Effects of Different Polypropylene and Ammonium Lignosulfonate Contents on the Crystallization Behavior, Rheological Behaviors, and Mechanical Properties of Ethylene Propylene Diene Monomer/ Polypropylene/ Ammonium Lignosulfonate Composites

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Thermoplastic elastomer (TPE), made from ethylene propylene diene monomer (EPDM) and polypropylene (PP) based on reactive blending, has excellent processing performance and characteristics and a wide range of applications. However, there are currently no reports in the literature regarding the usage of TPE in making composite boards. In this paper, EPDM, PP, and ammonium lignosulfonate (AL) were used as the raw materials, polyethylene wax was used as the plasticizer, and a dicumyl peroxide vulcanization system with dynamic vulcanization was used to make a new kind of composite material. This research studied the influences of the PP and AL contents on the crystallization behavior, mechanical properties, and rheological properties of the composites. The results showed that the PP content had a noticeable impact on the performance of the composites. The AL content had a major impact on the modulus of elasticity of the composite board. Accordingly, this kind of composite material can be used as an elastomer material for the core layer of laminated flooring.

Keywords: Polypropylene (PP); Ammonium lignosulfonate (AL); Morphology; Rheological properties; Mechanical properties

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INTRODUCTION

Polypropylene (PP) is a highly crystalline thermoplastic resin with configuration regularization. It is a popular compound because of its low cost and good performance in regard to its abrasive resistance, heat resistance, chemical stability, electrical properties, and processing properties. However, because of its poor resistance to cold and aging, the impact strength and toughness of PP are not satisfactory at lower temperatures. Consequently, its application is restricted (da Costa *et al.* 2006). A number of techniques have been employed to reinforce and toughen PP, including the addition of various elastomers as modifiers. The modification of a thermoplastic material with an elastomer has demonstrated a four-fold increase in the impact strength (da Silva and Coutinho 1996; Jiang *et al.* 2000) The thermoplastic polyolefin (TPV) compounded with ethylene propylene diene monomer (EPDM) and PP during dynamic vulcanization has both a rubber elasticity and thermos plasticity; hence, it is widely used in the automotive, construction, and electronics fields, and has maintained a fast growth rate every year.

Lignin is the second most abundant natural polymer in the plant world, next to cellulose. It is also the only natural resource that can provide renewable aromatic compounds (Rastogi and Dwivedi 2008; Stewart 2008). As a by-product of the pulp and paper industry (Belgacem *et al.* 2003; Fan and Zhan 2008), the annual output of lignosulfonate is approximately one million tons (Belgacem *el al.* 2003; El Mansouri and Salvadó 2006), but the utilization rate is low. Most lignin is disposed of as waste or burned, which not only wastes resources, but also pollutes the environment (Mohan *et al.* 2006). Lignosulfonate is a water-soluble anionic surfactant; as such, it has a characteristic surface activity and has many applications (Palmqvist *et al.* 2006; Vishtal and Kraslawski 2011; Chandra *et al.* 2015; Khazieva *et al.* 2015), including as an adhesive for drilling (Zhang and Yin 2002), detergent, glue, animal feed, particleboards (Jin *et al.* 2010), and cement additive (Grierson *et al*. 2005; Ansari and Pawlik 2007). Recently, there have many studies on the composite material combined from lignosulfonate with some polymer materials to improve the composite performances, including flame retardancy (Lu *et al.* 2018), thermal properties and thermal stabilization (Shao *et al*. 2017), dispersion property (Liu 2018), conductivity (Arvinte *et al.* 2017; Shao *et al.* 2018), spinnability (Ouyang *et al*. 2017), dye-adsorption performance (Lü *et al*. 2017), absorbency (Lv *et al.* 2018), crystallization behavior (Ye *et al.* 2017), and so on.

In this study, a new type of thermoplastic polymer material was made by mixing EPDM, PP, and ammonium lignosulfonate (AL). The effects of the PP and AL contents on the properties of the EPDM/PP/AL composites were systematically investigated.

EXPERIMENTAL

Materials

Extrusion-grade isotactic PP was purchased from Sinopec Maoming Branch (Maoming, China), and its model number is PPH-T03 (Melt Mass-flow Rate (MFR) = 3.0 g/10 min ± 0.5 g/10 min). The EPDM was supplied by Petro China Jilin Petrochemical Company (Jilin, China), and its model number is J-3080P (density = 0.87 g/cm^3; 70.9% ethylene content; Mooney Viscosity (ML) (4125 °C) = 74 dN•m; 4.2% ENB content). The AL was purchased from Shenyang Xingzhenghe Chemical Co., Ltd. (Shenyang, China) and was used without any further purification. Its composition was as follows: 4.8 wt.% moisture, 10.8 wt.% ash, 51.7 wt.% total lignin, and 26.9 wt.% carbohydrates.

Methods

Composite preparation

The preparation of the EPDM/PP/AL composites was performed in an intermeshing co-rotating twin-screw extruder (SH30, Nanjing Rubber Machinery Plant, Nanjing, China). The EPDM, PP, and AL were mixed according to the quality percentage. The EPDM content was 100 phr, and the PP and AL contents were 50 phr, 100 phr, and 150 phr. After mixing, the vulcanizing agent, active agent, and plasticizer (Table 1) were added into the blends. Following this step, the blends were mixed in a high-speed mixer (SHR-10A, Zhangjiagang Tonghe Plastic Machinery Co., Ltd., Zhangjiagang, China) at 750 rpm for 5 min to 8 min to guarantee that the materials were mixed evenly. The premixes were dynamically vulcanized in a specific twin-screw extruder. The rotation speed of the screw axis and the temperature in the extruder are given in Table 2. The composite was placed between the parallel flat plates (200 mm × 300 mm) of a mechanically controlled oil-heated press (SL-6, Harbin Special Plastic Products Co., Ltd., Harbin, China) for the final pressing process. The composite was pressed at 175 °C for 5 min according to a pre-programmed hot-pressing schedule. In this process, a 3-mm steel thickness gage was used to control the thickness of the board. Seven panels were produced for each of the target conditions. To obtain the final boards, 30 mm were trimmed off the edges and the final board dimensions were 150 mm × 220 mm × 3.3 mm. The panels were stored at room temperature for 2 d prior to the analyses described below.

