Effect of Electron Beam Irradiation on Chlorinated Polyethylene/Vinyl Acetate/Nitrile Rubber Blend System

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Abstract. The blends of chlorinated polyethylene (CPE), ethylene-vinyl acetate copolymer (EVA) and nitrile rubber (NBR) were mixed and irradiated by electron beam. The effects of chlorinated polyethylene and electron irradiation on the structure and properties of blends were studied. The mechanical properties, crosslinking degree, crystallization properties, structure and morphology of EVA/NBR/CPE composites were characterized. The results showed that the addition of 25phr CPE had a significant effect on the capacity increase of EVA/NBR blend system, and the mechanical properties of the composites increased first and then decreased, the degree of crosslinking and the glass transition temperature increased while the crystallization temperature and enthalpy decreased. Electron beam irradiation induced hydrogen extraction reaction, formed a cross-linking structure, enhanced the phase interface bonding, and produced a synergistic effect with CPE volume-increasing EVA/NBR blend system.

1. Introduction
The thermal shrinkable material is a kind of functional material with shape memory. In order to meet the actual demanding, the performance requirements have been extended from simple coating and insulation to flame retardant, oil resistance, radiation resistance, low temperature resistance and comprehensive performance. Since single material is hard to meet these, blending modification is a simple, economical and feasible way to realize the multi-function of thermal shrinkable materials. Materials with different properties have been introduced into the thermal shrinkable material system [1, 2], however, most of the polymers are incompatible or less compatible owing to the varies of property. It is an effective method to modify the blending system with compatibilizer [3-5]. Chlorinated polyethylene (CPE) is an effective compatibilizer used in polymer material blending to improve the compatibility of blending system [6]. In addition, studies on using radiation modification to improve the compatibility of polymer blend system have been reported [7, 8], and even some researchers have further studied how compatibilizer combined with radiation modification can improve the compatibility of blend system [9]. However, the study of using CPE as compatibilizer combined with irradiation to improve blending compatibility has not been reported.
In this work, CPE was used as compatibilizer and combined with electron beam irradiation to modify the blend system of EVA and NBR, and the synergistic effect of electron beam irradiation and CPE on improving the compatibility of EVA/NBR blend system was studied, which provided the technical basis for preparing oil-resistant thermal shrinkable materials. This work, modified the property of the ethylene/vinyl acetate copolymer (EVA) and nitrile butadiene rubber (NBR) blend system through the approach of the combination of compatible solvent using the CPE and electron beam irradiation, explored the collaboration effect of using electron beam irradiation and CPE for improving the compatibility of EVA/NBR blend system, and provided the technical foundation for preparing thermal-shrinkable material of oil-proof.

2. Experiments

2.1. Materials
Nitrile rubber (NBR), 6240, Acrylonitrile content 34%, Mooney viscosity 41 Pa·s, South Korea's LG chemical company; Ethylene-vinyl acetate copolymer (EVA), EVA14-2, VA content14%, The melt flow rate 2g/10min, Beijing Yanshan Petrochemical co., LTD; Chlorinated polyethylene (CPE), 240B, with chlorine content 40%, Residual crystallinity 25%, Hunan Yixiang chemical co. LTD. Xylene (≥ 99%).

2.2. Instruments and equipment
Open plastic mixing miller, SK-160B, Shanghai Sinan rubber machinery co. LTD; Tablet machine KY-3201-30, kaiyan mechanical equipment factory, Houjie, Dongguan city; Electron accelerator, DD1.2, beam of 1.0mA, Shanghai Pioneer Motor Factory; Microcomputer controlled electronic universal testing machine, WDT II-10, Shenzhen Kaiqiangli Experimental Instrument co., LTD. Differential Scanning Calorimeter (DSC), DSC 204 F1, Netzsch, Germany. Scanning Electron Microscope (SEM), FEI Sirion200, Philips, Netherlands. Fourier Infrared Spectroscopy (FTIR) Nicolet IS5, Thermo Fisher Technologies.

2.3. Preparation
The weight ratio of EVA to NBR is 5:5, and the raw material is added to the open-type refining machine for mixing, and 5 to 30 phr of CPE is added, and the kneading temperature is controlled at 120 to 140°C. The kneaded blend was tableted by a tableting machine under 130°C. The prepared tablet was encapsulated in a polyethylene bag and subjected to electron accelerator for crosslinking under air to obtain a sample of different composition EVA/NBR/CPE composite materials.

