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Morphology Study of Peroxide-Induced Dynamically Vulcanized Polypropylene/Ethylene-Propylene-Diene Monomer/Zinc Dimethacrylate Blends during Tensile Deformation

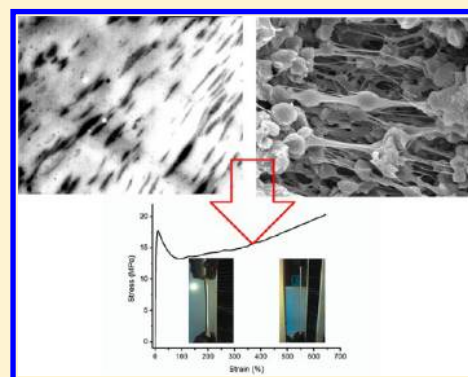
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ABSTRACT: Polypropylene (PP)/ethylene-propylene-diene monomer (EPDM)/zinc dimethacrylate (ZDMA) blend (EPDM/PP ratio of 30/70) with remarkable extensibility was successfully prepared via peroxide dynamic vulcanization. The uniaxial tensile properties, crystallization behavior, structure, and morphology during stretching were investigated. The tensile process study showed that the PP/EPDM/ZDMA blend exhibited the rubbery-like behavior with an elongation beyond 600%. The ZDMA graft-product domain increased the compatibility and interfacial adhesion between rubber and PP phases, while it reduced the crystallinity of the PP phase. On the basis of TEM and SEM analyses, we found that the cross-linked rubber particles could be elongated and oriented along the tensile direction, whereas the ZDMA graft-product domain “encapsulated” rubber phase together, acting as a “bridge” between elongated rubber phases and the PP phase during uniaxial stretching. The stress could be effectively transferred from the PP phase to the numerous elongated rubber phases due to the excellent compatibility and interfacial adhesion between rubber and PP phases, resulting in the rubbery-like behavior.



1. INTRODUCTION

Thermoplastic olefin blends (TPOs) typically containing ethylene propylene diene terpolymer and polypropylene (PP) have many commercial applications including automotive interior and exterior parts.¹ Especially, the un-cross-linked PP/ethylene-propylene-diene (EPDM) blends² and dynamically vulcanized PP/EPDM blends (TPVs)^{3,4} have generated considerable attention due to their wide industrial applications. During the dynamic vulcanization process, the EPDM phase is cross-linked under intensive mixing, resulting in a fine dispersion in the PP phase.⁵ The composition of EPDM and PP components determines the structure and the potential end-use properties of PP/EPDM blends.⁶ The EPDM-rich blends are used as a thermoplastic elastomer (TPE), while the PP-rich blends are applied as rubber toughened plastics. Typical PP/EPDM TPVs are formulated with high elastomer/thermoplastic ratios.⁷ These materials combine the melt processability of the thermoplastics and the elastic and mechanical properties of the cross-linked rubbers.⁸

Zinc dimethacrylate (ZDMA) is highly reactive in the presence of free radicals and readily reacts with polymers. In recent years, it has been found that rubbers can be reinforced by a high loading of ZDMA without conventional fillers such as carbon black and silica.^{9–12} ZDMA can be polymerized to graft onto rubber chains to enhance the cross-linked network of rubbers during peroxide vulcanization.^{8–12} Considering the

possible reactions of ZDMA with EPDM and even with PP in the peroxide free radical reaction, it is feasible to introduce ZDMA into PP/EPDM blends via peroxide dynamic vulcanization, and hence to enhance the interfacial adhesion between PP and EPDM with improved blend performance.

Although there are some reports on the dynamic vulcanization of PP/EPDM with ZDMA, the studies mainly concern the importance of ZDMA in minimizing beta scission of PP during peroxide vulcanization in EPDM-rich ratio. F. R. de Risi and J. W. M. Noordermeer¹³ evaluated (meth)acrylate coagents with peroxide in PP/EPDM and found that more stable free radicals were formed by positioning of the radical on the coagent molecules which limited chain fragmentation of the PP. Ping et al.¹⁴ reported the effects of in situ prepared ZDMA on the properties of dynamically vulcanized PP/EPDM (30/70, w/w), and found that ZDMA reduced the degradation of PP and improved the mechanical properties of the resultant blends.

The authors noticed that few references reported details dealing with the cross-linked PP/EPDM/ZDMA blends in a PP-rich ratio to date, and hence, a series of studies on using ZDMA to improve the compatibility and adhesion between the EPDM phase and the PP phase have been commenced.^{15,16} We

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found that ZDMA indeed reacted with PP and EPDM during peroxide dynamic vulcanization. A unique structure with the EPDM particles surrounded by a “gray zone” was observed for the first time by using transmission electron microscopy (TEM) examination, which was associated with the creation of new polymeric structures (poly-ZDMA graft products).¹⁶

The dynamically vulcanized PP/EPDM/ZDMA blends exhibited remarkable toughness and extensibility.¹⁶ Particularly, the elongation of the cross-linked PP/EPDM/ZDMA blend (EPDM/PP ratio of 30/70) exceeded 400% with obvious rubbery-like characteristics at large elongation.¹⁶ Generally, to achieve the desired elastic properties, the chosen EPDM/PP ratio is often larger than 50/50 and more specifically around 60/40.¹⁷ Therefore, the remarkable extensibility of dynamically vulcanized PP-rich blends with ZDMA may offer routes to the design of PP/EPDM-based TPOs for diversified applications.

