

Mechanical Properties and Morphological Structures Relationship of Blends Based on Sulfated EPDM Ionomer and Polypropylene

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ABSTRACT: The mechanical properties and morphological structures of blends based on Zn^{2+} neutralized low degree sulfated ethylene propylene diene monomer rubber (Zn-SEPDM) ionomer and polypropylene (PP) were studied. It was found that Zn^{2+} neutralized low degree sulfated EPDM ionomer and PP blends, which are new thermoplastic elastomeric materials, have better mechanical properties than those of PP/EPDM blend. Theoretical analysis of tensile data suggests that there is an increase of the extent of interaction between PP and EPDM in the presence of a low

degree of Zn^{2+} , which is also an indicator of better interfacial adhesion between PP and Zn-SEPDM than that between PP and EPDM. SEM results proved that the finer dispersed phase sizes and the shorter interparticle distances are the main reasons for the improved mechanical properties of the PP/EPDM blend. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1504–1510, 2004

Key words: ionomers; polypropylene (PP); mechanical properties; morphology; thermoplastics

INTRODUCTION

Thermoplastic elastomeric materials have been widely used in wire and cable products, especially in the mineral, electric equipment, and automobile industries. The most commonly used method of obtaining thermoplastic elastomeric materials is to toughen plastic and blends of rubber and plastic, such as POE (ethylene-1-octene copolymer)-toughened polypropylene (PP) and PP/ethylene propylene diene monomer rubber (EPDM) blends.^{1–5} The main defects of toughened plastic or rubber/plastic blends are their poor stress and strain properties. The stress and strain properties of toughened plastic and blends of rubber and plastic may be increased by incorporating compatibilizers and crosslinking bonds in these blends.^{6–11} The main disadvantages of toughened plastics with compatibilizers or vulcanized elastomer are their strict conditions of process and that they cannot be recycled. The use of ionomers in elastomers offers feasible ways of producing easily processable and recyclable elastomeric materials because they will form ionic interactions, under ambient conditions, to increase the tensile properties and ionic interactions will break at elevated temperature to achieve easy processing conditions.^{12–14}

The incorporation of ionic groups into organic polymers yields ionomers. The presence of even a small amount of ionic groups exerts a profound effect on the physical properties of the polymer.^{15–18} The ionic groups present in the polymers interact to form strong intermolecular ionic aggregates, which increase the adhesion of plastic and form the interlocked network structure in rubber/plastic blends. The mechanical properties of the ionomer depend on the ionic moiety, the counterion type, the degree of neutralization, the flexibility of the backbone polymer, and the presence of plasticizers. Using Zn^{2+} neutralized sulfated EPDM and PP blends to obtain elastomers was first investigated by the Exxon Company.^{14,19–22} Lundberg et al. reported that the blends of sulfonated elastomers with crystalline polyolefin¹⁴ and elastomeric blend compositions have improved weathering stability.¹⁹ Makowski et al. investigated the elastomeric blend compositions of a sulfonated elastomeric polymer²⁰ and elastomeric compositions.²¹ Bock et al. studied thermoplastic elastomer compositions.²² These ionic crosslinking elastomers are all based on their high ion concentrations to form ion aggregates. The main defects of these materials are their high viscosities and poor elasticity. Great quantities of plasticizers are used to obtain flexible materials.

In the present study, IR spectroscopy was used to evaluate the effectiveness of Zn^{2+} neutralized sulfated EPDM. Mechanical properties and morphological structure of a set of blends of PP and EPDM or Zn-SEPDM, with different contents of the low degree

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Zn^{2+} , were investigated; fractured etched morphology was also studied to determine the ionic interaction between the Zn-SEPDM and PP matrix.

EXPERIMENTAL

Materials

Polypropylene used in this study was isotactic polypropylene [iPP, Novatel H57541; GPC method, MW: 300,000 (Japan Polychem Corp., Tokyo, Japan)], with a density of 0.90 g/mm^3 and melt flow rate of 3.7 g/10 min (GB 3682-83). EPDM was Novdel IP 4770R supplied by the DuPont Dow Corp. (Midland, MI; Mooney viscosity, ASTM D-1646, ML_{1+4} at 125°C : 70; typical MW, GPC: 200,000; ethylene, mass%, ASTM D-3900: 70; ENB, mass%, ASTM D-6047: 4.9; MWD, characteristic DuPont Dow method EPRG-2: medium). Zinc acetate (AR), sulfuric acid (AR), and acetic anhydride used were supplied by the Shanghai Chemical Reagent Co. (China).