Table 1. Amounts of Vulcanizing Agents, Active Agents, and Plasticizer

DCP (phr)	TAIC (phr)	PE wax (phr)
2	0.5	2.5
3	1	
4	1.5	

DCP = dicumyl peroxide; TAIC = triallyl isocyanurate; PE wax = polyethylene wax

Table 2. Rotation Speed of the Screw Axis and Temperature in the Extruder

Rotation Speed (rpm)	Temperature (°C)						
	First Zone	Second Zone	Third Zone	Fourth Zone	Fifth Zone	Sixth Zone	Seventh Zone
50	145	155	165	170	170	165	160
100	145	160	175	180	180	175	165
150	145	165	180	190	190	180	165

Scanning electron microscopy

The composite microstructures were analyzed with scanning electron microscopy (SEM) (Quanta200, FEI, Hillsboro, OR, USA) at 10.0 kV. Prior to the SEM analysis, the sample surfaces were coated with a thin layer of gold using an ion sputter coater to make the samples conductive.

X-ray diffraction analysis

X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (D/max 2200, Rigaku, Japan) operating with Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 30 mA in the 2θ range from 5° to 50°, with the scan rate set to 5° min^{-1} .

Rotational rheological properties

The pellets prepared for the EPDM/PP/AL composites were injection-molded into test samples measuring 25 mm (diameter) × 2.2 mm (thickness) using a mini injection molder (Haake MiniJet, Thermo Scientific, Hanau, Germany). Prior to testing, the sample was heated to 200 °C and equilibrated for 5 min to erase the previous thermal and deformation history. Tests were run using a rotational rheometer (Discovery HR-2, TA Instruments, New Castle, DE, USA) equipped with a pair of parallel plates (2 mm in working distance and 25 mm in diameter). The dynamic frequency sweep was run at 200 °C from 0.01 rad/s to 100 rad/s at a 0.5% strain amplitude in the linear region. Three replicates were tested for each formulation.

Mechanical properties

Dumbbell-shaped tensile specimens with the dimensions 165 mm × 13 mm × 3 mm were measured using a universal mechanical machine (RGT-20A, Shenzhen Regear Instrument Cooperation, Shenzhen, China) according to ASTM D638-14 (2014). The tests were conducted at a crosshead speed of 5 mm/min and the deflections were measured using a 50-mm extensometer (RGT-20A, Shenzhen Regear Instrument Cooperation, Shenzhen, China).

Specimens with the dimensions 80 mm × 13 mm × 3 mm were measured under three-point bending using the universal mechanical machine in accordance with ASTM D790-17 (2017). A crosshead speed of 5 mm/min and a span length of 56 mm were used for the test.

Analysis method

SPSS13.0 was used for data statistics and analysis. Analysis of covariance was used for analysis of the influence of the content of PP and AL on the properties of EPDM/PP/AL composites. The Duncan new multiple range test (DMRT) was used to compare the mechanical properties and rheological properties of composites. The letters A, B, and C were used to indicate the significance of differences. If the letters are the same, it means the difference is not significant. If the letters are different, it means the difference is significant.

RESULTS AND DISCUSSION

Mechanical Properties of the Composites

The amount of EPDM used was fixed, and the amount of PP and AL used were varied. This was assumed to have a fixed effect, and the performances of the EPDM/PP/AL composites were analyzed using the linear mixed model of the type III test. Table 3 shows that the mechanical properties of the composites were significantly affected by the amount of PP, while the tensile modulus, flexural strength, and flexural modulus were all significantly affected by the amount of AL.

Table 3. Variance Analysis of the Linear Mixed Model for the Mechanical Properties with Different PP and AL Contents

Source	Tensile Strength (MPa)		Tensile Modulus (GPa)		Flexural Strength (MPa)		Flexural Modulus (GPa)	
	F	Sig.	F	Sig.	F	Sig.	F	Sig.
Intercept	5061	0.000	3556	0.000	7408	0.000	2661	0.000
PP Content (phr)	115.8	0.000	5.781	0.004	336.4	0.000	32.61	0.000
AL Content (phr)	2.215	0.114	88.37	0.000	9.928	0.000	127.6	0.000

Effects of the PP content on the mechanical performances of the composites

Table 4 shows the standard deviations of the mechanical test results of the EPDM/PP/AL composites with different PP contents. Figure 1 shows that the amount of PP had a significant influence on the mechanical properties of the EPDM/PP/AL composites.