In this work, we mainly focused on the morphology of the dynamically vulcanized PP/EPDM/ZDMA blends with an EPDM/PP ratio of 30/70 during stretching, aiming to get an insight into the relationship of the rubber phase and large extensibility of the blends. The morphology, structural, crystallization behavior and tensile properties of the as-prepared blends were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and tensile test.

2. EXPERIMENTAL SECTION

2.1. Materials. Polypropylene (PP, HP500N, MFI = 12 g/10 min (210 °C, 2.16 kg)) was purchased from CNOOC & Shell Petrochemicals Company Limited. 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 Co. (China). Zinc dimethacrylate (ZDMA) was purchased from Xian Organic Chemical Technology Plant (Shanxi, People's Republic of China). Dicumyl peroxide (DCP) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and was purified by anhydrous alcohol recrystallization before use. The other chemicals were used as received.

2.2. Sample Preparation. The two-step processing method was employed to prepare the PP/EPDM/ZDMA blends, in which the EPDM and ZDMA were mixed to get rubber compounds first, and then the rubber compounds were blended with pure PP melt.

The EPDM/ZDMA (100/30) compound was prepared in a two-roll mill at room temperature. The PP/EPDM/ZDMA (70/30/9) blends were prepared in an internal mixer (Haake Rheocord 90) by the melt mixing of the components at a temperature which was not higher than 170 °C and at a rotor speed of 40 rpm. Particularly, the temperature for adding ZDMA was maintained as close to 165 °C as possible, avoiding the quick decomposition of DCP at a higher temperature (the half-life of DCP at 170 °C was approximately 1 min). PP was first shear-melted, and then, EPDM/ZDMA compound was added. When the torque was stable, DCP (1% weight of EPDM component) was added and the mixing was continued until the final stable torque was reached. Subsequently, the composites were removed from the cavity of the internal mixer and cooled down to room temperature. The block of the blends was chopped into small granules. The specimens for mechanical testing were prepared by an injection molding machine (TTI-160F, Welltec Machinery & Equipment Co. Ltd., China). The

nozzle temperature was maintained at 210 °C, and the injection pressure was at 60 MPa.

2.3. Tensile Test. Standard tensile tests were conducted on dumbbell shaped specimens using a universal testing instrument (Shimadzu AG-1, 10 kN, Japan) in tensile mode at room temperature. The test speed was kept at 50 mm/min, according to ASTM D638-2003 standard.

2.4. Dynamic Mechanical Analysis. The dynamic mechanical behavior of the peroxide dynamical vulcanized blends was determined using a dynamic mechanical analyzer (Gabo Qualimeter Testanlagen GmbH; Germany) with tensile mode at 10 Hz and a heating rate of 3 °C/min in the temperature range from −100 to 100 °C. The samples were prepared as a cut strip with a size of 30 mm × 6 mm × 4 mm.

2.5. Scanning Electron Microscopy. A Nova NanoSEM 430 (FEI Company, USA) was used to investigate the phase morphology of the blends. In order to observe the cross-linked EPDM phase, the samples were subjected to hot xylene wash to remove the PP phase at the surface and then dried sufficiently. Before morphological observation, the surface of the samples was coated with a thin layer of gold to prevent electrostatic charging build-up during observation.

2.6. Transmission Electron Microscopy. The specimens were ultramicrotomed into thin sections of about 100 nm in thickness with a Leica EMUC6 under 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.

2.7. Differential Scanning Calorimetry. The crystallinity was studied by means of a NETZSCH DSC 204 F1 (German) differential scanning calorimeter. Samples of about 5 mg were heated to 200 °C at a rate of 10 °C/min under a nitrogen atmosphere and held at 200 °C for 5 min to eliminate the thermal history. Afterward, the samples were cooled to 20 °C at a rate of 10 °C/min, holding at about 3 min at 20 °C, and then heated again to 200 °C at a heating rate of 10 °C/min. The crystallinity was calculated from the heat of fusion using 209 J/g as the heat of fusion of 100% isotactic PP.

3. RESULTS AND DISCUSSION

3.1. The Tensile Characteristics. All the standard dumbbell shaped specimens show a good repeatability (repeated three times) of the tensile property; thus, the stress–strain curves shown in Figure 1 are the typical resultant curves for every sample. The average value of tensile test data also is listed in Table 1.

The beta scission of PP cannot be avoided completely during peroxide vulcanization even in the presence of ZDMA;¹⁵ thus, we added a small quantity of DCP (0.1% weight of PP) into PP during melt mixing. This measurement was done to compare the tensile properties of the PP/EPDM/ZDMA blend and PP in a relatively fair condition. As clearly shown in Figure 1a, the PP/DCP exhibits a brittle failure without yielding. The tensile strength is about 36 MPa, and the elongation at break is only about 15%. This may be due to the degradation of PP caused by DCP and increased crystallinity (see the crystallization parameters in Table 2). For the neat PP, the deformation processes typical of a tough plastic during the uniaxial tension can be observed in sequence in Figure 1b. These processes include elastic deformation, yield point, strain softening, development of larger deformation, and stress hardening. The necking down region began at a strain of about 25%. The yield stress of PP is 36 MPa which is equal to the tensile strength of

