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Preparation and Study of EPDM Composites with High Volume Resistance Retention Rate

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Abstract

LDPE/ EPDM composites were prepared by mechanical blending method. The effects of two compatibilizers MA/Zn and CPE on the vulcanization properties, mechanical properties, aging resistance and electrical properties of the composites were studied. The results showed that the addition of two kinds of compatibility significantly improved the compatibility of LDPE and EPDM. Compared with CPE, the addition of MA/Zn can improve the properties of the composites better. The mechanical and electrical properties of the composite were improved by the addition of MA/Zn compatibilizer. The volume resistivity of sample L3M2 is the highest at room temperature and 125 ℃, which are 19.8×10^{13}Ω·m and 16.8×10^{12}Ω·m, respectively. Compared with L3, the increase was 26.1% and 25.8%, respectively. The tensile strength is 14.1MPa, which is 90.5% higher than L3.

Keywords

EPDM; Vulcanization Characteristics; Unsaturated Zinc Carboxylate; Volume Resistivity; Dielectric Properties.

1. Introduction

EPDM is widely used in automotive parts, waterproof materials for construction, wire and cable insulation, heat-resistant hose, tape, automotive seals and shock absorbing products due to its molecular main chain saturation and excellent aging resistance[1]. Submersible oil pump cable is a kind of special cable used with submersible oil pump. With the development of oil field, the application range of submersible oil pump cable is gradually increasing[2]. The working environment in oil Wells is harsh, often in high temperature, high pressure and oil-bearing corrosive environment.

In wire and cable products, insulation is undoubtedly one of the most important properties. However, according to the existing research, the insulation performance of EPDM insulation layer at high temperature is seriously decreased, and the volume resistance retention rate from 20℃ to 125℃ is only about 1%, which greatly reduces the life and safety of the cable[3]. Therefore, how to improve the volume resistance retention rate of EPDM rubber at high temperature is an urgent problem to be solved.

The conductive mechanism of polymer is ionic conductance, and the volume resistivity of EPDM decreases with the increase of temperature, that is, it has a negative resistance temperature coefficient[4]. The relationship between ρv and thermodynamic temperature T is:

$$\rho_V = A_e^{E/RT}$$

In the formula, Ae is inversely proportional to the concentration of impurity ions. E is the activation energy of ion migration. Plot 1/T with lnρv to obtain A line, from which the slope of the line can be found E and the intercept can be found A[5]. It can be seen that the concentration

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of impurity ions determines the value of resistivity, and the activation energy of ion migration determines the speed of the change of volume resistivity with temperature.

Low density polyethylene (LDPE) is a linear polymer with branch chains, which has good electrical insulation, easy processing, chemical stability and ductility. It is also widely used in the field of wire and cable[6].

In this paper, a rubber and plastic blending scheme was studied to improve the ion migration activation energy of EPDM, that is, EPDM mixed with low density polyethylene (LDPE). The results show that the addition of LDPE significantly increases the high temperature volume resistivity of EPDM composites, but significantly decreases the mechanical properties of the blends, which is due to the thermodynamic incompatibility of EPDM and LDPE. In order to solve this problem, two compatibilizers were added to the formula to improve the adhesion of the two phases and to form a uniform island structure of the blend. The effects of rubber and plastic ratio, compatibilizer type and addition amount on the physical and electrical properties of the blends were studied, and EPDM composites with stable volume resistivity at high temperature were successfully prepared.

2. Experimental Part

2.1. Raw Materials

The raw materials used in the experiment are shown in Table 1:

Table 1. Specification and manufacturer of raw materials required for experiment.