Table 4. Descriptive Statistics for the Mechanical Properties with Different PP Contents

	PP Content (phr)	N	Mean	Std. Deviation	Std. Error	Minimum	Maximum
Flexural Strength	50	48	7.677	1.117	0.161	5.691	10.545
	100	50	12.180	1.836	0.260	9.661	17.003
	150	50	16.700	2.891	0.409	9.769	22.037
Flexural Modulus	50	47	0.437	0.287	0.042	0.129	1.220
	100	50	0.460	0.194	0.027	0.213	0.977
	150	50	0.644	0.139	0.020	0.428	0.985
Tensile Strength	50	38	4.677	0.843	0.137	2.802	6.402
	100	44	6.681	1.072	0.162	4.115	8.807
	150	41	8.041	1.807	0.282	4.774	11.280
Tensile Modulus	50	38	0.117	0.053	0.009	0.029	0.220
	100	44	0.110	0.024	0.004	0.063	0.171
	150	41	0.122	0.027	0.004	0.067	0.174

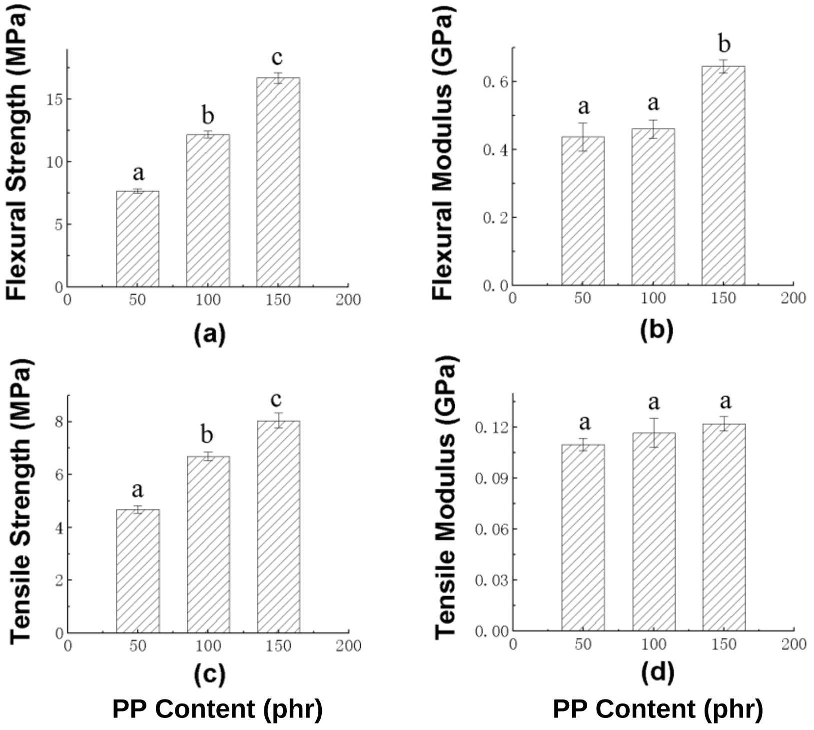
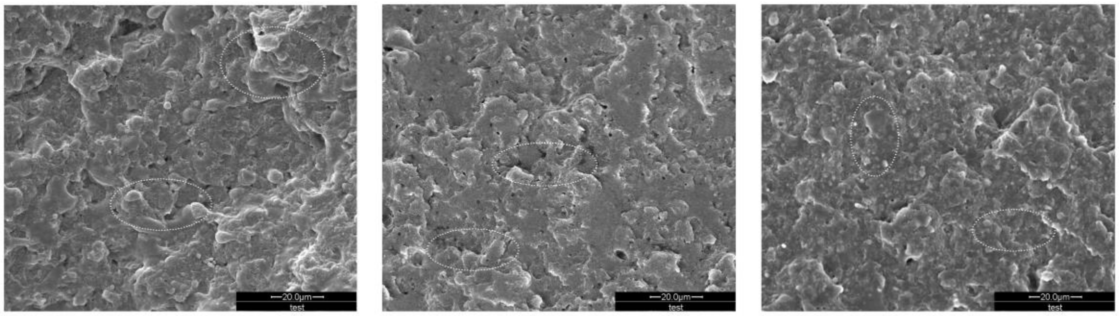


Fig. 1. Effects of the different PP contents on the mechanical properties of the composites: (a) flexural strength, (b) flexural modulus, (c) tensile strength, and (d) tensile modulus

The flexural strength, flexural modulus, tensile strength, and tensile modulus of the composites increased with an increase in the amount of PP. The flexural and tensile strengths had significant differences when the PP dosage was 50 phr, 100 phr, and 150 phr. This was because the PP is a crystalline polymer (Mandal *et al.* 2014); therefore, when its content increased, the crystallinity of the EPDM/PP/AL composite increased. As such, the composite material had a better resistance performance to external forces. These factors led to a better mechanical performance. This conclusion is consistent with previous results reported in the literature (Choudhary *et al.* 1991; Shibryaeva *et al.* 2001; Humbert *et al.* 2011). Also, the tensile and flexural moduli of the composites increased as the PP content increased. This was because the elastic modulus and degree of crystallinity of the composites have a linear relationship (Niesten and Gaymans 2001; Humbert *et al.* 2011; Xiong *et al.* 2011). The PP content of the EPDM/PP/AL composites led to an increase in the crystallinity of the composite material; thus, the elastic modulus of the composite was improved.

Figure 2 shows the SEM photos for the EPDM/PP/AL composites with different PP contents. The EPDM particles with different PP contents were all at the micron level distributed uniformly as an “island” in the “sea” phase of the PP and formed an obvious “sea-island” two-phase structure. With an increasing PP content, the particle size of the EPDM particles decreased and the interfacial compatibility improved. When the PP content was 50 phr, the EPDM particle size was the largest and the phase interface was clear. This was probably because of the following reasons. When the rubber content is high, EPDM particles easily coalesce. Also, when the PP content was 100 phr, the EPDM particle size decreased and the combination of the two phases improved, but there was still a lot of phase interface. Lastly, when the PP content was 150 phr, the EPDM particle size was the smallest with more uniform dispersion and the phase interface was greatly reduced, which indicated that the two phases were closely combined. This was why the mechanical properties of the composites were improved with an increase in the PP content.