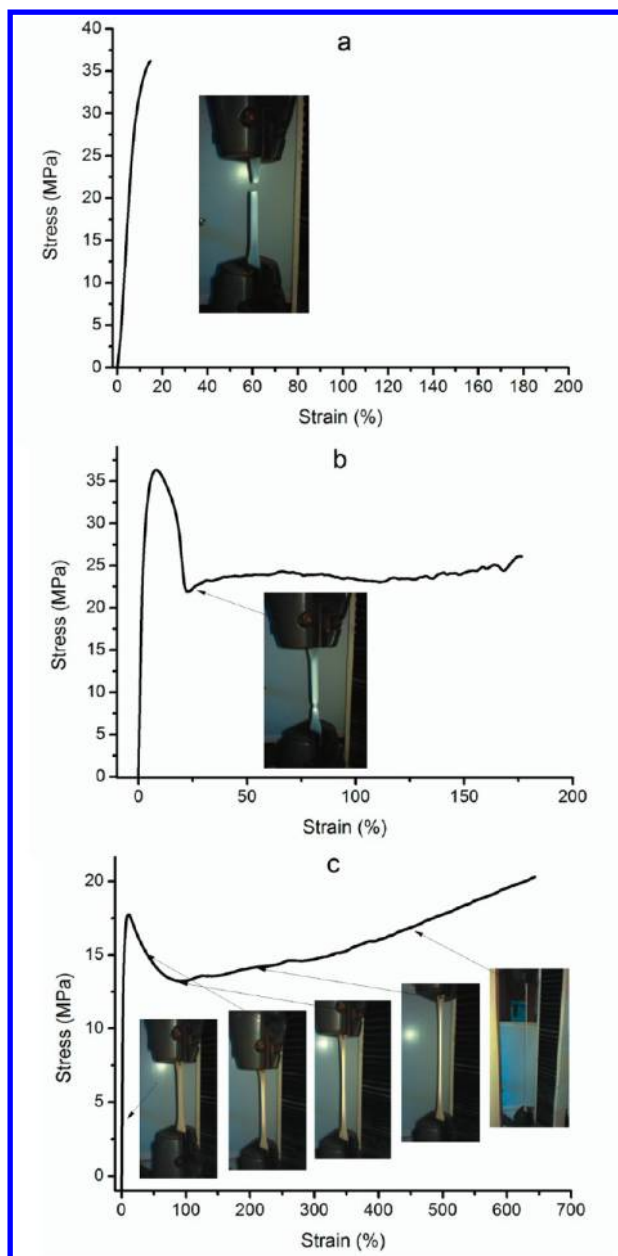


Figure 1. Tensile testing of (a) PP/DCP, (b) PP, and (c) PP/EPDM/ZDMA (70/30/9) blend.

Table 1. The Data of Tensile Property of PP/DCP, PP, and PP/EPDM/ZDMA (70/30/9)

sample	yield stress (MPa)	break stress (MPa)	elongation at break (%)
PP/DCP	36.2 ± 0.5	36.2 ± 0.5	15 ± 3
PP	36.4 ± 0.5	26.1 ± 0.5	177 ± 10
PP/EPDM/ZDMA (70/30/9)	17.6 ± 0.4	20.9 ± 0.4	645 ± 50

Table 2. Crystallization Parameters for Samples

sample	X_c (%)	T_c (°C)	T_o (°C)
PP	45.6	104.0	112.5
PP/DCP	48.4	114.4	125.0
PP/EPDM (70/30)	47.6	114.7	124.0
PP/EPDM/ZDMA (70/30/9)	40.9	116.4	127.3

PP/DCP. The break strain of PP is about 170%; however, the break stress (about 26 MPa) does not exceed the yield stress in this experiment.

Regardless of the processing conditions or cure state, the tensile properties of PP are altered significantly by the rubber phase (EPDM/ZDMA). As shown in Figure 1c, the dynamically cross-linked PP/EPDM/ZDMA (70/30/9) blend exhibits an excellent extensibility with an elongation beyond 600%. Another interesting feature of the PP/EPDM/ZDMA blend is the rubbery-like behavior shown under tensile load after the yield stress, showing no necking down region. The PP/EPDM/ZDMA blend also shows a yield point at about 15% strain. The yield stress is 17.6 MPa, whereas the break stress is nearly 21 MPa which is higher than the yield stress. It should be noted that the EPDM phase is not entirely responsible for the excellent extensibility—it is well-known that the EPDM/PP ratio is often larger than 50/50 (wt/wt%) to achieve the elastic properties. We believe that the remarkable extensibility and the high break stress are attributed to the incorporation of ZDMA. The increase of the tensile stress of the PP/EPDM/ZDMA blend beyond 100% strain (Figure 1c) may be mainly contributed by the EPDM phase reinforced by ZDMA. As a reacting type of reinforcing agent for rubbers, ZDMA can polymerize to graft onto rubber chains to enhance the cross-linked network during peroxide curing, resulting in good hardness, tensile and tear strength of rubbers.^{9–12} In addition, the large extensibility reveals that ZDMA not only increases the strength, leading to the formation of stiffer rubber particles, but also increases the interactions between EPDM and PP phases, leading to the blend extension of 600–700%.