2.4. Characterization
The gel content of the EVA/NBR/CPE composite was tested in accordance with GB/T 18474-2001. The fragment of 0.1–0.2mm was cut from the composite samples, and the quality of each sample was controlled at 0.5–1.0g. The sample was wrapped with a 200-mesh stainless steel mesh and placed in a xylene solution at 140°C for 8h. The gel content was obtained by calculating the ratio of the mass of the undissolved portion of the sample to the total mass. The test was performed 5 times in parallel and the results were averaged. The thermal performance of EVA/NBR/CPE composites was evaluated by differential scanning calorimeter (rise and temperature drop rate 10°C/min), and the effect of irradiation on the crystallization properties of EVA/NBR composites was investigated. The material samples were frozen by liquid nitrogen and then brittle. The fracture morphology was observed by scanning electron microscopy (SEM). The molecular structure of the material was characterized by Fourier transform infrared spectroscopy (FTIR) with a wavelength range of 7800-350 cm\(^{-1}\) and tested by the attenuated total reflectance (ATR) method.
3. Result and Discussion

Figure 1a shows the mechanical properties of different compositions of EVA/NBR/CPE composites. The tensile strength and elongation at break of the composites decreased significantly with the addition of CPE, indicating that the small addition did not play a fine dispersion effect on the EVA and NBR blends; when the addition amount exceeded 15phr, the elongation at break and tensile strength began to increase gradually, and when the addition amount reached 25phr, the elongation at break reached the maximum. Further increasing the CPE, the tensile strength and elongation at break of the blend system were significantly reduced. From the curve in the figure, it can be determined that the amount of CPE added should be controlled between 22.5-27.5phr.

Figure 1b shows the effect of electron beam irradiation on the mechanical properties of different compositions of EVA/NBR/CPE composites. It can be seen from Fig. 1b that after the addition of 25phr of the ternary blend system, the tensile strength of the ternary blend has greatly improved throughout the dosage range. In addition, with the increase of the radiation dose, the tensile strength of CPE modified composite material reached its maximum value when the radiation dose was 80kGy. In low irradiation dose, CPE modified the elongation at break of the ternary blend modification of EVA/NBR binary blend system before a larger increase, when the irradiation dose increases to a certain value, the elongation at break of the ternary blend system are increased with the increase of irradiation dose reduced quickly, and EVA/NBR binary blend system of elongation at break decreased slower, this is mainly due to higher crosslinking degree under the same irradiation dose.

Figure 2 shows the effect of electron beam irradiation on the gel content of EVA/NBR/CPE composites. As can be seen from figure 2, the gel content of EVA/NBR composite material shows an increasing trend with the increase of irradiation dose, among which, the gel content increases significantly at the stage of low irradiation dose, and tends to moderate at the stage of high irradiation dose. Under the same irradiation dose, the gel content of the blend material with added solvent CPE was higher, indicating that it was easier to cross link after adding CPE. This is mainly because the crosslinking mainly occurs in the amorphous region of the polymer, the CPE crystallinity is very low, and it basically exists in the amorphous form. After adding CPE, the crosslinking reaction is more likely to occur.
Figure 2. Effect of electron beam irradiation on gel content of EVA/NBR/CPE composite materials.

Figure 3 shows the effect of electron beam irradiation on the crystallization properties of EVA/NBR/CPE composites. It can be seen from Fig. 3 that the composite material has the remarkable characteristics of EVA and NBR, namely, the crystallization zone characteristics of the EVA in the high temperature region and the glass transition characteristics of the NBR in the low temperature region. The glass transition temperature (Tg) and the crystallization temperature (Tc) and crystallization enthalpy (ΔHc) are shown in Table 1. As can be seen from table 1, when the compatibilizer CPE was added to EVA/NBR blend system, the glass transition temperature and crystallization temperature of the blend material increased and the crystallization enthalpy decreased. When the composite material is irradiated at a certain dose, due to the cross-linking structure generated inside and the formation of a non-melting and non-melting cross-linking network, the Tg of the material is improved to some extent compared with that before the irradiation, and increases with the growing of the irradiation dose. The crystallization temperature Tc and crystallization enthalpy ΔHc of the composite material decrease with the increase of the irradiation dose, which is mainly caused by the damage to the crystallization area of the composite material. When it comes to a 160 kGy irradiation dose, ΔHc reduced about 15%, and the Tc decreased nearly 4℃. ΔHc is proportional to the crystallinity, so the crystallinity of the composite material also decreases with the increase of the radiation dose.