50 phr PP 100 phr PP 150 phr PP

(a) (b) (c)

Fig. 2. SEM photos of the EPDM/PP/AL composite with different PP contents: (a) 50 phr, (b) 100 phr, and (c) 150 phr

Effects of the AL content on the mechanical performances of the composites

The main innovation of this paper was the addition of AL to the blends as the main raw material. Therefore, the key research focus of this paper was to determine the influence of different AL contents on the properties of the composite materials. In this paper, the AL amounts were 50 phr, 100 phr, and 150 phr, and the composite properties were studied accordingly. Table 5 shows the standard deviations of the mechanical test results of the EPDM/PP/AL composites with different AL contents. Figure 3 shows that the flexural and tensile moduli of the EPDM/PP/AL composites increased with an increasing AL content, and the difference was significant. This was because the AL functional groups can impart colloid properties (Areskogh and Henriksson 2011).

Table 5. Descriptive Statistics for the Mechanical Properties with Different AL Contents

	AL Content (phr)	N	Mean	Std. Deviation	Std. Error	Minimum	Maximum
Flexural Strength	50	44	11.138	4.192	0.632	5.691	20.370
	100	54	12.630	4.271	0.581	5.969	22.037
	150	50	12.807	4.109	0.581	6.925	21.282
Flexural Modulus	50	44	0.316	0.159	0.024	0.129	0.668
	100	54	0.486	0.123	0.017	0.189	0.747
	150	49	0.727	0.203	0.029	0.350	1.220
Tensile Strength	50	41	6.535	1.901	0.297	2.802	9.850
	100	42	6.841	1.999	0.308	4.039	11.280
	150	40	6.152	1.704	0.269	3.420	9.952
Tensile Modulus	50	41	0.085	0.026	0.004	0.029	0.132
	100	42	0.120	0.024	0.004	0.056	0.179
	150	40	0.145	0.031	0.005	0.084	0.220

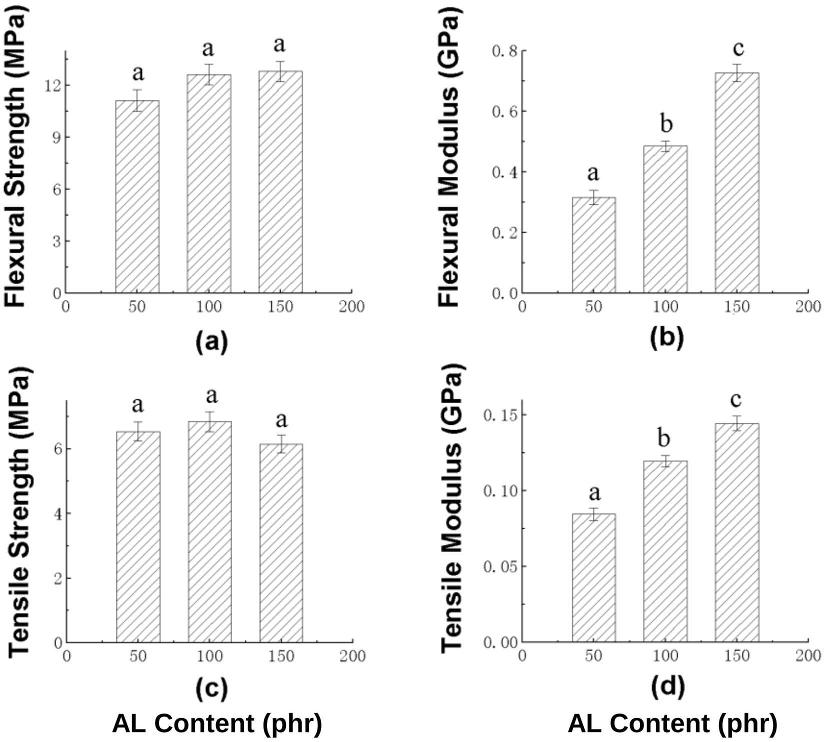
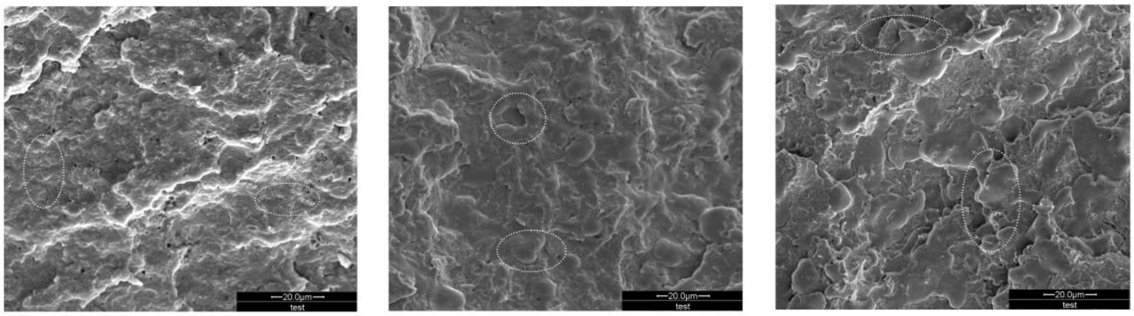


Fig. 3. Effect of the different AL contents on the mechanical properties of the composites: (a) flexural strength, (b) flexural modulus, (c) tensile strength, and (d) tensile modulus

As the AL content increased, the viscosity and elastic modulus of the EPDM/PP/AL composites increased. This indicated that the function of AL in the composite system was similar to the function of natural lignin in plant fibers and had a reinforcing effect on a mixed system. Additionally, AL can produce free radicals under a high temperature shearing force (Shen *et al.* 2013). These free radicals can combine with side chains of rubber molecules, improve the ability of composite materials to resist deformation, and improve the composite stiffness.

