Preparation and properties of ethylene-vinyl acetate grafted acrylonitrile

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Abstract

Ethylene-vinyl acetate copolymer (EVA) was functionalized to varying degrees with acrylonitrile (AN) by melt grafting processes. Fourier transform infrared spectra (FT-IR) confirmed that AN was successfully grafted onto the EVA. High resistance meter, electronic universal testing machine, etc have studied the influencing factors of grafting process and the effect of grafting rate on oil resistance, mechanical properties and electrical properties. The results show that the optimal grafting process is that the dosage of AN is 8.0 wt%, the dosage of styrene (St) is 5.0 wt%, the dosage of Dilauroyl peroxide (LPO) is 0.4 wt% of the total amount of AN and St, and the grafting rate is 1.24%. With the increase of the amount of LPO and AN, the grafting rate first increased and then decreased. The grafting rate increases, so that the oil resistance, volume resistivity, and breakdown field strength of the grafted product are gradually increased. When the grafting rate is 1.24%, the volume resistivity is $1.63 \times 10^{13}$ Ω·m, which is significantly improved compared with pure EVA, and the breakdown field strength is 23.26 kV mm⁻¹, which is 12.3% higher than pure EVA.

1. Introduction

Cable is an indispensable and important infrastructure in social production and life [1]. It is widely used in various sectors of the national economy and occupies a very important position. With the rapid development of national economy and the continuous progress of science and technology, the use of cables is rising sharply.

Ethylene-vinyl acetate (EVA) has been widely used in insulation layer and sheath layer of cable due to its outstanding mechanical properties, processability and ozone resistance [1]. However, its oil resistance and dielectric properties cannot meet industrial requirements in some special uses, such as oilfield cable, locomotive cable [2]. Hence, modification of EVA to improve its comprehensive performance has been a hot topic in recent years.

Common methods of modifying EVA include: physical blending modification [3], dynamic vulcanization modification [4–6], and grafting modification [7].

The method of physical blending to modify the oil resistance of polyolefin has the advantages of simple process, convenient operation, moderate cost, and strong designability [8, 9]. Zou et al [10] blended NBR and EVA, added flame retardants: magnesium hydroxide (MH), organic montmorillonite (OMMT) and red phosphorus to the system, and added inorganic filler nano-silica (SiO₂). And molybdenum trioxide (MoO₃) to prepare composite materials. Their research results show that the addition of nano-SiO₂ and MoO₃ can significantly improve the oil resistance, tensile strength and flame retardancy of the blend system, and the smoke density is also significantly reduced.

Dynamic vulcanization refers to a thermoplastic vulcanize preparation method in which the rubber is continuously cut by shearing force during the rubber vulcanization process to make it uniformly dispersed in the continuous phase of the resin. Lu [11] dynamically vulcanized two EVAs with similar chemical structures to
prepare oil-resistant thermoplastic dynamic vulcanizates, and studied the structure and oil resistance of the products. The prepared thermoplastic dynamic vulcanizate has good oil resistance.

The biggest problem of physical blending modified EVA is poor dispersion and uneven dispersion of the blend, which will have a great impact on the performance of the composite material. Dynamic vulcanization modified EVA also has the problem of poor compatibility. The plastic phase and the rubber phase have poor compatibility and are prone to phase separation, which has a great impact on the performance of the vulcanized product. It is necessary to add a compatibilizer to increase the compatibility of the two. This will make the preparation process cumbersome and complicated. Compared with the two, the product prepared by grafted-modified EVA has better performance and better stability.

Jin [12] grafted maleic anhydride (MAH) onto EVA by a melting method, and prepared a graft product with excellent oil resistance and electrical properties. The EVA part of the graft product has a good relationship with the polyolefin material. Compatibility, MAH has good compatibility with polar materials. Therefore, the prepared graft polymer can be used as a compatibilizer for composite materials. Compared with blended modified and dynamically vulcanized modified EVA, the product prepared by grafted modified EVA has better performance and better stability.

Acrylonitrile (AN) has a strong polar cyano group (—CN). It is a monomer with excellent comprehensive performance. It is often used to synthesize oil-resistant polymers [13] and graft modified polyolefins to improve polyolefins performance.

