{\gamma_{\text{H}_2\text{O}}^p + \gamma^p} \right) \quad (1)$$

$$(1 + \cos \theta_{\text{CH}_2\text{I}_2}) \gamma_{\text{CH}_2\text{I}_2} = 4 \left(\frac{\gamma_{\text{CH}_2\text{I}_2}^d \gamma^d}{\gamma_{\text{CH}_2\text{I}_2}^d + \gamma^d} + \frac{\gamma_{\text{CH}_2\text{I}_2}^p \gamma^p}{\gamma_{\text{CH}_2\text{I}_2}^p + \gamma^p} \right) \quad (2)$$

in which $\gamma = \gamma^d + \gamma^p$, $\gamma_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}}^d + \gamma_{\text{H}_2\text{O}}^p$, $\gamma_{\text{CH}_2\text{I}_2} = \gamma_{\text{CH}_2\text{I}_2}^d + \gamma_{\text{CH}_2\text{I}_2}^p$, γ is surface tension, d is dispersion component, p is polar component, and $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$ are contact angles of the polymer with water and diiodomethane, respectively. The numerical values used are $\gamma_{\text{H}_2\text{O}}^d = 22.1$ dyn/cm, $\gamma_{\text{H}_2\text{O}}^p = 50.7$ dyn/cm, $\gamma_{\text{CH}_2\text{I}_2}^d = 44.1$ dyn/cm, and $\gamma_{\text{CH}_2\text{I}_2}^p = 6.7$ dyn/cm.²³ The interfacial tension of PP/EPDM, PP/ZDMA, and EPDM/ZDMA pare is calculated from surface tension by using the geometric mean equation:²⁴

$$\gamma_{\text{AB}} = \gamma_{\text{A}} + \gamma_{\text{B}} - 2(\gamma_{\text{A}}^d \gamma_{\text{B}}^d)^{1/2} - 2(\gamma_{\text{A}}^p \gamma_{\text{B}}^p)^{1/2} \quad (3)$$

where γ_{AB} is the interfacial tension and γ_{A} and γ_{B} are the surface tensions of the two materials in contact.

Generally speaking, the selective localization of filler in the component phase in the polymer blend is governed by thermodynamic factors.²⁵ During mixing before the addition of DCP, three different interfaces are probably formed: PP/EPDM, PP/ZDMA, and EPDM/ZDMA. The calculated interfacial tension values of PP/ZDMA, EPDM/ZDMA, and PP/EPDM are 22.99, 22.41, and 0.14 mN/m, respectively. The values of PP/ZDMA and EPDM/ZDMA are quite similar, which indicates that the migration of some ZDMA from EPDM phase to PP phase is a thermodynamically favorable process.