Preparation of Zn^{2+} neutralized sulfated EPDM

Acetyl sulfate preparation

First, acetic anhydride was cooled below -10°C , and a corresponding volume of 96% sulfuric acid was added. The solution was stirred and finally 1,2-dichloroethane (DCE) was added. The product obtained was maintained at 0°C in an ice bath until it was added to the reaction medium.

Sulfonation reaction

Sulfonation was carried out according to the procedure described by Makowski et al.^{20,23} In an agitated reactor, the polymer was dissolved in cyclohexane at $60\text{--}70^\circ\text{C}$ and purged with nitrogen, after which the acetyl sulfate, prepared as described above, was added. The solution was stirred and purged with nitrogen during the experiment. The reaction was terminated by being precipitated into methanol or water after the desired reaction time.

Neutralization reaction

The neutralization reaction was carried out after the sulfonation reaction was terminated. Then the solution was stirred and precipitated into the extra zinc sulfate solution of ethanol and water and purged with nitrogen during the experiment. The product was obtained after the desired reaction time.

The reaction equation is shown in Figure 1.

The complete removal of residual acid and salt from the final product after the neutralization reaction is important because it can interfere with the properties of the final product. The dried polymer was cut into

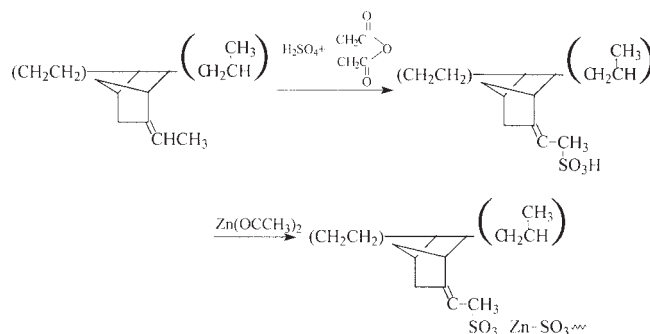


Figure 1 Reaction equation of Zn^{2+} neutralized sulfated EPDM.

small pieces and washed once with boiling deionized water and many times with cold water until the neutral pH of sewage was obtained. It was finally vacuum dried at 80°C for 3 days.

Sample preparation

Prescribed amounts of PP and EPDM (or Zn-SEPDM) were mixed in a Haake Rheocord 90 internal mixer (Haake, Bersdorff, Germany). Samples were obtained when the torque was maintained at a constant value. Some samples were removed for analysis of the ion concentration by weighing the ZnO that remained after heating to 1200°C in a muffle furnace. The dumb-bell-shape test pieces were cut after being compressed by a press vulcanizer at 170°C , according to the Chinese standard GB/T 1040-92.

Characterization

FTIR spectroscopy

The obtained samples were pressed into films of $100 \mu\text{m}$ thickness. A Perkin-Elmer FTIR instrument (Perkin Elmer Cetus Instruments, Norwalk, CT) was used to obtain the results.

Mechanical properties

Mechanical properties were measured on an Instron-4302 tensile tester according to GB/T 1042-92.

Morphology observation

The phase morphology of the blends was examined by scanning electron microscopy (SEM; Model S520; Hitachi, Osaka, Japan). Specimens were prepared by immersing test pieces in liquid nitrogen before breaking. The fractured surfaces of the test pieces were coated with gold.

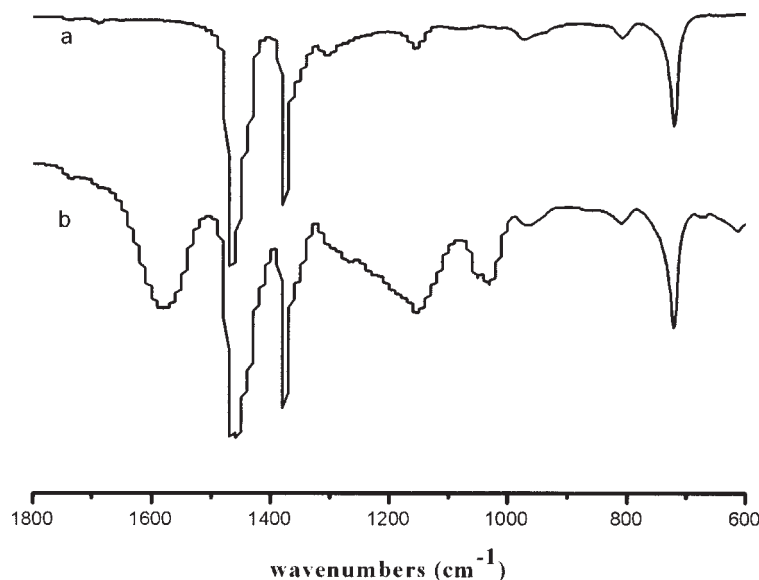


Figure 2 FTIR spectra of neat EPDM and Zn-SEPDM: (a) EPDM, (b) 0.06 mol % Zn-SEPDM.