At present, there is no report about the grafting of AN on EVA. In this paper, LPO is selected as the initiator, and AN is grafted onto EVA by the melting method. The optimal process of the grafting reaction is determined, and the amount of initiator and monomer for butt grafting are studied. The influence of the grafting rate, and the oil resistance, mechanical properties, electrical properties, crystallization temperature and melting temperature of the grafted product were studied.

In this paper, EVA was modified by grafting AN onto EVA to synthesize EVA-g-AN (EVA-g-AN) through melt grafting, and the molecular structure of EVA-g-AN was characterized by FTIR. The effects of reaction conditions, such as LPO dosage, AN dosage on the grafting ratio were discussed. Moreover, the oil
resistance, breakdown strength and volume resistivity of EVA-g-AN were evaluated with respect to different level of AN content.

The effects of grafting ratio on oil resistance, breakdown strength and volume resistivity were studied. Laid the foundation for the preparation of oil-resistant cable materials.

2. Experimental

2.1. Materials
Ethylene-Vinyl Acetate Copolymer (EVA), Exxon Chemical; Acrylonitrile (AN), Eco Reagent; Styrene (St), Sigma Aldrich; Dilauroyl Peroxide (LPO), Zibo Huigangchuan Chemical Industry; Antioxidant Agent 1010, Jingtianwei Chemical; Xylene, Guangfu Fine Chemical; N,N-Dimethylformamide (DMF), Fuyu Fine Chemical.

2.2. Samples preparation of EVA-g-AN
Weigh AN, St, LPO according to a certain ratio and mix them to make a solution. Weigh 50g of EVA into the prepared solution to fully swell, mix the swelled EVA and antioxidant 1010 evenly, at 140 °C, 50 rpm the grafted product was prepared by mixing in a torque rheometer under the above conditions. The N-grafting reaction mechanism is shown in figure 1.

The grafted product was heated to reflux with xylene for 1 h, precipitated with ethanol, filtered with suction, and immersed in DMF for 72 h to remove monomers and self-polymers that did not participate in the grafting reaction. A flat vulcanizer was used to make sheet samples of different thicknesses for performance testing.

2.3. Characterization
Fourier transform infrared (FTIR) spectra of EVA and EVA-g-AN were recorded using a Nicolet iS10 spectrometer in the wave number range of 4000–400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. The cyano group stretching vibration absorption of AN at 2240 cm$^{-1}$ was used to determine the extent of grafting by using the 1740 cm$^{-1}$ band (due to carbonyl absorption of the EVA polymer) as a reference. The ratio of absorption areas of peaks at 2240 and 1740 cm$^{-1}$ ($A_{2240}/A_{1740}$) was calculated. The grafting degree was obtained from a calibration curve established by using EVA blends containing known amount of AN.

Differential scanning calorimetry (DSC) was performed by a PerkinElmer DSC equipped with Pyris software to investigate the melting temperature and the heat of fusion. Samples of approximately 8 mg were encapsulated in standard aluminum pans. The scanning temperature was ranging from 40 °C to 200 °C with a heating/cooling rate of 10 °C min$^{-1}$ under a nitrogen atmosphere. The first heating was to eliminate the thermal history of the samples. The melting temperature and the heat of fusion values were obtained from the second heating curve.

Oil resistance of unmodified EVA and grafted EVA was conducted according to GB/T 1690–2010. The dumbbell-shaped samples were immersed in IRM 903 oil at room temperature for 168 h. After the stipulated period, the samples were removed from the oil, cleaned and wiped with tissue paper to eliminate the excess oil from the surface for oil resistance test. Oil resistance was reported in terms of the changes in volume, mass and tensile properties after oil immersion.

DC breakdown strength of the sample was measured using a HT-100 dielectric strength tester at room temperature. A film with a thickness of around 100 μm was sandwiched between two opposing plate electrodes. The lower electrode was grounded, whereas the upper was connected to the DC source. To prevent surface flashover, the electrodes and the sample were immersed in silicone oil during the test. An increasing electric field was applied to the film at a rate of 1 kV/s until breakdown occurred. The breakdown field strength can be calculated according to

$$E_b = \frac{U_b}{d}$$  \hspace{1cm} (1)

where $E_b$ represents breakdown strength, $U_b$ is the breakdown voltage, and $d$ is the sample thickness at the breakdown spot. Fifteen films were tested for each sample, and a two-parameter Weibull statistical distribution method was employed for data analysis.