3.2. Poly-ZDMA Graft-Products Domain. Figure 2 depicts the temperature dependence of $\tan \delta$ at 10 Hz for

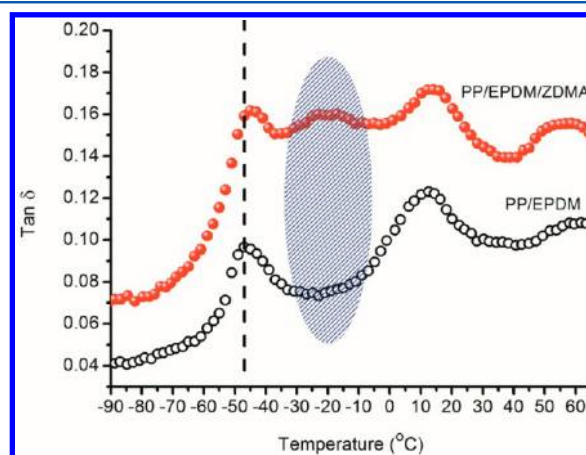


Figure 2. Temperature dependency of $\tan \delta$ at 10 Hz for peroxide dynamical vulcanized PP/EPDM (70/30) binary blend and PP/EPDM/ZDMA (70/30/9) ternary blend.

the PP/EPDM (70/30) binary blend and the PP/EPDM/ZDMA (70/30/9) ternary blend. Two $\tan \delta$ peaks correspond to the glass transition temperatures (T_g) of PP (about 15 °C) and EPDM (about −48 °C), respectively. The $\tan \delta$ peak for the EPDM phase shifted to higher temperature (about −45 °C) is due to the fact that the polymerization of ZDMA increased the cross-link density of the EPDM phase.^{10–14} Furthermore, a small peak appearing at about −20 °C is observed in the curve of the PP/EPDM/ZDMA ternary blends. This new peak is associated with the possible poly-ZDMA graft-products

(possibly the EPDM-g-(poly-ZDMA)-g-PP or (poly-ZDMA)-g-PP).

The TEM image of the PP/EPDM/ZDMA (70/30/9) blend is depicted in Figure 3. Here the rubber phase appears as the

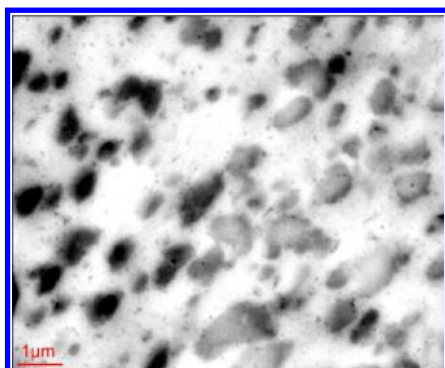


Figure 3. TEM image of the peroxide dynamical vulcanized PP/EPDM/ZDMA (70/30/9) blend.

darker “larger” particles and PP as the bright areas. The rubber particles are the cross-linked EPDM phase which is reinforced by ZDMA.^{9–12} However, most of the lighter areas are filled with gray domains containing numerous small particles. We thought that those “gray domains” might contain the creation of new polymeric structures (poly-ZDMA graft products domain) which should be responsible for the new relaxation peaks between those of EPDM and PP (Figure 2). All the rubber particles seem to be surrounded or connected by the

gray domains. It is thought that the rubbery-like behavior is related to the “gray domains” encapsulating rubber particles.

The onset crystallization temperature (T_o), the crystallization peak temperature (T_c), and the crystallinity ($X_c\%$) are summarized in Table 2. The PP/DCP shows higher crystallinity than PP, which explains the low elongation at break of the PP/DCP. The PP/EPDM/ZDMA blend shows a lower crystallinity of the PP phase and a higher onset crystallization temperature than the PP/EPDM blend. The higher onset crystallization temperature suggests that something in direct contact with PP molecules serves as an effective nucleating agent for the crystallization, which may be the poly-ZDMA graft-products. On the other hand, the poly-ZDMA graft-products enhance the compatibility between EPDM and PP which restricts the rearrangement of PP macromolecule segments during the crystallization process. In addition, PP involved in the free radical reaction with EPDM and ZDMA also increases the amorphous region of the PP phase. As a result, the crystallinity of the PP/EPDM/ZDMA blend is much lower than that of the PP/EPDM blend.

3.3. Deformation of Rubber Phase. The deformation of the rubber phase was investigated by TEM. We selected two stages during stretching to observe the shape of the deformed rubber phase. The sample was stretched to the fixed elongation; then, the middle part was ultramicrotomed into thin pieces along the longitudinal stretching direction. As can be seen in Figure 4a and b, the rubber particles are deformed to be thin and long because of the decrease in thickness or width of parallel area of the sample. The oriented PP molecules force the