The flexural and tensile strengths of the composites were not significantly influenced by the AL content. The flexural strength increased with an increase in the AL content. The tensile strength increased at first and then decreased as the AL content increased. When the AL dosage was 100 phr, the tensile strength of the composites was at its highest. These results were not consistent with the research results of Toriz *et al.* (2002), who studied PP and lignosulfonate composites. According to Toriz *et al.* (2002), the tensile and flexural strengths of the composites decreased with an increase in the lignosulfonate dosage. This was because of the existence of EPDM in the composite. Lignin can increase the mechanical properties of EPDM (Zhang and Ding 2001; Xu *et al.* 2015). Accordingly, with certain increases in the lignin content, the mechanical properties of the EPDM/PP/AL composites increased.

Figure 4 shows the SEM photos of the EPDM/PP/AL composites with different AL contents. The photos show that with increases in the lignin content, the composite interface condition worsened and the phase interface became clearer. When the lignin content was 50 phr, the specimen section had a good continuity and interfacial bonding, without obvious classification between the different phases. When the lignin content was 100 phr, the specimen section had a good continuity and close interfacial bonding, but there was obvious separation between the different phases. When the lignin content was 150 phr, the phase interface was clear and the gap between the phases became bigger. The stress concentration increased, which led to a decrease in the tensile strength of the composite.



50 phr AL 100 phr AL 150 phr AL

(a) (b) (c)

Fig. 4. SEM photos of the EPDM/PP/AL composites with different AL contents: (a) 50 phr, (b) 100 phr and (c) 150 phr

Rheological Properties of the Composites

Table 6 lists the effects of the different PP and AL dosages on the rheological properties of the EPDM/PP/AL composites. The results showed that the PP content had significant impacts on the rheological properties. Furthermore, the AL content had significant impacts on the storage and loss moduli of the composites.

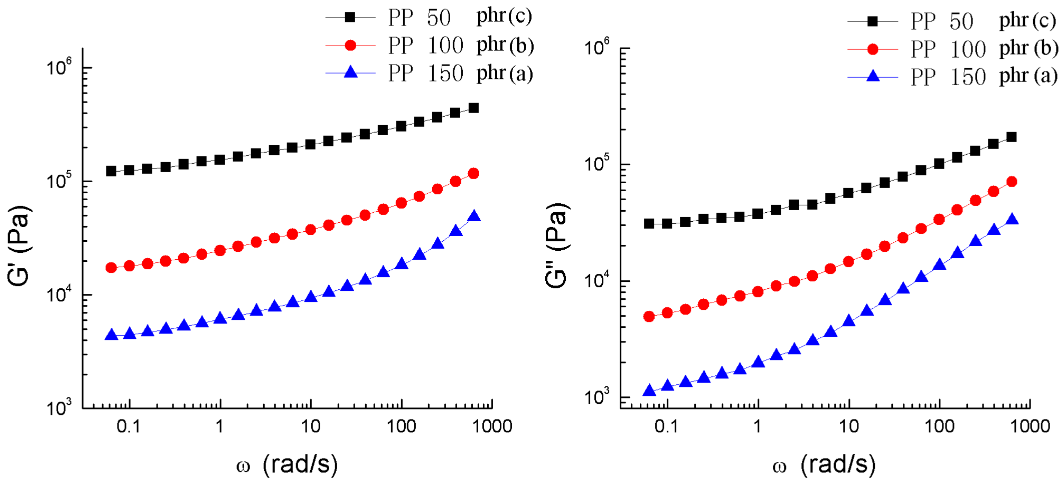
Table 6. Variance Analysis of the Linear Mixed Model for the Rheological Properties with Different PP and AL Contents

Source	*G'*		*G"*		*η**	
	F	Sig.	F	Sig.	F	Sig.
Intercept	763.972	0.000	457.740	0.000	39.250	0.000
PP Content (phr)	374.521	0.000	145.201	0.000	23.186	0.000
AL Content (phr)	56.848	0.000	39.236	0.000	2.978	0.052

G' = storage modulus; *G"* = loss modulus; *η** = complex viscosity

Effects of the PP content on the rheological performance of the composite

Figures 5 and 6 show that the PP content had significant effects on the rheological properties of the EPDM/PP/AL composites.



(a) **(b)**

Fig. 5. Relationship of the storage (a) and loss moduli (b) with the different PP contents

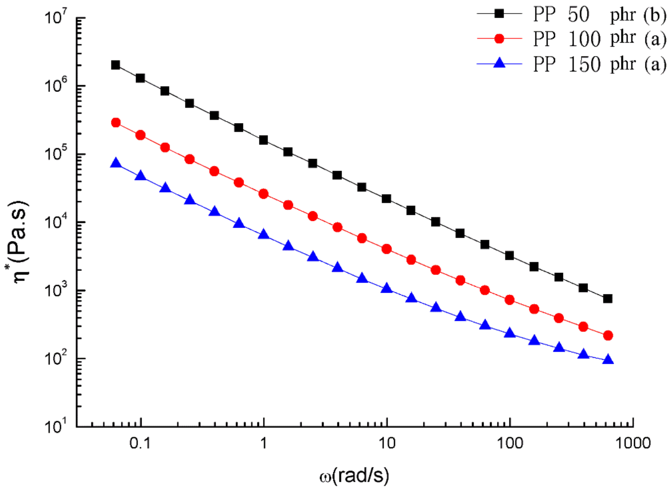
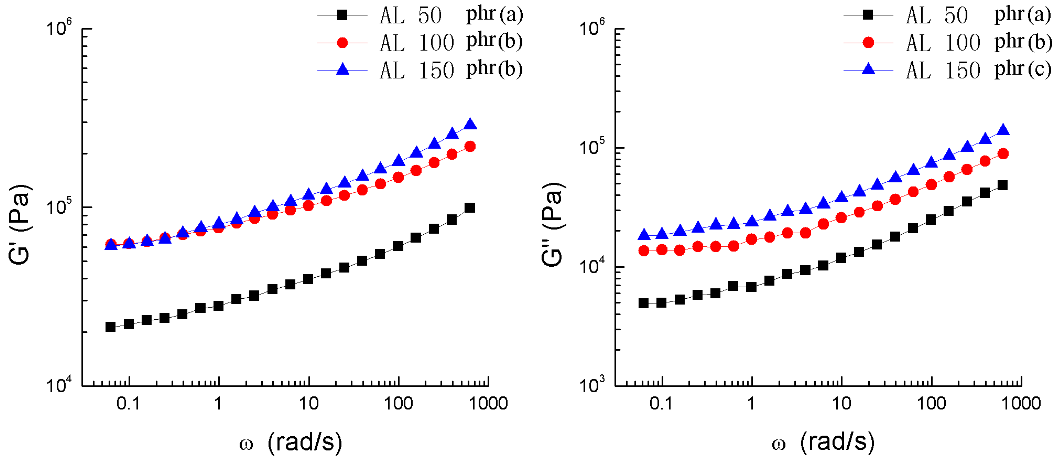