Figure 3. DSC of EVA/NBR/CPE composites with different components irradiated by electron beam.
Table 1. Crystallization properties of EVA/NBR/CPE composites irradiated by electron beam.

| Sample | $T_g/°C$ | $T_c/°C$ | $\Delta H_c/(J \cdot g^{-1})$ |
|--------|----------|----------|-----------------------------|
| 1      | -36.00   | 70.94    | 22.18                       |
| 2      | -23.47   | 72.63    | 16.07                       |
| 3      | -22.03   | 72.13    | 15.09                       |
| 4      | -16.70   | 70.11    | 14.63                       |
| 5      | -12.63   | 68.50    | 13.71                       |

Figure 4 shows infrared spectra of EVA/NBR/CPE composite materials with different components before and after irradiation.

As can be seen from figure 4, EVA/NBR and EVA/NBR/CPE infrared spectral characteristic peak absorption bands are basically consistent, 2916cm$^{-1}$, 2848cm$^{-1}$, 1439cm$^{-1}$ and 719cm$^{-1}$ are anti-CH$_2$ anti-symmetric expansion, symmetric expansion, varying angle and in-plane swing, 1738cm$^{-1}$ is -C=O expansion vibration, 1370cm$^{-1}$ and 969cm$^{-1}$ are -CH$_3$ symmetric expansion angle and out-of-plane bend, and 1239cm$^{-1}$ and 1020cm$^{-1}$ are C-O-C anti-symmetric expansion and symmetric expansion.

The characteristic absorption peak intensity of the composites after irradiation has been weakened to some extent, indicating that dehydrogenation reaction has occurred [10], forming a tertiary carbon or quaternary carbon structure, ie, a symmetric carbon framework structure, resulting in weakening of the absorption band. In addition, the EVA/NBR/CPE composite material produced a new peak at 1662 cm$^{-1}$ after irradiation, which may be caused by the dechlorination of the material owing to the irradiation process and the formation of C=C.

Figure 5 shows the cross-sectional morphology of EVA/NBR/CPE composites with different compositions. Figure 6 shows the effect of electron beam irradiation on the structure of EVA/NBR/CPE composites. It can be seen from Figure 5 that when the blend ratio of EVA to NBR is 5:5, the appearance of the composite material is clearly phase-separated, the interface is clear, and the larger nitrile rubber particles are dispersed in the EVA matrix, when 25 parts by mass of CPE is added, the rubber particles are significantly smaller and the dispersion is more uniform.

It can be seen from Fig. 6 that the phase interface becomes blurred after the addition of 25phr ternary blend system is irradiated at 80kGy [11], it shows that due to the cross-linking reaction caused by irradiation, a three-dimensional crosslinked structure is produced, and the interfacial bonding of the blending system is strengthened, so that the compatibility of the three-phase blending system is further improved, and the mechanical properties of the blending system are combined with electron beam
irradiation. The effect of compatibilizer CPE and electron beam irradiation has a synergistic effect on improving the compatibility of EVA/NBR blends.

![Figure 5. Sectional morphology of EVA/NBR/CPE composites with different compositions a EVA/NBR (5/5) b EVA/NBR/CPE(5/5/2.5).](image1)

![Figure 6. Effect of Electron Beam Irradiation on the Structure of EVA/NBR/CPE Composites (a EVA/NBR/CPE (5/5/2.5)-0kGy b EVA/NBR/CPE(5/5/2.5)-80kGy).](image2)

4. Conclusion
Adding 22.5 to 27.5phr of CPE in the EVA / NBR blending system can achieve fine dispersion; When the amount is 25phr, CPE has the most significant capacity-enhancing effect on the EVA / NBR blend system. Electron beam irradiation initiates a dehydrogenation reaction and forms a crosslinked structure, which improves the mechanical properties and glass transition temperature of the composite material and reduces the crystallization temperature and crystallization enthalpy of the composite material. And it has synergistic effect with the CPE capacity-enhancing EVA / NBR blending system.

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