RESULTS AND DISCUSSION

FTIR study

Figure 2 shows the infrared spectra of neat EPDM and Zn^{2+} neutralized sulfated EPDM, with an ion concentration of 0.06 mol/100 g (0.06 mol % Zn-SEPDM). According to spectrum (b) of Zn-SEPDM, it can be deduced that the band observed at 1026 cm^{-1} is attributed to the S=O stretching mode and 1221 cm^{-1} is attributed to the asymmetric stretching of S=O. A medium peak at 614 cm^{-1} is attributed to the stretching mode of S—O and the band at 1575 cm^{-1} results from the zinc sulfate ion. The difference between these two spectra proved that the Zn^{2+} neutralized sulfated EPDM ionomer was obtained by this two-step reaction.

Mechanical properties

The mechanical properties of neat polymer and the blends, measured at ambient temperature, are summarized in Table I.

From Table I, it can be seen that the mechanical properties of PP/EPDM blends are significantly improved by using Zn^{2+} neutralized low degree sulfated EPDM, especially the properties of stress and strain at break. It can also be seen that the blend of PP/0.06 mol % Zn-SEPDM has sufficiently high stress and strain at break characteristics for use as elastomeric materials. The higher mechanical properties observed in the case of ionomeric polyblends is caused by the formation of a technologically compatible blend, wherein the intermolecular ionic interactions act as a compatibilizer.

The changes of mechanical properties of PP, by blending EPDM or Zn-SEPDM with PP, can be directly seen in Figure 3. The neat PP is a rigid and strong plastic material. The soft and toughened PP can be obtained by blending EPDM with it, although strain and stress at break dramatically decrease because of the low interfacial adhesion between PP and EPDM and poor dispersion structure of EPDM in PP. The strain and stress at break can be substantially improved by doping Zn^{2+} in PP/EPDM. When the ion concentration of Zn-SEPDM is very low (e.g., 0.03 mol

TABLE I
Mechanical Properties of PP/EPDM and PP/Zn-SEPDM Blends^a

Sample	Yield stress (MPa)	Stress at break (MPa)	Strain at break (%)
PP/EPDM	8 (± 0.20)	11 (± 1)	563 (± 15)
PP/0.02 mol % Zn-SEPDM	9 (± 0.5)	13 (± 1)	598 (± 30)
PP/0.03 mol % Zn-SEPDM	11 (± 1)	17 (± 2)	727 (± 51)
PP/0.05 mol % Zn-SEPDM	12 (± 1.5)	21 (± 2)	698 (± 45)
PP/0.06 mol % Zn-SEPDM	13 (± 1.5)	30 (± 3)	627 (± 34)
PP/0.08 mol % Zn-SEPDM	11 (± 1)	22 (± 1)	564 (± 20)

^a The mixed ratio of each blend is 50 : 50 by weight with eight replications of the data.

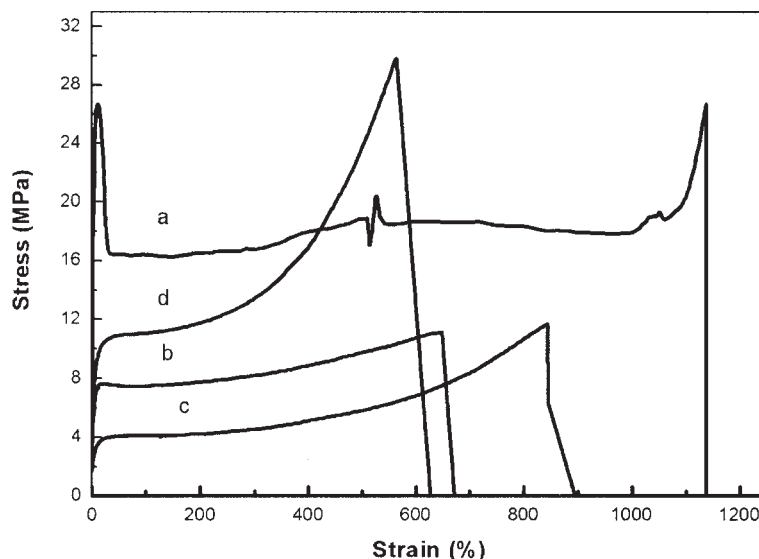


Figure 3 Stress-strain curves of neat PP, PP/EPDM, and PP/Zn-SEPDM blends: (a) neat PP, (b) PP/EPDM, (c) PP/0.03 mol % Zn-SEPDM, (d) PP/0.06 mol % Zn-SEPDM.