Fig. 6. Relationship of the complex viscosity of the composite with the different PP contents

Specifically, there were significant differences in the storage and loss moduli between the three different dosages of PP. The storage and loss moduli were the highest when the PP content was 50 phr, and they decreased as the PP content reached 100 phr. When the PP content was 150 phr, these values were the lowest. The complex viscosity of the composites had similar trends. These results were in compliance with the results of a study done by Zhou *et al.* (2008) on high-density polyethylene/PP/EPDM blends. These results were because of the “island” of EPDM scattered in the “sea” of PP within the blend system containing EPDM, PP, and AL (Sengers *et al.* 2004). The AL worked as a reinforcing agent in the system. The increase in the PP content led to an increase in the “sea” area and a reduction in the density of the EPDM. Therefore, the viscosity of the system was reduced and the storage and loss moduli of the system decreased.

Effects of the AL content on the rheological performances of the composites

Figure 7 shows that the AL content had a significant effect on the storage and loss moduli of the EPDM/PP/AL composites. With an increase in the AL dosage, the storage and loss moduli of the composites increased.



(a) **(b)**

Fig. 7. Relationship of the storage (a) and loss moduli (b) with the different AL contents

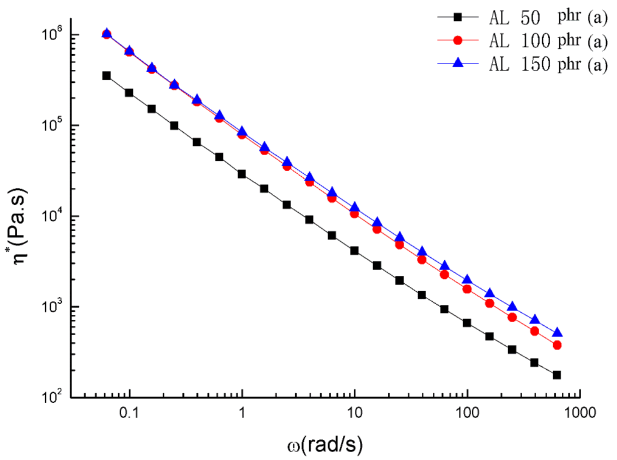


Fig. 8. Relationship of the complex viscosity with different AL contents

Figure 8 shows that the AL content had little impact on the complex viscosity of the composites, but the value increased with an increase in the AL content. This was a result of the AL molecule size being larger and the hindrance on the aromatic ring being large; as such, the molecule was not easy to move (Dong *et al.* 2008). Similarly, under a high temperature shear force, there were interactions between the free radicals of the AL (Shen *et al.* 2013) and side chain of the EPDM molecule (Xu *et al.* 2015). These interactions led to an increased viscosity, as well as an increase in the storage and loss moduli of the composites.

Crystallization Behavior of the Composites

Table 7 shows that the amount of PP and AL has a significant influence on the crystallization behavior of EPDM/PP/AL composites. The content of PP has a significant effect on the peak area and peak height of the crystallization, and the content of AL has a significant effect on the peak area and the full width half maximum (FWHM) of the crystallization peak of the composites.

Table 7. Variance Analysis of the Linear Mixed Model for the XRD diagrams data with Different PP and AL Contents

Source	Peak Area		Peak Height		FWHM	
	F	Sig.	F	Sig.	F	Sig.
Intercept	375.079	0.000	457.344	0.000	1113.141	0.000
PP Content (phr)	11.296	0.000	5.523	0.005	1.904	0.152
AL Content (phr)	3.208	0.043	0.899	0.409	3.014	0.052

Effects of the PP content on the miscibility of the composite

Figure 9 shows that the diffraction peak area, peak height and FWHM of the composites increase with the increase of PP contents.