Raw materials	Specification	Manufacturer
EPDM(J-4045)	Muney viscosity 45 (ML_{1+4}100°C), ethylene content 49.0%~55.0%	Jilin Petrochemical Company, petrochina Co.,LTD
Antioxidant RD	Purity ≥99.0%	Hubei Nona Technology Co.,LTD
ZnO	Analytically pure	Shanghai Yuanye Bio-technology Co., LTD
Silane coupling agent A172	Analytically pure	Nanjing Nengde New Material Technology Co., LTD
Silane treatment clay	1500 mesh	Shanxi Jinyukolin Technology Co., LTD
Talc powder	5000 mesh	Haicheng Zhicheng Powder Manufacturing Co., LTD
Dicumyl peroxide (DCP)	Purity ≥99.0%	Norion Chemicals (Ningbo) Co., LTD
Cyclohexane	Purity ≥99.0%	Jinan Trangenesis Chemical Co., LTD.=
ZDMA, ZMMA	≥100 mesh	Nanjing Youyou Auxiliary Chemical Co., LTD

2.2. Instruments and Equipment

The instruments and equipment required for the experiment are shown in Table 2:

Table 2. The instruments and equipment required for the experiment and their specifications and manufacturers

Instrument name	Model number	Manufacturer
Mixing mill	XK160	Qingdao Jinjiuzhou Rubber Machinery Co., LTD
Flat vulcanizing machine	XLB-400×400	Qingdao Jinjiuzhou Rubber Machinery Co., LTD
Electronic tensile testing machine	JSL-500N	Jiangdu Jingyi Testing Machinery Co., LTD
Infrared absorption spectrometer	VERTEX70	Bruker GMBH, Germany
Field Emission Electron Sweep Microscope	S-4800	Hitachi, Japan
High insulation resistance Tester	ZC-90F	Shanghai Taiou Electronics Co., LTD.
Air aging test box	SC-7015A	Dongguan Shuncheng Electronics Co., LTD
Shore hardness tester	XHS Shoer A	Yingkou Material Testing Machine Factory
Rotor-free vulcanizers	MDR-A1	Taiwan Youken Technology Co., LTD.
Contact Angle tester	JY-PHB	Chengde Youte Testing Instrument Manufacturing Co., LTD.
Dielectric constant tester	TH2829C	Tonghui Electronics Co., LTD
Voltage breakdown tester	KDZD5550	Wuhan Kaidi Zhengda Electric Co., LTD

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2.3. Sample Preparation

The mixer was heated up to 140℃ and the rotational speed was 30r/min. EPDM and LDPE were mixed evenly into the mixer according to the formula, and the compatible agent and other small materials were added after LDPE was melted and mixed evenly. After mixing for 10min, take out the compound and add the vulcanizing agent and the lower piece on the smelting machine, and park the label. The specific formula of the experiment is shown in Table 1.

After parking for 8h, weigh the 80-85g film into the mold, vulcanize it in the plate vulcanizer at 175℃ and 10mPa for 8min, and then park it.

Table 3. Experimental formula

	EPDM	LDPE	CPE	MA+ZnO
L0	100	0	0	0
L1	100	10	0	0
L2	100	20	0	0
L3	100	30	0	0
L3C2	100	30	2	0
L3C4	100	30	4	0
L3C6	100	30	6	0
L3M2	100	30	0	2
L3M4	100	30	0	4
L3M6	100	30	0	6

Basic formula: antioxidant RD 1.5, ZnO5, Paraffin 5, calcined clay 50, talc 15,DCP 3, TAIC 2.

2.4. Performance Testing and Characterization

2.4.1. Differential Scanning Calorimetry (DSC) Analysis

The 5mg sample was weighed and embedded in the crucible through the sampler and in the DSC chamber. The temperature is raised from 20℃/min to 150℃ under nitrogen atmosphere, and the influence of thermal history is eliminated at 150℃ for 5min. Cool at the same rate to -70℃ for 5min. In the temperature range of -70℃ to 150℃, the DSC test was carried out at 20℃,min[7].

2.4.2. Vulcanization Characteristics and Crosslinking Density

According to ISO-6502: 1999, the vulcanization characteristics of EPDM composites were tested by a rotor-free vulcanization instrument. Test condition: 175℃×8min.