%), the modulus of PP/Zn-SEPDM will decrease, the strain and stress at break will increase, and the stress-strain curve signifies its elastomeric property. By improving the ion concentration, the modulus and stress at break of PP/Zn-SEPDM blends will increase, but strain at break will decrease. Tough and strong materials can be obtained by the use of 0.06 mol % Zn-SEPDM blended with PP.

Predictive models were used to analyze the tensile strength of polymer blends to assess the level of interfacial interaction.^{24–27} Based on the relationship of area fraction to volume fraction of the inclusions, the dependency of the dispersed phase of the mechanical properties of the two phase blends is commonly expressed by the first power law and two-thirds power-law relationship. Three models were used to analyze the tensile strength results obtained in this study.

Model 1: Neilsen's first law model²⁴

$$\frac{\sigma_b}{\sigma_p} = (1 - \phi_1)S \quad (1)$$

Model 2: Neilsen's two-thirds power-law model²⁴

$$\frac{\sigma_b}{\sigma_p} = (1 - \phi_1^{2/3})S' \quad (2)$$

Model 3: Nicolais-Narkis model²⁵

$$\frac{\sigma_b}{\sigma_p} = (1 - K_b\phi_1^{2/3}) \quad (3)$$

where σ_b and σ_p represent the stress at break of the blends and the PP, respectively; ϕ_1 is the volume fraction of EPDM or Zn-SEPDM in the blends; and S and S' are the Neilsen's parameters in the first and two-thirds power-law models, respectively. K_b in the Nicolais-Narkis model is an adhesion parameter.

The maximum value of the parameter S and S' in eq. (1) is unity for "no stress concentration effect." The lower the value of S , the greater the stress concentration effect or poorer the adhesion, which is valid for filled polymer composites or blends. The weightage factor K_b in eq. (3) is an adhesion parameter, the maximum value of K_b being 1.21 for spherical inclusion of the minor phase with no adhesion.²⁶ The lower the value, the better the adhesion. The three models described above were used to analyze the tensile strength results for evaluation of interfacial adhesion, if any, by comparing the experimental values with those predicted by the models.^{26,27} The values of S , S' , and K_b are listed in Table II, showing a comparison

TABLE II
Values of Stress Concentration Parameters of PP/EPDM and PP/Zn-SEPDM Blends

Blend ^a	S	S'	K_b
PP/EPDM	0.81	1.10	0.94
PP/0.02 mol % Zn-SEPDM	0.96	1.30	0.82
PP/0.03 mol % Zn-SEPDM	1.26	1.70	0.59
PP/0.05 mol % Zn-SEPDM	1.50	2.10	0.35
PP/0.06 mol % Zn-SEPDM	2.22	3.00	-0.18
PP/0.08 mol % Zn-SEPDM	1.63	2.20	0.29

^a Volume fraction of EPDM or Zn-SEPDM in each sample = 0.5.