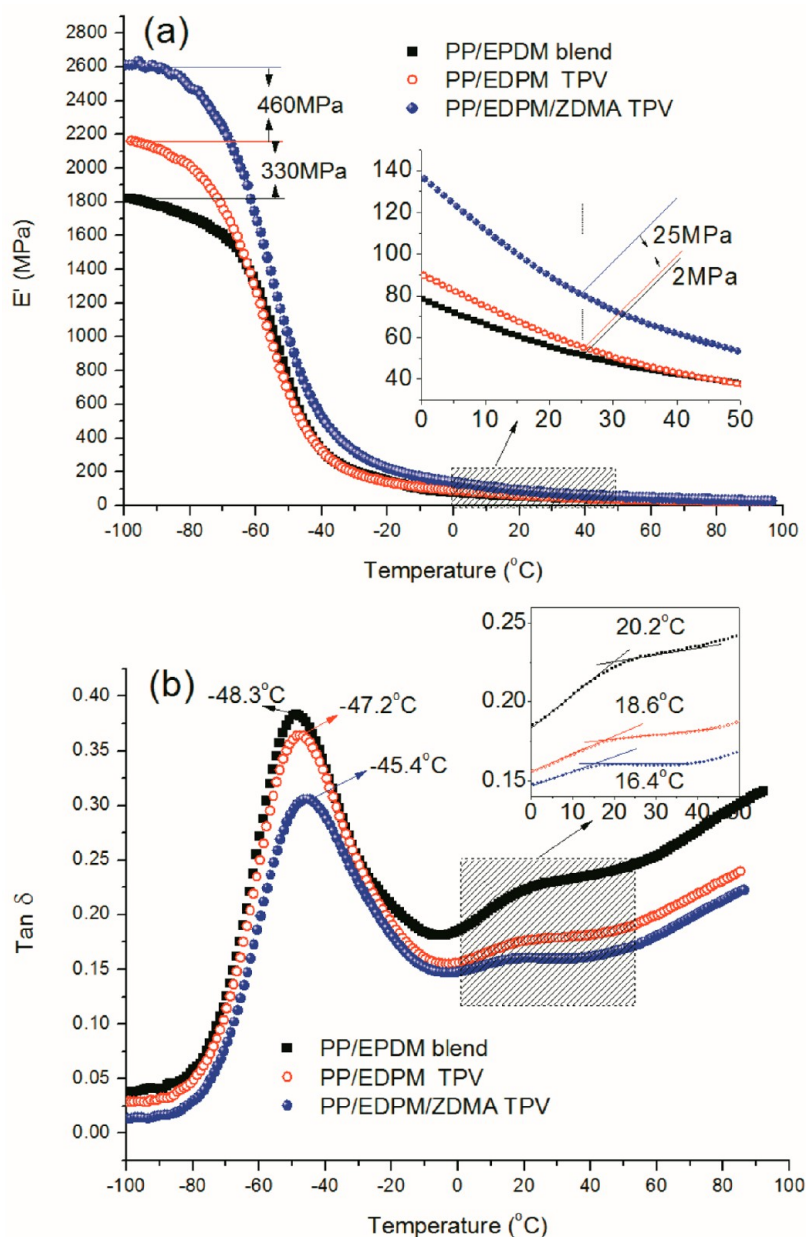


Figure 7. Storage modulus (a) and loss tangent (b) versus temperature for PP/EPDM blend, PP/EPDM TPV, and PP/EPDM/ZDMA TPV.

The mixing rate and size of the ZDMA are other factors that affect the migration of ZDMA from EPDM phase to PP phase. In fact, thermodynamic factors, for example, wetting coefficient, are less potent in the selective localization of large size filler. The size of ZDMA is on the micrometer level in this study, and thus part of ZDMA is still easy to migrate into PP phase during the intensive mixing (rotor speed of 80 rpm). After adding DCP, the ZDMA polymerized and reacted with both EPDM and PP, providing the possibility to result in the peculiar phase structures observed by TEM.

3.5. Dynamic Mechanical Analysis. DMA has been done to understand the dynamic response of the blend and TPVs. The dependency of storage modulus (E') obtained from oscillatory tension deformation as a function of temperature from -100 to 100 $^{\circ}\text{C}$ is given in Figure 7a. All samples show a steep decrease in E' value at the temperature range between -70 to -30 $^{\circ}\text{C}$, followed by a rubbery plateau. The PP/EPDM TPV shows a higher E' at the glass region than the PP/EPDM

blend, which can be well-explained by the cross-linked EPDM phase. The most exciting information, observed in this Figure, is the increase in modulus values at the whole region by the addition of the ZDMA. The E' at -100 $^{\circ}\text{C}$ increases from 2180 to 2640 MPa with the addition of 7phr ZDMA in the PP/EPDM matrix at a ratio of 30/70. The increase in E' at room temperature (25 $^{\circ}\text{C}$) is more obvious; the $\Delta E'$ between PP/EPDM/ZDMA TPV and PP/EPDM TPV is ~ 25 MPa, whereas $\Delta E'$ between PP/EPDM TPV and PP/EPDM blend is only ~ 2 MPa. Regardless of the gray zone with lots of nanoparticles observed by TEM, the polymerization of ZDMA in the EPDM phase reinforces the rubber particles very strongly,¹⁶ contributing to the increased E' . Furthermore, a denser rubber network can be achieved by ZDMA graft polymerizing onto rubber chains during peroxide curing, hence the increase in the hardness of the rubber particles. Meanwhile, in situ compatibilizing of ZDMA occurs at the interfacial layer between PP and EPDM through the reaction between the