The crosslinking density of EPDM composite was determined by equilibrium swelling method[8]. The specific test method was as follows: The EPDM was cut into sheets with the same shape and mass as m_0, and soaked in cyclohexane solvent at room temperature for 48h until the swelling equilibrium state was reached after constant weight[9]. The surface of the sample is cleaned and its mass m_1 is weighed, and the result is calculated by the following formulation:

$$V_e = \frac{\chi V_r^{\,2} + \ln(1 - V_r) + V_r}{V_0\left(0.5V_r - \sqrt[3]{V_r}\right)} \quad (1)$$

$$V_r = \frac{m_0}{m_0 + (m_1 - m_0)\frac{\rho_1}{\rho_0}} \quad (2)$$

Where, V_e is EPDM crosslinking density, unit is mol/cm^3. V_r is the volume fraction of rubber phase in the swelling sample. The molar volume of cyclohexane is V_0 = 106.4ml/mol. χ is the

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Flory-Huggins interaction parameter between EPDM and cyclohexane, which is 0.354. ρ_0 and ρ_1 are the densities of cyclohexane solvent and EPDM rubber at room temperature before swelling, which are 0.6749 g/cm^3 and 1.243 g/cm^3, respectively [10].

2.4.3. Mechanical Property

The Shore A hardness test is performed according to ISO 7619-1:2010 and is read after 3s of stress action. Tensile strength and elongation at break were tested using an electronic universal testing machine in accordance with ISO 37:2005. The sample is dumbbell type and the tensile rate is 500mm/s.

2.4.4. Aging Resistance

The samples were made into dumbbell samples and placed in a drying box at 125℃ for 168h. After aging, the mechanical properties were measured by standing at room temperature for 6h. The measurement standards and methods are the same as 1.4.3[11].

2.4.5. Electrical Performance Test

The volume resistivity was tested using the ZC-90F high insulation resistance measuring instrument according to ISO 14309:2019. The sample was circular and the test voltage was 1000V. The volume resistivity is calculated as follows:

$$\rho v = \mathrm{R}_x \frac{A}{h}$$

Where ρv is the volume resistivity (Ω·m). Rx is the measured volume resistance (Ω). A is the effective area of the protected electrode (m2). h is the average thickness of the sample (m) [12].

Volume resistivity tests at high temperatures are performed in accordance with IEC 62631-3-2019.

Dielectric properties are tested using Concept 50, a wideband dielectric analyzer with a frequency range of 100 to 10^{6}Hz.

3. Results and Discussion

3.1. EPDM Composite DSC Curve

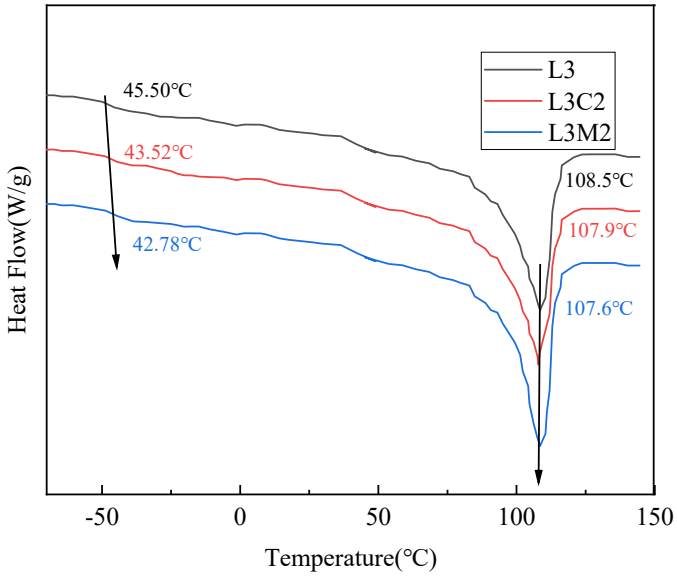

Figure 1. DSC curve of EPDM composites

The DSC curves of samples L3, L3C2 and L3M2 are shown in Figure 1. The glass transition temperature (Tg) of EPDM component and the melting temperature (Tm) of LDPE component

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can be seen in this experiment sample because EPDM and LDPE are not completely compatible. Among them, the Tg of EPDM and the Tm of LDPE in sample L3 without adding compatibilizer were 45.5℃ and 108.5℃ respectively. According to the DSC curves of samples L3C2 and L3M2, the glass transition temperature of EPDM component (43.52℃, 42.78℃) moves to the high temperature region after the addition of the two compatibants, and the melting temperature of LDPE (107.9℃, 107.6℃) moves to the low temperature region. The results show that the interface of thermoplastic LDPE and crosslinked EPDM is well combined, that is, the addition of compatibilizers can improve the compatibility of EPDM/LDPE polymer blends[13].