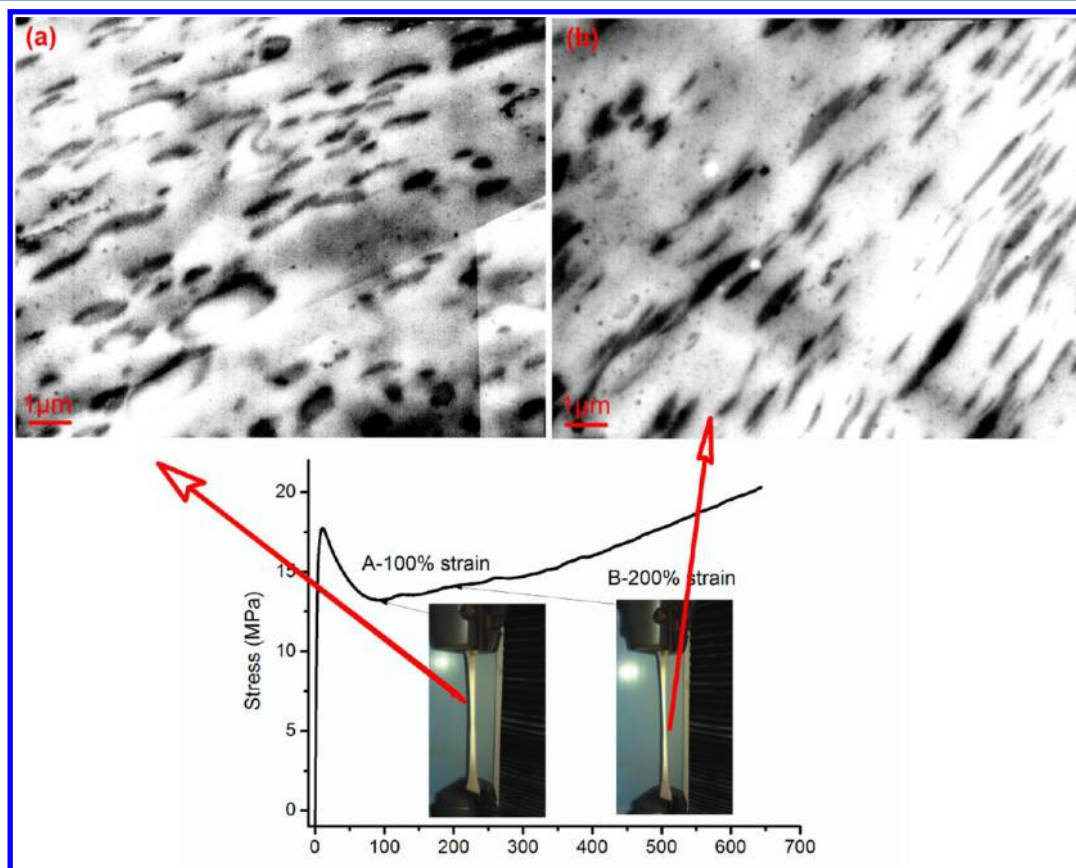


Figure 4. TEM images of the stretched PP/EPDM/ZDMA (70/30/9) blend: (a) 100% strain; (b) 200% strain; (c) deformed rubber phase at high magnification.

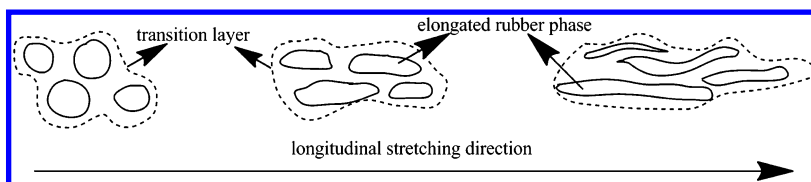


Figure 5. The possible schematic drawing of the evolution of morphology of PP/EPDM/ZDMA blend during stretching.

elongated rubber phase to be oriented. Although the rubber phase appears noncontinuous, it could be speculated that those particles were elongated to be rubber fibers which showed the trend of approaching each other (Figure 4b) at large elongation. Figure 4b also shows the good compatibility and interfacial adhesion between rubber and PP phases, without formation of cavities.¹⁸ During stretching, those gray domains “encapsulated” the rubber phase, acting as a “transition layer” between elongated rubber phases and the PP phase, should contribute to the high elongation of the PP/EPDM/ZDMA blend. The possible schematic drawing of the evolution of morphology during stretching is shown in Figure 5.

3.4. SEM Observation. Because the PP and non-cross-linked EPDM phase have been removed by the boiling xylene (etched by boiling xylene for 20 min), the particles with average dimension of about 1 μm shown in Figure 6 are the cross-

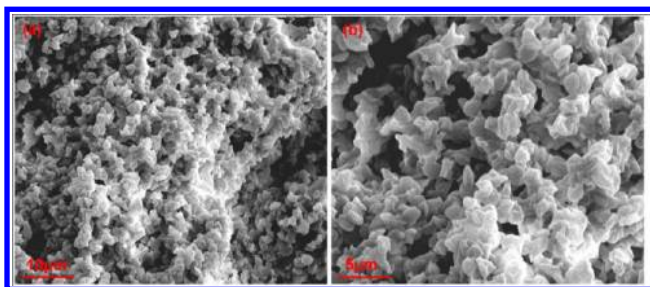


Figure 6. SEM images of the PP/EPDM/ZDMA blend etched by boiling xylene for 20 min: (a) $\times 5000$; (b) $\times 10000$.

linked rubber phase. The size of the rubber particle is much larger than that of our earlier results;¹⁶ this may be related to the lower rotor speed and higher ZDMA content employed in this experiment. The rubber particles agglomerated together because of the high temperature used for dissolving the PP matrix in boiling xylene.

Figure 7 shows the SEM micrographs obtained from the dumbbell specimen which was stretched to 200%. Numerous needle-like salient zones appear on the longitudinal stretching surface. No rubber particles are observed, and the needle-like

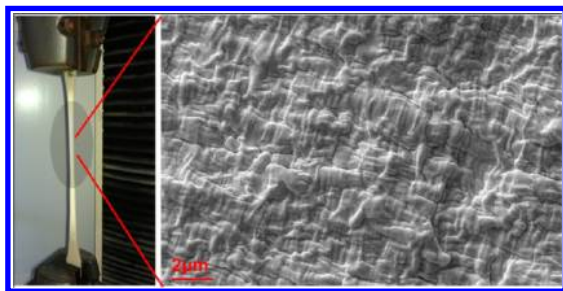


Figure 7. SEM images of the longitudinal stretching surface of the PP/EPDM/ZDMA blend which was stretched to 200%.

salient zones are associated with the stretched rubber phase combined with the PP matrix.