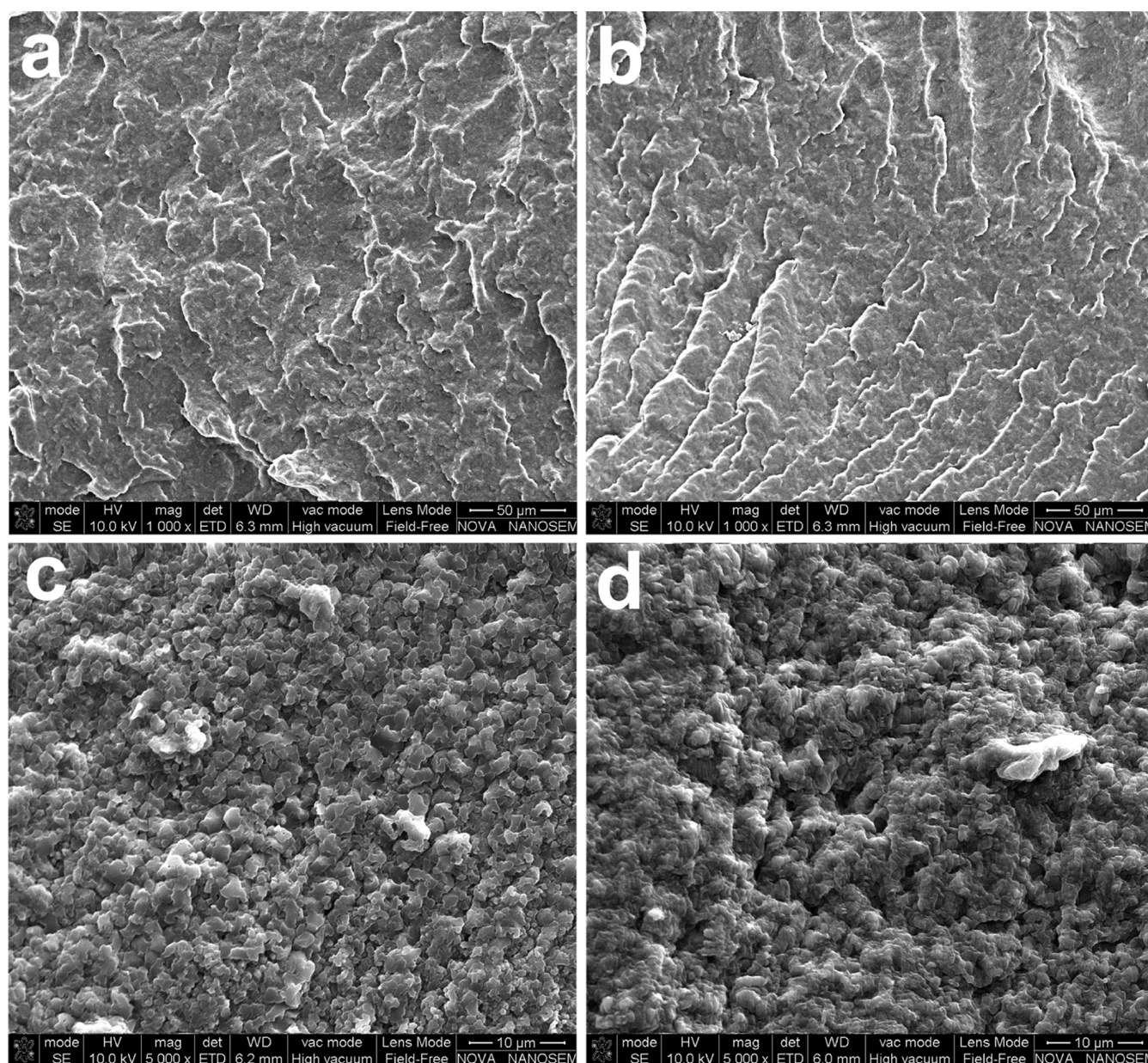


Figure 8. SEM micrographs: cryogenically fractured faces of (a) PP/EPDM TPV and (b) PP/EPDM/ZDMA TPV and xylene-etched cryogenically fractured faces of (c) PP/EPDM TPV and (d) PP/EPDM/ZDMA TPV.

double bonds of ZDMA and the free radicals generated in both EPDM and PP chains, which improved the interface adhesion between PP phase and reinforced EPDM particles. All of the above factors should be considered to explain the largely increased E' of PP/EPDM/ZDMA TPV.

The temperature corresponding to the maximum of $\tan \delta$ is usually related to the glass-to-rubber transition temperature (T_g). All samples presented two glass-transition temperatures: the strong one at around -47°C is related to the transition of the EPDM phase, and the weak one at $\sim 18^\circ\text{C}$ corresponds to the glass-rubber transition of the PP phase (tensile mode at 1 Hz and a heating rate of $3^\circ\text{C}/\text{min}$). For PP/EPDM blend and PP/EPDM TPV, dynamic vulcanization results in a slight increase in the $\tan \delta$ peak temperature related to EPDM phase and a slight decrease in the $\tan \delta$ peak temperature related to the PP phase (Figure 7b). Incorporation of ZDMA further increases $\tan \delta$ peak temperature of EPDM phase from -47.2

to -45.4°C and decreases $\tan \delta$ peak temperature of PP phase from 18.6 to 16.4°C . Furthermore, it can be observed that the $\tan \delta$ peak value and half-peak width of EPDM phase are decreased by ZDMA, which again indicates the decrease in chain mobility imparted by the increased cross-link density of EPDM phase. The lower $\tan \delta$ peak temperature for PP phase suggests an improvement of the interaction between the PP and rubber phases, promoted by the reaction of ZDMA, confirming the compatibilization effect.