3.2. Vulcanization Characteristic Analysis and Crosslinking Density

Table 4. Vulcanization characteristics of EPDM composites

	T_{S1}/s	T_{C10}/s	T_{C90}/s	MH/N·m	ML/N·m	MH-ML/N·m	CRI/min^{-1}
L0	50	27	251	3.04	0.21	2.83	29.85
L1	47	26	262	3.12	0.2	2.92	27.91
L2	48	26	258	3.22	0.21	3.01	28.57
L3	47	26	255	3.33	0.20	3.13	28.84
L3C2	48	28	246	3.38	0.22	3.16	30.30
L3C4	46	27	243	3.48	0.21	3.27	30.45
L3C6	47	26	239	3.54	0.2	3.34	31.91
L3M2	48	26	255	3.89	0.21	3.68	28.99
L3M4	47	26	258	3.76	0.20	3.56	28.43
L3M6	48	28	256	3.73	0.22	3.51	28.85

The vulcanization characteristic data of EPDM composites can be obtained from Table 4, where TC10 is the scorch time of EPDM composites; The size of the vulcanization index CRI reflects the speed of vulcanization, and the larger the CRI, the faster the vulcanization speed. The vulcanization index CRI is calculated as follows:

$$CRI = \frac{100}{T_{C90} - T_{S1}}$$

It can be concluded that the coking time and vulcanization index of EPDM composites have little effect on the processing safety and efficiency of EPDM composites with the difference of LDPE and compatibant addition amount[14].

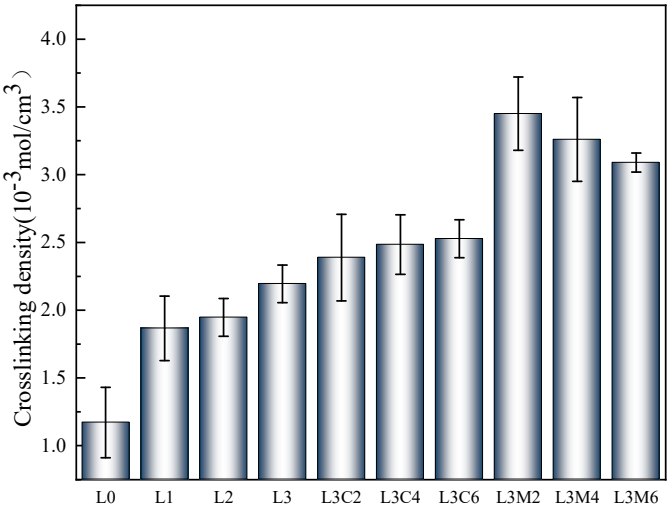

Figure 2. Crosslinking density of EPDM composites

The crosslinking density of EPDM composites measured by equilibrium expansion method is shown in Figure 2. With the increase of LDPE and compatibilizer CPE, the crosslinking density

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of the composite increased gradually. However, with the increase of compatibilizer MA/Zn addition, it gradually decreased but significantly increased compared with sample L0. The cross-linking density of sample L3M2 reached the highest, which increased by 194.6% compared with sample L0.

The crosslinking density of rubber is divided into chemical crosslinking density and physical crosslinking density. Physical cross-linking refers to the formation of bonds or entanglement between polymer chains through weak interactions, and chemical cross-linking refers to the formation of bonds between polymer chains through covalency. In this experiment, with the addition of compatibilizer, the compatibility between the two phases of the blend is improved, and the adhesion between the two phases is increased, so that the physical crosslinking density is increased.