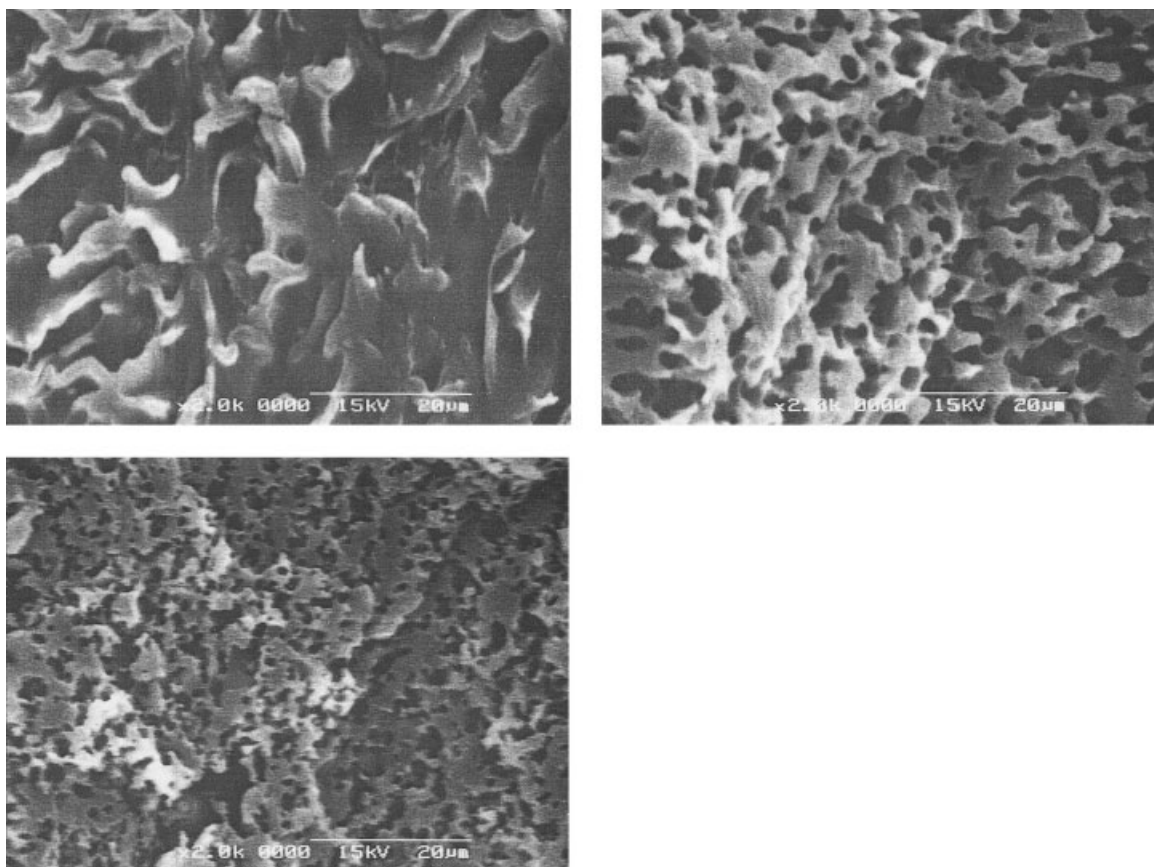


Figure 4 Scanning electron micrographs of fractured etched PP/EPDM blends: (a) PP/EPDM, (b) PP/0.03 mol % Zn-SEPDM, (c) PP/0.06 mol % Zn-SEPDM.

between the experimental data and theoretical models.

The same tendency was found from the analysis of S and S' , that the experimental values for PP/Zn-SEPDM blends are higher than that for the PP/EPDM blend. When the Zn^{2+} concentrations are less than 0.06 mol %, the values increase with increasing Zn^{2+} concentrations and vice versa. This confirms that all PP/Zn-SEPDM blends can take excessive stress because the interfacial adhesion is improved, compared to that of the PP/EPDM blend. From Table III, it can be seen that the values of S and S' of PP/0.06 mol % Zn-SEPDM blend are 2.22 and 3.00, respectively, which are much greater than that of the PP/EPDM blend, which confirms that the adoption of 0.06 mol % Zn^{2+} into EPDM can effectively eliminate stress concentration of PP/EPDM blends. The analysis of K_b also shows that all the values of blends are less than 1.21, showing that blends have interfacial adhesion between EPDM or Zn-SEPDM and PP in these blends, although the values of Zn-SEPDM blends have a much higher level of adhesion and the tendency is similar to the values of S and S' . A very important result can be seen in that the values of K_b for the PP/0.06 mol % Zn-SEPDM blend are less than zero,

showing that the stress at break of this blend is higher than that of neat PP. In addition to the much greater interfacial inhesion, the stress can be attributed to the strong ionic interaction between Zn-SEPDM and the PP matrix.