The volume resistivity was measured in accordance with ASTM D257–14 and done at room temperature by a ZC–36 high resistance meter equipped with three-electrode system.
3. Results and discussion

3.1. FT-IR analysis
FTIR was used extensively to investigate the grafting reaction. The FTIR spectra of the unmodified EVA and the EVA-g-AN are illustrated in figure 2. It can be seen that the absorption bands at 2849 cm$^{-1}$ and 1250 cm$^{-1}$ were attributed to C–H bending vibration of the EVA. The absorption bands at 1740 cm$^{-1}$ were assigned to the stretching vibration of carbonyl group (C=O). The pure EVA has unsaturated double bond characteristic peaks at 1560 cm$^{-1}$ and 1640 cm$^{-1}$, the graft EVA-g-AN did not appear this peak. This proves that the unsaturated double bonds in EVA participate in the grafting reaction and disappear. The graft EVA-g-AN appeared an obvious characteristic absorb peak of cyano group (C≡N) at 2240 cm$^{-1}$, but the pure EVA did not appear this peak. Because the graft EVA-g-AN have been refined, it is impossible for the existence of the uncombined AN in graft. This indicated that the monomer AN had been successfully grafted onto EVA macromolecular chain.

3.2. Effect of LPO dosage on grafting ratio of graft EVA-g-AN
Figure 3 shows the effect of LPO dosage ranging from 0.1 to 0.5 wt% on the grafting ratio when AN dosage is kept at 6 wt%. It can be seen from figure 3, the grafting ratio of EVA-g-AN increased first and then decreased as the increase of LPO dosage. When LPO dosage was 0.4 wt%, grafting ratio reached a maximum value of 0.81%. The reaction mechanism of grafting AN onto EVA was free radical polymerization. In the melting extrusion process,
the dodecanoyl radicals were generated by the homolytic cleavage reaction of the peroxy bond in the LPO at high temperature, which attacked EVA to form macromolecular radicals of EVA and then reacted with AN and obtained EVA-g-AN. When LPO dosage was low, the number of the free-radical sites on the EVA backbone increased with the increase of LPO dosage, which resulted in the increase of the grafting ratio. When LPO dosage was high, more macromolecular radicals generated, which accelerated the coupling termination reaction between the macromolecular radicals and reduced the grafting ratio. Therefore, the optimal LPO dosage was 0.4 wt% in this work.

3.3. Effect of AN dosage on grafting ratio of graft EVA-g-AN

Figure 4 shows the effect of AN dosage ranging from 2 to 10 wt% on the grafting ratio when LPO dosage is kept at 0.4 wt%. As shown in figure 4, as AN dosage was increased, the grafting ratio increased, but decreased when AN dosage exceeded 6 wt%. The experimental results may be explained by the fact that at low AN dosage, the diffusion of monomer molecules to the free-radical sites on the EVA backbone governed the grafting extent, and the contact chance between monomer molecules and the free-radical sites on the EVA backbone increased with the increase of AN dosage, which resulted in the increase of grafting ratio, whereas at higher monomer dosage, undesirable homopolymerization of monomer enhanced, which resulted in the decrease of grafting ratio.
3.4. DSC analysis

The DSC was used to investigate the effect of grafting degree on the thermal properties of EVA-g-AN. The heating thermograms of the pure EVA and EVA-g-AN with grafting degrees of 0.8% and 1.24% are shown in figure 5. For unmodified EVA, the corresponding values of melting temperature ($T_m$) and the heat of fusion ($\Delta H_f$) are 83.18 $^\circ$C and 50.8 J g$^{-1}$, respectively. For EVA-g-AN copolymers, the $T_m/\Delta H_f$ values are 82.38 $^\circ$C/45.4 J g$^{-1}$, 81.88 $^\circ$C/40.3 J g$^{-1}$ with increasing content of grafting. This was due to the fact that the grafted branches disrupted the regularity of the chain structures in EVA and prohibited the movements of the polymer segments, making the regular arrangement of the molecular chains more difficult.