3.3. Mechanical Property

Table 5. Experimental formula

Sample	Hardness(HA)	Tensile strength(MPa)	Elongation of break(%)
L0	72	12.6±0.5	149.8±5.1
L1	81	6.9±0.6	161±3.8
L2	82	7.2±0.4	220±6.3
L3	84	7.4±0.9	243±6.1
L3C2	81	11.6±0.8	274±12.3
L3C4	79	12.0±0.3	263±13.9
L3C6	76	13.1±0.4	243±10.8
L3M2	77	14.4±0.6	284±0.4
L3M4	78	13.9±0.7	266±0.4
L3M6	81	14.1±0.4	257±0.4

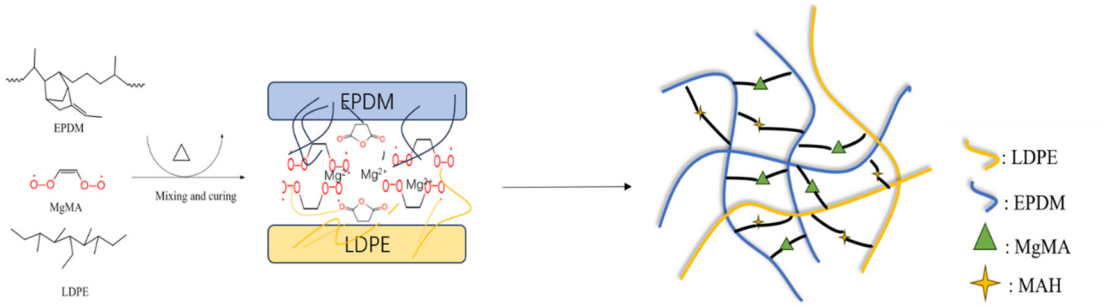

Figure 3. Mechanism of compatibilizer MA/Zn improving the compatibility of EPDM/LDPE composites

The mechanical properties of EPDM composites are shown in Table 5. With the increase of LDPE addition, the tensile strength of the composite decreases obviously. This was due to the thermodynamic incompatibility between EPDM and LDPE, so sample L3 was selected as the control group, in which compatibilizer was added. The addition of two compatibilizers significantly improved the mechanical properties of EPDM composites. The tensile strength of L3C6 is the highest, 13.1±0.4MPa, which is 77% higher than that of L3. The tensile strength of L3M2 is the highest in the MA/Zn samples, which is 14.4MPa, and the relative increase is 94.6%.

It can be seen from the data in Table 2 that the tensile strength changes differently with the increase of the two compatible doses. CPE is a random copolymer that does not contain reaction groups and does not participate in chemical reactions in the blending system as a compatibilizer. As a compatibilizer, CPE can cover EPDM colloidal particles in the blending system, play a connecting role in the two phases, and improve the compatibility between EPDM and LDPE to

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improve its mechanical properties. The disadvantage of non-reactive compatibants is that they are low in efficiency and require a large amount of addition to have a significant effect, which also explains the increase in tensile strength of the composite with the increase in the amount of CPE added.

3.4. Heat Resistance to Oxygen Aging

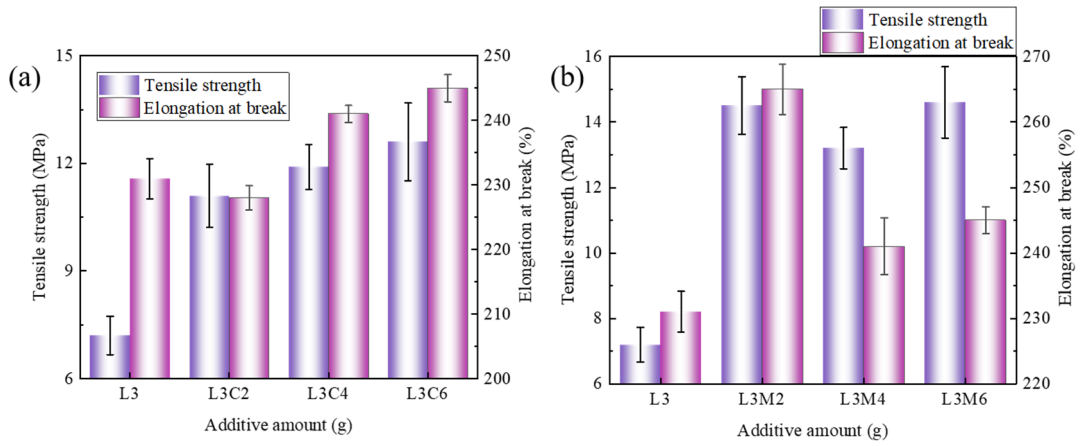

Figure 4. Effect of compatibilizers on thermal oxygen aging properties of EPDM composites