3.6. SEM Micrographs. We analyzed the effect of the ZDMA on the morphology of the PP/EPDM TPV. Hence, we used boiling xylene to etch the cryogenically fractured faces of PP/EPDM TPV and PP/EPDM/ZDMA TPV. For the cryogenically fractured surface of PP/EPDM TPV, a large number of random fringes formed during the cryogenic fracture process and a relative flat surface without any considerable plastic deformation of the ligaments is observed in Figure 8a. As

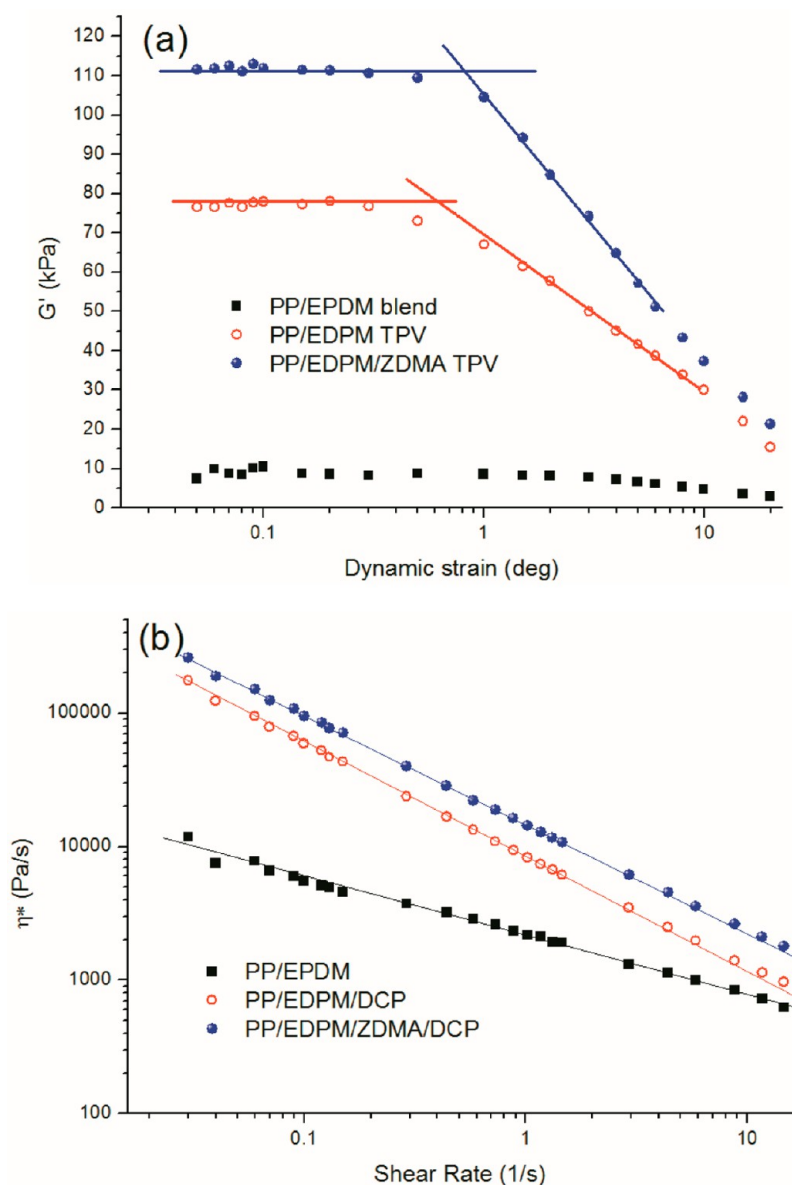


Figure 9. Rheological property of the material melts at 190 °C: (a) Dependence of storage modulus on strain amplitude and (b) dependence of complex viscosity on shear rate.

shown in Figure 8b, there are many oriented fringes with ridge-shaped erections on the cryogenically fractured surface of PP/EPDM/ZDMA TPV, which means that the material undergoes a light brittle failure process compared with PP/EPDM TPV. This implies good situ reactive compatibilization effect of ZDMA on PP and EPDM phase. After etched by boiling xylene, the observed particles shown in Figure 8c,d are the cross-linked rubber phase. Because the high temperatures were used for dissolving the PP matrix in boiling xylene, it is impossible to avoid agglomeration of the rubber particles. However, it still can be clearly seen that incorporation of ZDMA leads to size reduction of the cross-linked EPDM particles with dimensions of about 0.5 to 1 μm ; this is consistent with the observation from TEM.