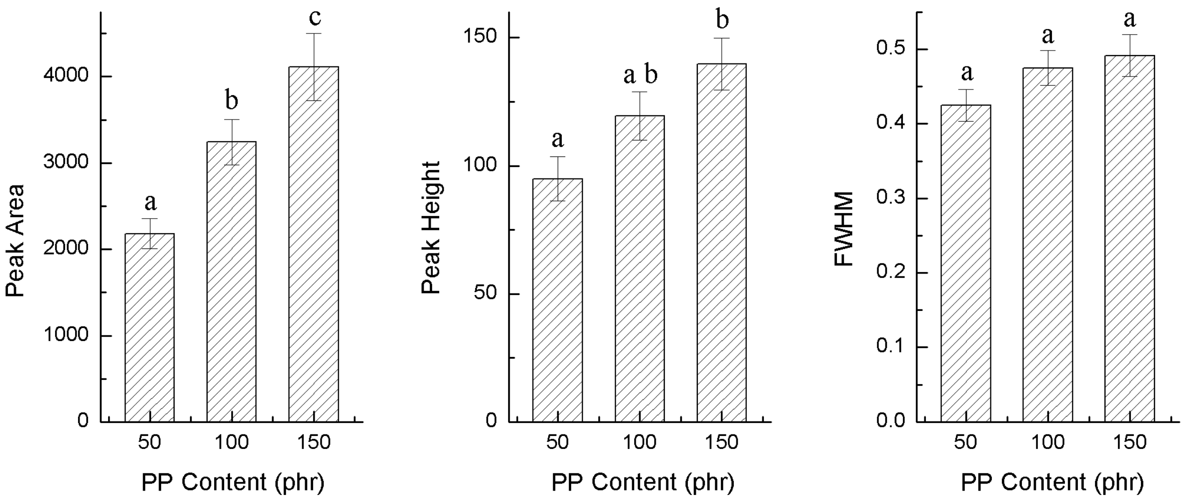


Fig. 9. XRD diagrams data of the composite with the different PP contents

Especially for the diffraction peak area which has significant differences. As shown in Fig. 10, with the increase of PP content the diffraction peaks intensity of the composite increases. But the main diffraction peaks remain the same positions, and they are in the same crystal structure. This indicates that the crystallinity of the mixed system increases with the increase of PP content. This is because PP is the main crystalline substance in the mixed system, so that the amount of PP has a significant effect on the crystallization behavior of the composites. This conclusion is consistent with previous studies.

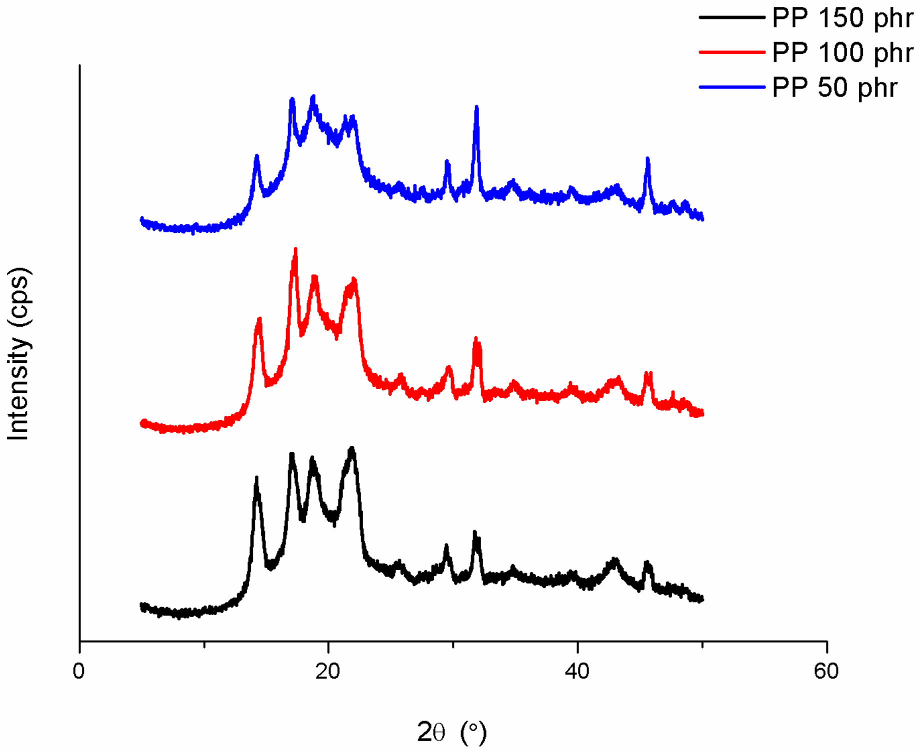


Fig. 10. XRD patterns of the composite with the different PP contents

Effects of the AL content on the miscibility of the composite

Figure 11 shows that the peak area and peak height of the composites decreased with the increase of Al content. And the difference was significant between the AL content in 50phr and 150phr. The FWHM of the composites increased with the increase of AL content, and there were significant differences between AL content in 50 phr and 150 phr. This is because AL content had significant impact on the viscosity of the composite system and the viscosity increased with the increases of AL content, which led to the uneven dispersion of the components in the system. This hampers the intermolecular force of polypropylene and reduces the crystallization area. With the increase of AL content, the strength of the composite increased, but the overall crystallization level of the composites decreased. The results are consistent with the study carried by Kong *et al.* (2015), who research on the AL content effects on the crystallization while they preparing lignin-based polyester polyols.

Figure 12 shows the XRD patterns of EPDM/PP/AL composites with different Al contents. It is apparent from the figure that the diffraction peak strength of the EPDM/PP/AL composites decreased with the increase of Al content, but the main diffraction peaks remained in the same position, which means that they are the same crystal structure. This indicates that the PP is the main crystalline substance in the system, and the AL only affected the crystallization process of PP. The molecular chain of AL does not pass through the crystallization of PP. It only plays a local effect in the amorphous region of PP. This conclusion is consistent with the study carried by Jiang and Jiang (1999), who studied the crystallinity of the dynamically vulcanized EPDM/PP.