FIG. 4 shows the mechanical properties of EPDM composite samples after aging at 125℃ for 168h. It can be seen from the figure that the tensile strength of the two compatibilizers after aging is significantly improved compared with L3. Among them, the tensile strength of sample L3M6 reaches the highest 14.6MPa, which is 102.8% higher than that of L3.

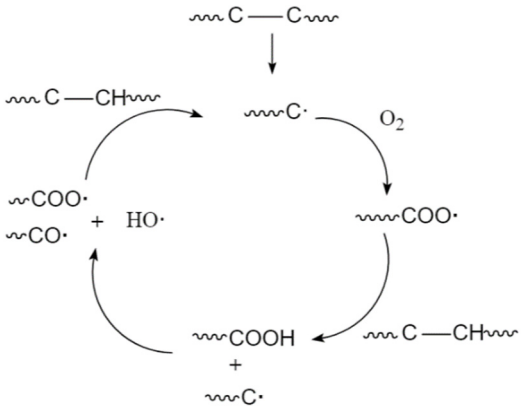

Figure 5. Schematic diagram of EPDM aging process

3.5. Electrical Property

FIG. 6 shows the electrical properties of EPDM composites. It can be seen from FIG. 6 (a) that the relative dielectric constant of sample L0 has little change under the influence of frequency. The relative dielectric constant of sample L3 increases after LDPE is added. The changes were also different after the addition of compatibilizers. The addition of non-reactive compatibant CPE decreases the relative dielectric constant and does not change significantly with frequency. This is because CPE is non-polar and has little effect on the matrix. The reactive compatibilizer MA/Zn contains polar groups, in which the inherent dipole moment participates in the polarization process under the action of electric field, resulting in the increase of the relative dielectric constant. With the increase of frequency, the dipole moment polarization changes with the change of electric field, resulting in a decrease in the relative dielectric constant.

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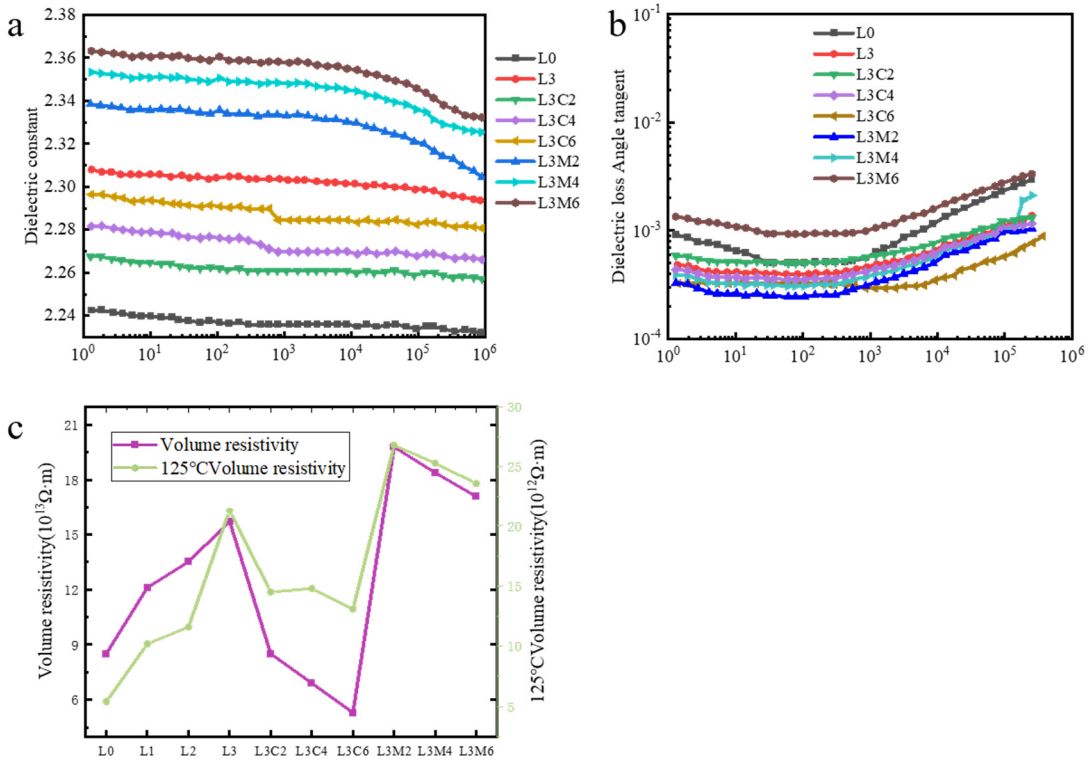