In general, during mixing the dispersion of EPDM in the blend mainly depends on both the viscosity difference between EPDM and PP and the interaction between EPDM particles.³ The former favors the formation of dispersed EPDM and the latter is opposite. When curing agent is added, both the

viscosity difference between EPDM and PP and the interaction between EPDM particles are increased. At this time, it may be that the effect of shear on the morphology of the blends is dominant and intense shear results in dispersion of EPDM particles in the blend. After that, the viscosity difference between EPDM and PP plays the critical role, leading to the EPDM particles being immobilized by cross-links and breaking down into small droplets under the applied shear field.⁴ Under such conditions, the size of the EPDM particles decreases. In the present study, the intense shear (rotor speed of 80 rpm) and a sharp viscosity difference between EPDM and PP after the addition of DCP are some of the reasons behind the resultant smaller size of the cross-linked rubber particles because the ZDMA largely promoted the cross-linking process and increased the cross-link density of the EPDM phase in the presence of free radicals. The size reduction also directly enlarges the contact area that adds additional benefits to interface interaction between the phases.

3.7. Rheological Properties. The dependence of storage modulus (G') on the strain amplitude at very low strain values delivers an understanding about the impact of the filler networking within the polymer matrix. In general, for a filled rubber, the G' decreases with increasing strain, which is called “Payne effect”²⁶ and yields information about filler–filler networking in the rubber matrix. In the present investigations, the plots of G' versus strain amplitude of the PP/EPDM blend, PP/EPDM TPV, and PP/EPDM/ZDMA TPV are shown in Figure 9a. It is evident from this Figure that the PP/EPDM blend does almost not undergo any change in G' with increasing strain because the EPDM phase is melted at the test temperature. However, a strong dependency can be observed for the TPVs. Here the rubber phase is cured during dynamic vulcanization and, obviously, those observed rubber particles in SEM, being cross-linked, build “filler–filler”-like networking in the PP melt. The PP/EPDM/ZDMA TPV shows a higher G' value than the PP/EPDM TPV, which is reasonably attributed to the ZDMA reinforced EPDM particles with higher dense cross-links. The possible transition field surrounding the rubber particles (Figure 6) fulfills the demand to remain in contact with each other. Meanwhile, the role of the improved interface interaction between PP and rubber phase adds difficulties for the whole material melt to deform under stress, leading to the obviously increased storage modulus. In addition, the observed nanoparticles from TEM may also yield contribution to the G' .

Moreover, it is quite interesting to discuss the critical strain value (γ_c) at which nonlinear behavior starts. As shown in Figure 9a, a higher γ_c value at $\sim 0.8^\circ$ can be observed for the PP/EPDM/ZDMA TPV, whereas a higher γ_c value at 0.5° can be observed for the PP/EPDM TPV. These findings can only be explained if there is a stronger interaction between cross-linked rubber particles and between particles and PP phase, resulting in the formation of stronger physical networks, hence more strain dependency of G' for the PP/EPDM/ZDMA TPV at the molten state.

It is clearly seen in Figure 9b that all of the materials demonstrate shear thinning behavior. Dynamic vulcanization leads to the increase in complex viscosity as a result of the formation of cross-linked EPDM particles. Incorporation of ZDMA leads to the further increase in complex viscosity of the TPV. Moreover, PP/EPDM/ZDMA TPV shows a gently descending trend of complex viscosity at high shear rate region, compared with PP/EPDM TPV. In polymer blends, the viscosity depends on interfacial thickness and adhesion as well as the characteristics of bulk polymers because interlayer slip may occur along with orientation and disentanglement on the application of shear stress. Thus this behavior is attributed to the presence of interconnected agglomerates formed by the dynamically vulcanized rubber particles throughout the PP matrix as well as the improved interphases interlayer for PP/EPDM/ZDMA TPV. Nevertheless, the result of rheological property of the material melts at 190°C quite agrees satisfactorily with the phase structure previously discussed, indicating the good in situ reactive compatibilization of ZDMA on PP/EPDM TPV.