3.5. Oil resistance

The results of oil resistance based on the changes in volume, mass and tensile properties of EVA-g-AN with different grafting degrees before and after immersing in oil for 72 h at 40 $^\circ$C are presented in figure 6. It can be seen that the rate of change of mass, volume and tensile properties decreased as the grafting degree increased, indicating enhanced oil resistance. The increment of acrylonitrile content plays an excellent effect on the oil resistance of the grafted EVA. There was an excellent compatibility between the non-polarity oil molecules and the weakly polar EVA. A large number of oil molecules entered the EVA matrix directly per unit of time, so the properties such as volume and mass varied greatly. When AN was grafted onto EVA, a certain number of strong polarity cyano groups were introduced, which extremely excluded to the non-polar oil molecules and availably
prevented oil molecules diffusing into the EVA matrix directly. On the other hand, due to the strong dipole moment of cyano groups, the intermolecular forces increased, resulting in a higher cohesive energy density, which was defined as the energy required to separate all the molecules in a given material from each other. Thus, the EVA grafted with AN become more resistant to the solvent attack, leading to an increase in oil resistance.

3.6. DC breakdown strength

Weibull plots of the dc breakdown strength of the EVA-g-AN samples with different grafting degrees are shown in figure 7, and the corresponding parameters are listed in table 1. It can be seen that the breakdown strength and increased gradually with the increase of grafting degree. When the grafting degree was 1.24%, the breakdown strength was the largest value of 23.26 kV mm$^{-1}$, which was 12.3% higher than that of pure EVA. The shape factor also increased from 24.89 of pure EVA to 36.20 of EVA-g-AN with grafting degree of 1.2%, indicating that the stability of breakdown was improved. Carrier capture sites play a positive part on breakdown performance. It is well known that cyanogroup can act as deep traps. Therefore, when AN was grafted onto EVA molecular chain, a certain amount of deep traps were introduced into the system. The deep traps can absorb charge carrier energy through interaction and reduce carrier mobility, which weakened carrier collision with the EVA molecular chain. In addition, the homo-charges formed in the vicinity of the electrodes due to carrier trapping by deep traps, enhancing the electric field required for charge injection. Thus, the breakdown performance was improved.

3.7. DC volume resistivity

The electrical performance of the insulation materials is of critical importance for the power cable application. A high insulation resistance is desirable to minimize the cost of cable dielectric losses. Figure 8 shows the dependence of volume resistivity of pure EVA and EVA grafted with AN on the grafting degree. The volume resistivity shows essentially an identical tendency with the breakdown strength. As the grafting degree increased, the volume resistivity of EVA grafted with AN increased. As explained above, the deep traps introduced by cyanogroup in EVA-g-AN can capture the charge carriers and slow down the motion of them in the charge transport process. At the meantime, the charge layer near the electrode can inhibit the further injection of carriers. In consequence, the mobility and number of the charge carriers reduced, leading to an increase in volume resistivity of EVA-g-AN.

Table 1. Characteristic breakdown field strength and shape factor of different grafting degrees.

| Grafting degree/% | 0     | 0.14 | 0.5   | 0.8   | 1.24  |
|------------------|-------|------|-------|-------|-------|
| DC breakdown field strength (kV mm$^{-1}$) | 20.72 | 21.08 | 21.63 | 21.99 | 23.26 |
| Shape factor     | 24.89 | 28.40 | 33.63 | 34.50 | 36.20 |

Figure 8. Influence of grafting degree on volume resistivity.
4. Conclusions

(1) The optimal process of the grafting reaction was determined: the amount of AN was 8.0 wt%, the amount of St was 5.0 wt%, and the amount of LPO was 0.4 wt% of the total amount of AN and St. The grafted product was the best graft. The rate is 1.24%. As the content of LPO and AN increases, the grafting rate first increases and then decreases. The excess of monomer and initiator will cause the self-polymerization reaction to occur.

(2) The increase in grafting rate reduces the melting temperature (Tm) and the heat of fusion (ΔHf), improves oil resistance, the volume resistivity and breakdown field strength. When the grafting rate is 1.24%, the volume resistivity of the grafted product is $1.63 \times 10^{13} \Omega \cdot m$, which is significantly improved compared with pure EVA, and the breakdown field strength is 23.26 kV mm$^{-1}$, which is 12.3% higher than pure EVA.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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