In order to further investigate the inside structure of the elongated sample, a procedure was developed to selectively remove the PP matrix. This is accomplished by selection of a suitable etch time for dissolution of the partial-PP phase with xylene. In our experiment, the longitudinal stretching surface of the stretched specimen was etched with xylene at 100 $^{\circ}\text{C}$ for 3 min to remove the part of the PP phase in the surface layer. The SEM micrographs of the etched surface are shown in Figure 8. Numerous “particles” are connected by nanometer

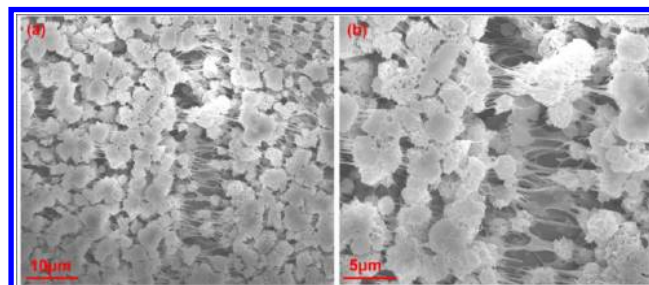


Figure 8. SEM images of the longitudinal stretching surface of the PP/EPDM/ZDMA blend which was stretched to 200% after being etched with xylene at 100 $^{\circ}\text{C}$ for 3 min: (a) $\times 5000$; (b) $\times 10000$.

scale fiber-like threads along the stretching direction. The average size of the “particles” is obviously larger than those observed in Figure 6, and the “particles” seem to be somewhat flat. This is because the observed “particles” are not the pure cross-linked rubber phase, as they should contain residual PP. Upon elongation in tensile testing, the PP continuous phase was stretched, and at the same time, the rubber particles were forced to be elongated. After partial dissolution of the PP phase, the residual PP could not yield enough stress to maintain the deformation of the rubber particles. Subsequently, the deformed particles were drawn back by the elastic EPDM domain effectively, resulting in the peculiar morphology shown in Figure 8.

Figure 9 shows that the surface of the “rubber particle” is very rough because of the residual PP. Figure 9a shows that two “rubber particles” are connected by several fiber-like threads in

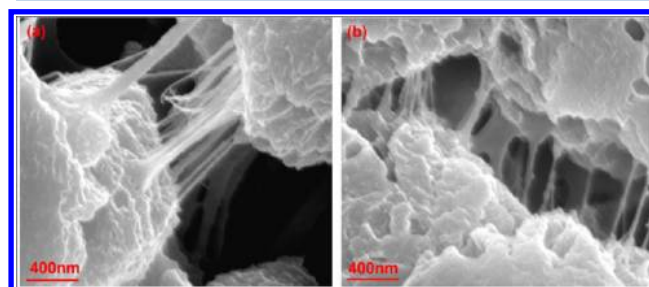


Figure 9. SEM images of the “fiber-like threads” at large magnification.

the range of tens of nanometers. Obviously, most of those fiber-like threads maintain their stretched status under the retraction force of the rubber phase. Moreover, those threads attached on the surface of the “rubber particle” firmly, confirming the excellent interfacial adhesion between threads and particles. Figure 9b shows the single thread with uneven diameter distribution. The surface of the thread is very rough. Thus, these fiber-like threads may be the stretched rubber phase combined with the gray materials which are observed by TEM.

Figure 10 shows the longitudinal stretching surface of the 200% stretched specimen which was etched with xylene at 100

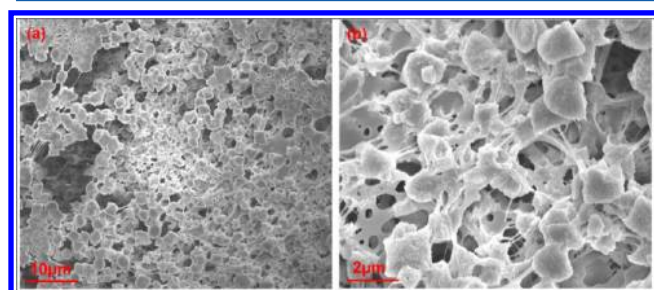


Figure 10. SEM images of the longitudinal stretching surface of the PP/EPDM/ZDMA blend which was stretched to 200% after being etched with xylene at 100 °C for 5 min: (a) $\times 2500$; (b) $\times 20000$.

°C for 5 min. The average size of the particles is smaller than that observed in Figure 8, which indicates that more PP phase has been removed. Furthermore, most of the rubber particles on the top layer are spherical, indicating that the deformed particles can be drawn back by the elastic EPDM domain effectively without the stresses of the PP phase. It can be imagined that the cross-linked rubber particles are elongated under the force of the stretched PP phase, and dispersed evenly in the stretched sample. In Figure 10b, it is interesting that the “film-like” materials are found in deeper layers which are lightly etched. We speculate that those “film-like” materials might contain the amorphous PP. After removal of the amorphous PP, the “film” broke up and led to the formation of the fiber-like threads. Most of those “film-like” materials appear in the deeper layers because of the retained stress of the unetched PP phase. We also believe that those “film-like” materials or fiber-like threads contribute to the rubber-like behavior.