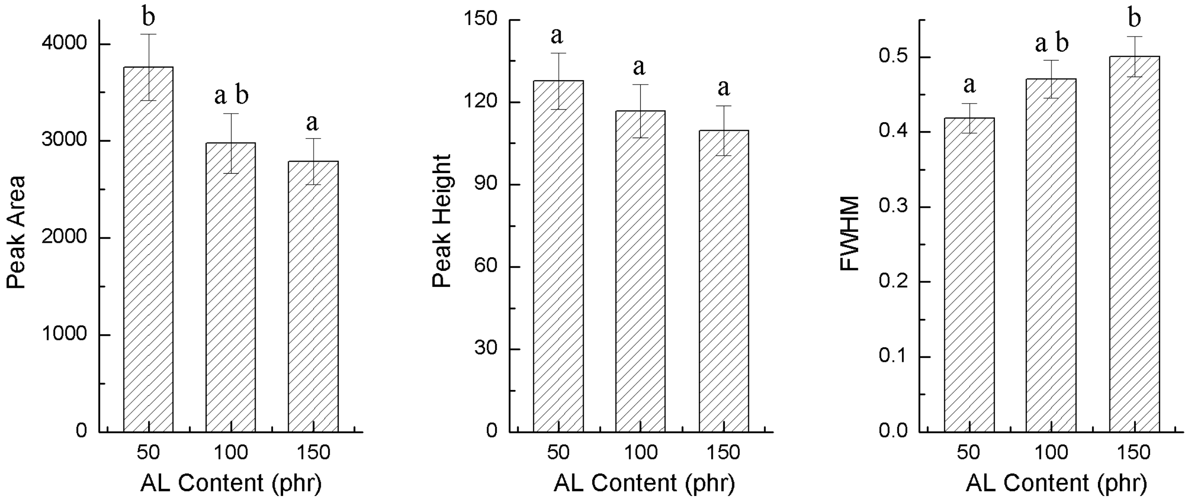


Fig. 11. XRD diagrams data of the composite with the different AL contents

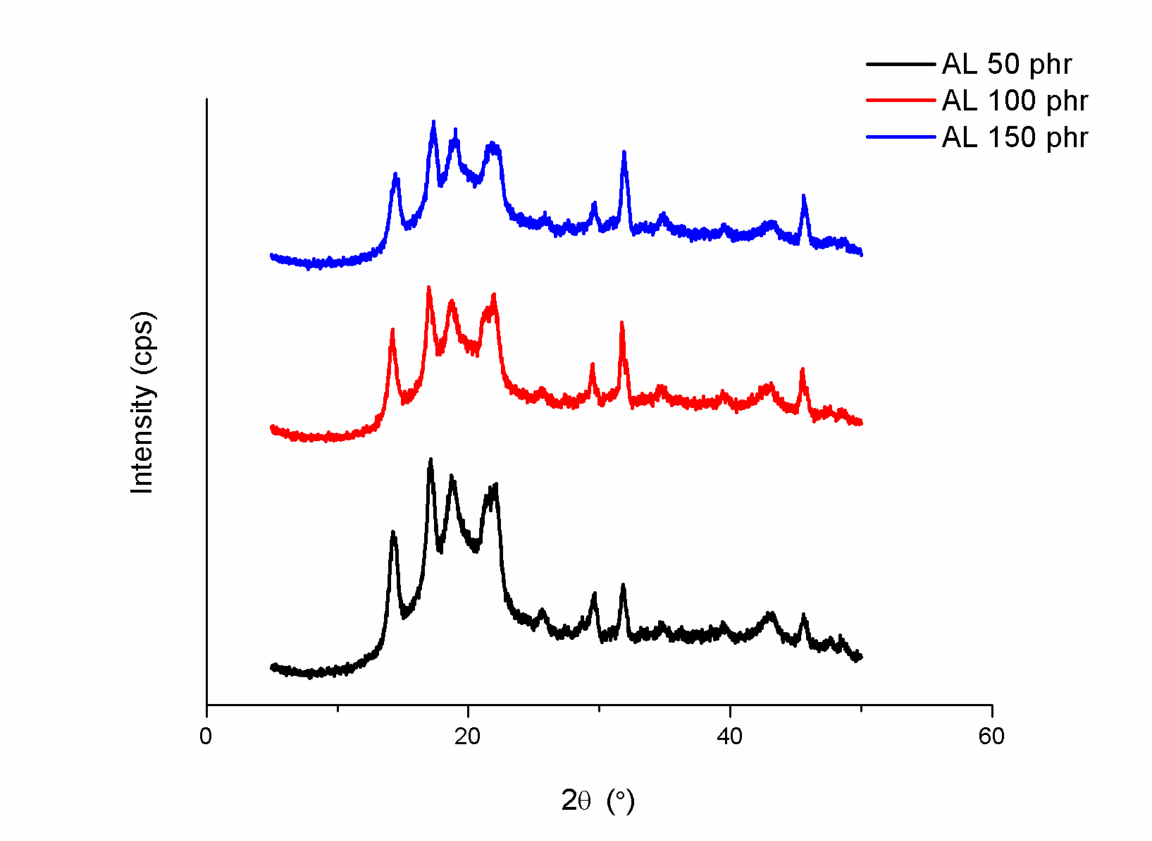


Fig. 12. XRD patterns of the composite with the different AL contents

CONCLUSIONS

EPDM/PP/AL composites were made using a dynamic vulcanization method with a peroxide vulcanization system. The effects of the PP and AL contents on the properties of the EPDM/PP/AL composites were studied. The main conclusions were as follows:

1. The effect of the PP amount on the properties of the composites was significant. With an increase in the PP content, crystallinity and the strength of the composites increased, the viscosity decreased, the mechanical properties were improved, and the plastic characteristics were more significant.
2. The amount of AL had a significant influence on the modulus of elasticity of the composite. With an increase in the AL content, the modulus of elasticity of the composites increased as well. Similarly, the viscosity of the composites increased with an increase in the AL content. However, the viscosity increase was insignificant when the content of AL exceeded 100 phr. The crystallinity of the composite decreases with the increase of AL content.
3. When the PP and AL contents were both 100 phr, the composite had the best comprehensive performance and is suitable for use as the core layer of elastic materials in composite flooring.

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