Fractured surface morphology observation

The fractured surface morphology of PP/EPDM and Zn-SEPDM blends was studied by SEM and the results are shown in Figure 4(a), (b), and (c). To elucidate the dispersion morphology of the PP phases and Zn-SEPDM or EPDM phases, the fractures were etched to remove the Zn-SEPDM or EPDM phases by immersing the specimens to the mixed solution of sulfuric acid, phosphoric acid, and dichromate acid at 70°C for 5 min. SEM micrographs show the PP matrix (gray sections) that remained after the Zn-SEPDM or EPDM phase was extracted.^{2,10,27} It is evident from extraction results shown in the SEM that, in the equal weight ratio blends of PP/EPDM, the PP phases will form the continuous phase and EPDM or Zn-SEPDM phases are dispersed in the PP phases, but the sizes of phase domains are significantly different. For the rubber-toughened plastic, because the molecular chains of

rubbers are softer than those of plastics, the movement of molecular chains of rubbers will be restricted by that of plastics and the rubber will be curled to form dispersion phases, even in the equal weight ratio blends.

In general, it is considered that the toughness of polymer materials depends on stress concentration and craze strength. The rubber phase dispersed in the plastic phase plays important roles: first of all it will induce many crazes at the center of the stress concentration domain and, on the other hand, it will control the development of the craze without formation of fatal cracks. The dispersion morphology and the adhesion of the interlayer of the blends will affect the toughness of the rubber-toughened plastic polymer. According to the theory proposed by Wu, based on EPDM-toughened PA-66²⁸ (which is used in many rubber-toughened plastics)

$$d_c = T_c [(\pi/6\phi_r)^{1/3} - 1]^{-1} \quad (4)$$

where d_c is the critical particle diameter, T_c is the critical interparticle distance, and ϕ_r is the rubber volume fraction.

Continuation of the rubber phase plays an important role in determining the toughness and strength of rubber-toughened plastic. The stress field will apply to the isolated plastic particles and the whole stress field will be separated, sustained by every particle. The critical particle diameter d_c is a material property of the matrix, independent of the rubber volume fraction and particle size. From eq. (4), it can be deduced that, if the rubber volume fraction ϕ_r is fixed, the critical interparticle distance T_c will be determined by the morphology of rubber. Mechanical analysis shows that the interfacial adhesions are much different between blends of PP/EPDM and PP/Zn-SEPDM, and the phase domains will be affected by interfacial adhesion. From Figure 4(a), it can be seen that the PP phase and the EPDM phase form a large phase domain because of self-aggregation induced by poor interfacial adhesions. Most phase domains are larger than 15 μm . The finer phase domain can be seen in Figure 4(b) and (c). The mean phase domain size, which is less than 10 μm , can be seen in Figure 4(b) and those less than 5 μm can be seen in Figure 4(c).

The strength of polymer is determined by the breakdown of the chemical bond and that of the blend is determined by the van der Waals attraction. Because the van der Waals attraction is much less than that of the chemical bond, the strength of many blends is much less than that of the corresponding polymer, especially in the incompatible blends. The most commonly used method to improve the strength of incompatible blends is increasing the interfacial adhesion to decrease the distance of van der Waals attraction or incorporating a chemical bond to form the crosslink-

ing network. From Figure 4(a), the incompatible polymers PP and EPDM are simply mixed; the two phases can be clearly seen. The EPDM phase will form a dispersed phase because it is soft. The strength of the blend is determined by the van der Waals attraction of PP and EPDM. Because the domain phase is larger and the interparticle distance is much greater, the van der Waals attraction is very weak. From Figure 4(b) and (c), the more even and finer phase domains can be seen and the distance of van der Waals attraction is much shorter. However, the ion concentration in PP/0.03 mol % Zn-SEPDM blend is too low to form the ionic interaction across the entire blend, and so the increase of stress at break is attributed to the increase of van der Waals attraction. In PP/0.06 mol % Zn-SEPDM blend, there are enough ions to form ionic interactions across the entire blend, so the continuous structure of the PP phase and Zn-SEPDM phase dispersed in it, and adhesion on it, can be seen in Figure 4(c). In PP/0.06 mol % Zn-SEPDM blend, the ions have dual effects: first, these are polar groups and thus increase the interfacial adhesion between PP and Zn-SEPDM; second, the ionic interaction across the entire PP and Zn-SEPDM blend will form.

CONCLUSION

1. It was found that Zn^{2+} neutralized low degree sulfated EPDM and PP blends have better mechanical properties than those of the PP/EPDM blend.
2. The theoretical analysis of tensile properties suggests that there is an increase in the extent of interaction between PP and EPDM in the presence of low-degree Zn^{2+} , which is also an indication of better interfacial adhesion between PP and Zn-SEPDM than that between PP and EPDM.
3. SEM results confirmed that the finer dispersed phase sizes and the smaller interparticle distances are the main reasons for the improvement of the mechanical properties of PP/EPDM blends.

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