In order to further support the observation of an elongated rubber phase, the longitudinal stretching surface of a PP/EPDM/ZDMA blend which was stretched to 300% was etched with xylene at 100 °C for 7 min. A typical elongation of rubber particles domain can be observed from Figure 11. General views of the morphologies at lower magnifications are shown in Figure 11a and b, and more details are provided in Figure 11c and d at higher magnifications. Note that the PP continuous phase has been removed, and it is impossible to avoid retraction and agglomeration of the rubber phase. Nevertheless, a lot of the elongated rubber phases still maintain the strongly elongated status because of the retained PP in deeper layers. Higher magnification micrographs of the elongated rubber particles in Figure 11c and d indicate that they indeed can be stretched to be rubber fibers with high elasticity. Most rubber particles were elongated, whereas the poly-ZDMA graft-product domains act as a “bridge” to “connect” those rubber fibers during uniaxial stretching; at the same time, the stretched PP phase functions as a “container” to fix the elongation status of the rubber phase. At large strains, almost all of the “rubber

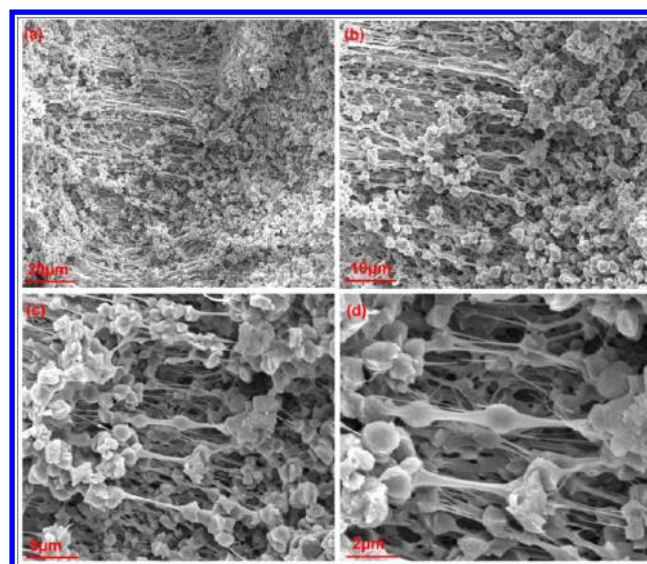


Figure 11. SEM images of the longitudinal stretching surface of the PP/EPDM/ZDMA blend which was stretched to 300% after being etched with xylene at 100 °C for 7 min: (a) $\times 2500$; (b) $\times 5000$; (c) $\times 10000$; (d) $\times 20000$.

fibers” were oriented along the tensile direction; the stress could be effectively transferred from the PP phase to the elongated rubber phase due to the excellent compatibility and interfacial adhesion between rubber and PP phases. As a result, the stress increases with strain, which should be reflected in the tensile strength of the cross-linked rubber phase, resulting in the rubbery-like behavior.

Figure 12 shows the longitudinal stretching surfaces of a PP/EPDM/ZDMA blend which was stretched to break and then

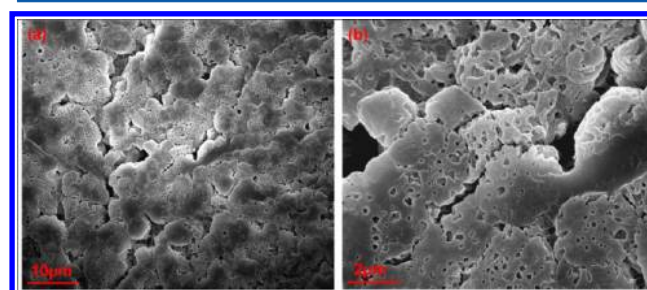


Figure 12. SEM images of the longitudinal stretching surface of the PP/EPDM/ZDMA blend which was stretched to break after being etched with boiling xylene for 20 min: (a) $\times 5000$; (b) $\times 20000$.

etched with boiling xylene for 20 min. After the PP phase was removed completely, the resultant morphology was quite different. No elongated rubber phase can be seen; the large blocks shown in Figure 12 are the cross-linked EPDM phase. However, they seem to have “coalesced” into larger agglomerations. Without the support of the PP phase, the strongly elastic recoil caused the elongated rubber phases to be bonded together rather than dispersing in the boiling xylene. The high temperature and long time used for complete dissolution of the PP matrix may be some other reasons causing this peculiar morphology.