Figure 6. Electrical properties of EPDM composites (a) relative dielectric constant; (b) dielectric loss; (c) Volume resistivity at room temperature and 125℃

FIG. 6 (b) shows the variation of dielectric loss of EPDM composite with frequency. It can be seen from FIG. 6 (b) that the dielectric loss of EPDM composites decreases first and then increases with the change of frequency. After the addition of compatibilizer MA/Zn, the dielectric loss of the sample decreases first and then increases with the addition of the compatibilizer MA/Zn. There are two main reasons for this change: first, the inherent dipole moment contained in Ma polarizes in the electric field, resulting in increased relaxation polarization loss; second, the dissociation energy of MgMA generated during processing is small, and dissociation occurs under the action of electric field. The dielectric loss of composite material is increased. When the addition amount is low, the two have less influence on the dielectric loss of the composite material, resulting in the above phenomenon.

Figure 6 (c) shows the volume resistivity diagram of EPDM composites at room temperature and 125℃. Compared with L3, the volume resistivity changes at room temperature and 125℃ are the same after adding two compatibilities. After the addition of CPE, the volume resistivity of the composite at room temperature and 125℃ is significantly reduced, which is because the volume resistivity of CPE vulcanizate is 1-2 orders lower than that of EPDM vulcanizate, and the filling of CPE leads to the decline of the volume resistivity of EPDM composite. The addition of MA/Zn significantly increases the volume resistivity of EPDM composites, which is due to the increase of internal crosslinking degree of the composites and the decrease of free volume in the system, resulting in the decrease of carrier mobility, resulting in a significant increase in the volume resistivity of EPDM composites at room temperature and 125℃. The volume resistivity of sample L3M2 reached the highest at room temperature and 125 ℃, which were 19.8×1013Ω·m and 16.8×1012Ω·m, respectively. Compared with L3, it increased by 26.1% and 25.8% respectively.

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4. Conclusion

The effects of rubber and plastic ratio, compatibilizer type and addition amount on physical properties, vulcanization properties and electrical properties of blends were studied. The main conclusions are as follows:

(1): With the increase of LDPE addition, the volume resistivity of EPDM composite material at room temperature and high temperature increases significantly, but the tensile strength decreases significantly and the hardness increases significantly. When the LDPE addition amount is 30phr, the tensile strength is 7.4MPa and the hardness is 84.

(2): The addition of compatibilizer CPE can improve the compatibility between EPDM and LDPE. With the increase of MA/Zn addition, the mechanical properties of the composite increased, but the electrical properties decreased significantly. The volume resistivity of sample L3C6 at room temperature and 125℃ is 5.3×1013Ω·m and 12.1×1012Ω·m, respectively.

(3): The addition of compatibilizer MA/Zn can improve the compatibility between EPDM and LDPE. Compared with CPE, the addition of MA/Zn has a better effect on the improvement of the properties of the composites. With the addition of compatibilizer MA/Zn, the mechanical and electrical properties of the composites are improved significantly. The volume resistivity of sample L3M2 reached the highest at room temperature and 125℃, which were 19.8×1013Ω·m and 16.8×1012Ω·m, respectively. Compared with L3, they increased by 26.1% and 25.8% respectively. The tensile strength is 14.1MPa, which is 90.5% higher than that of L3.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgments

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