3.8. Mechanical Properties. The significant improvements in the mechanical properties of the resultant materials further well annotate the excellent in situ reactive compatibilization of ZDMA on PP/EPDM TPV. Figure 10 shows the mechanical properties of the PP/EPDM blend, PP/EPDM TPV, and PP/EPDM/ZDMA TPV. As shown in Figure 10a, for PP/EPDM TPV, it exhibits the tensile strength of 5.3 MPa and tear

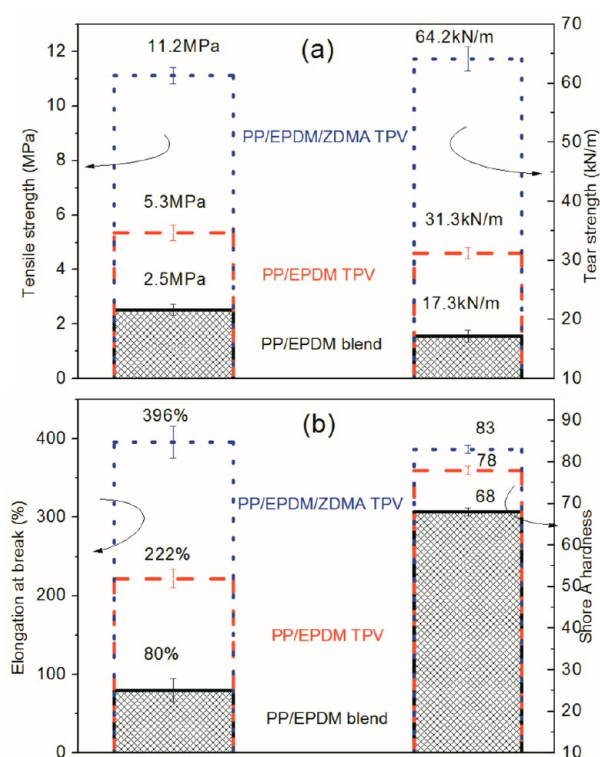


Figure 10. Mechanical properties of the PP/EPDM blend, PP/EPDM TPV, and PP/EPDM/ZDMA TPV: (a) tensile strength and tear strength and (b) elongation at break and hardness.

strength of 31.3 kN/m, higher than the 2.5 MPa and 17.3 kN/m of PP/EPDM blend (nearly two times), indicating that the significant improvements in the properties can be achieved by vulcanizing the EPDM phase. However, after incorporation of ZDMA, the tensile strength and tear strength of PP/EPDM/ZDMA TPV are increased up to 11.2 MPa and 64.2 kN/m, respectively, much higher than that of PP/EPDM TPV (more than two times). Figure 10b shows the similar increment in elongation at break and hardness for the materials. The elongation at break and hardness increase from 80% and 68 to 222% and 78 after dynamic vulcanization, respectively, and further increase to 396% and 83 after incorporation of ZDMA. The ZDMA-reinforced EPDM phase and the improved interface adhesion between PP and EPDM by ZDMA should be the two main reasons for the remarkable increased mechanical properties of PP/EPDM/ZDMA TPV. In particular, the large increase in elongation of PP/EPDM/ZDMA TPV verifies the good physical interaction between the ZDMA reinforced rubber phase and PP phase through the thick transition layer which originated from the DCP-induced dynamic vulcanization in the presence of ZDMA.²⁷

4. CONCLUSIONS

The role of ZDMA as a potent in situ reactive compatibilizer as well as an effective reinforcing agent in the TPV based on PP and EPDM has been investigated. EPDM and ZDMA were mixed to get rubber compounds first; then, the rubber compounds were blended with PP melt, at last, the blend was dynamically vulcanized in the presence of peroxide. It is observed that the ZDMA migrates from EPDM phase to PP phase during mixing and reacts with EPDM and PP after addition of DCP, and results in a peculiar phase structure that

rubber particles are surrounded and “bonded” by a thick transition zone which containing numerous of nanoparticles with dimensions of about 20–30 nm. Meanwhile, incorporation of ZDMA leads to size reduction of the cross-linked EPDM particles with dimensions of about 0.5 to 1 μm . The in situ reactive compatibilization of ZDMA provides a strong reinforcement to the interfacial reaction between PP and EPDM phase, resulting in significant improvements in the rheological and mechanical properties of the resultant materials.

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Notes

The authors declare no competing financial interest.

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