CONCLUSIONS

This study focused on the morphology of the dynamically vulcanized PP/EPDM/ZDMA blends during stretching. In summary, the dynamically cross-linked PP/EPDM/ZDMA (EPDM/PP = 30/70) blend exhibits an excellent extensibility with an elongation beyond 600% and a rubbery-like behavior shown under tensile load after the yield stress. The poly-ZDMA graft-products resulting from peroxide dynamical vulcanization increase the compatibility and interfacial adhesion between the rubber and PP phases but reduce the crystallinity of the PP phase. The dispersed rubber particles are elongated and oriented along the tensile direction, whereas the “fiber-like threads” bonded the rubber phase together, acting as a “bridge” between elongated rubber phases and the PP phase during uniaxial stretching. The stress could be effectively transferred from the PP phase to the numerous elongated rubber phases due to the excellent compatibility and interfacial adhesion between rubber and PP phases, resulting in the rubbery-like behavior.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Li, C. Q.; Zhao, Q. N.; Deng, H.; Chen, C.; Wang, K.; Zhang, Q.; Chen, F.; Fu, Q. Preparation, Structure and Properties of Thermoplastic Olefin Nanocomposites Containing Functionalized Carbon Nanotubes. *Polym. Int.* **2011**, *60*, 1629–1637.
- (2) Martin, G.; Barres, C.; Sonntag, P.; Garois, N.; Cassagnau, P. Continuous Morphology and Stress Relaxation Behaviour of Unfilled and Silica Filled PP/EPDM Blends. *Mater. Chem. Phys.* **2009**, *113*, 889–898.
- (3) Ao, Y. H.; Sun, S. L.; Tan, Z. Y.; Zhou, C.; Zhang, H. X. Compatibilization of PP/EPDM Blends by Grafting Acrylic Acid to Polypropylene and Epoxidizing the Diene in EPDM. *J. Appl. Polym. Sci.* **2006**, *102*, 3949–3954.
- (4) Yazdani, H.; Morshedien, J.; Khonakdar, H. A. Effect of Maleated Polypropylene and Impact Modifiers on the Morphology and Mechanical Properties of PP/Mica Composites. *Polym. Compos.* **2006**, *27*, 614–620.
- (5) Antunes, C. F.; Machado, A. V.; van Duin, M. Morphology Development and Phase Inversion during Dynamic Vulcanisation of EPDM/PP Blends. *Eur. Polym. J.* **2011**, *47*, 1447–1459.
- (6) Min, K. T.; Kima, G. H. Uncross-Linked Polypropylene (PP)/Ethylene-Propylene-Diene (EPDM)/Multi Walled Carbon Nanotube (MWCNT) and Dynamically Vulcanized PP/EPDM/MWCNT Nanocomposites. *Polym. Adv. Technol.* **2011**, *22*, 2273–2278.
- (7) Wang, Z. B.; Wang, L. J.; Wang, X.; Hao, C. C. Deformation Reversibility Enhancement of Thermoplastic Vulcanizates Based on High Density Polyethylene and Ethylene-Propylene-Diene Terpolymer. *Mater. Chem. Phys.* **2012**, *134*, 1185–1189.
- (8) l’Abee, 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*, 1758–1768.
- (9) Chen, Y. K.; Xu, C. H. Specific Nonlinear Viscoelasticity Behaviors of Natural Rubber and Zinc Dimethacrylate Composites Due to Multi-Crosslinking Bond Interaction by Using Rubber Process Analyzer 2000. *Polym. Compos.* **2011**, *32*, 1593–1601.
- (10) Lu, Y. L.; Liu, L.; Tian, M.; Geng, H. P.; Zhang, L. Q. Study on Mechanical Properties of Elastomers Reinforced by Zinc Dimethacrylate. *Eur. Polym. J.* **2005**, *41*, 589–598.
- (11) Nie, Y. J.; Huang, G. S.; Qu, L. L.; Zhang, P.; Weng, G. S.; Wu, J. R. Cure Kinetics and Morphology of Natural Rubber Reinforced by the In Situ Polymerization of Zinc Dimethacrylate. *J. Appl. Polym. Sci.* **2010**, *115*, 99–106.
- (12) Peng, Z. L.; Liang, X.; Zhang, Y. X.; Zhang, Y. Reinforcement of EPDM by In Situ Prepared Zinc Dimethacrylate. *J. Appl. Polym. Sci.* **2002**, *84*, 1339–1345.
- (13) de Risi, F. R.; Noordermeer, J. W. M. Effect of Methacrylate Coagents on Peroxide Cured PP/EPDM Thermoplastic Vulcanizates. *Rubber Chem. Technol.* **2007**, *80*, 83–99.
- (14) He, P.; Peng, Z. L.; Ren, W. T.; Zhang, Y.; Zhang, Y. X. Ethylene Propylene Dienemonomer/Polypropylene Thermoplastic Elastomermodified with in Situ Prepared Zinc Dimethacrylate. *China Synth. Rubber Ind.* **2006**, *29*, 435–438.
- (15) Chen, Y. K.; Xu, C. H.; Cao, L. M.; Wang, Y. P.; Cao, X. D. PP/EPDM-Based Dynamically Vulcanized Thermoplastic Olefin with Zinc Dimethacrylate: Preparation, Rheology, Morphology, Crystallization and Mechanical Properties. *Polym. Test.* **2012**, *31*, 728–736.
- (16) Chen, Y. K.; Xu, C. H.; Cao, L. M.; Cao, X. D. Highly Toughened Polypropylene/Ethylene-Propylene-Diene Monomer/Zinc Dimethacrylate Ternary Blends Prepared via Peroxide-Induced Dynamic Vulcanization. *Mater. Chem. Phys.* **2013**, *138*, 63–71.
- (17) Shahbikian, S.; Carreau, P. J.; Heuzey, M.-C.; Ellul, M. D.; Cheng, J.; Shirodkar, P.; Nadella, H. P. Morphology Development of EPDM/PP Uncross-Linked/Dynamically Cross-Linked Blends. *Polym. Eng. Sci.* **2012**, *52*, 309–322.
- (18) Bitinis, N.; Sanz, A.; Nogales, A.; Verdejo, R.; Lopez-Manchado, M. A.; Ezquerro, T. A. Deformation Mechanisms in Poly(lactic Acid)/Natural Rubber/Organoclay Bionanocomposites as Revealed by Synchrotron X-ray Scattering. *Soft Matter* **2012**, *8*, 8990–8997.