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Silane grafting and crosslinking of ethylene–octene copolymer

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Abstract

Vinyl trimethoxysilane (VTMS) and vinyl triethoxysilane (VTES) grafted ethylene–octene copolymer (POE) were prepared in the melt process. The effects of silane concentration, reaction time and temperature on the silane grafting were investigated, and the grafting reaction was in situ monitored using the differential scanning calorimetry (DSC). The silane grafted POE was characterized by the Fourier transform infrared spectroscopy (FTIR) and melt flow index (MFI). MFI data of the silane grafted POE show that the MFI value is affected not only by DCP concentration, but also by silane concentration. The difference of gel content between VTMS and VTES crosslinked POE indicates that for POE, the grafting reaction activity of VTES is higher than that of VTMS. Moreover, the thermal behavior and mechanical properties of the crosslinked POE were also studied. It has been found that the thermal stability and mechanical properties of the silane crosslinked POE are greatly improved.
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Keywords: Ethylene–octene copolymer; Silane crosslinking; Mechanical properties; Thermal behavior

1. Introduction

Crosslinking is an important way to improve the thermal and chemical resistance of polyolefins (PO). There are three main crosslinking methods, i.e. radiation crosslinking, peroxide crosslinking and silane crosslinking [1–6]. Among the three crosslinking methods, silane crosslinking is cost-effective and easily operated [7], and thus it is commonly employed to produce wire and cables, plastic pipes, etc.

To produce silane crosslinked polymers, vinylsilanes are first grafted onto the backbones of polymers, and the grafted polymers are then hydrolyzed in the warm water to form silane crosslinked ones with siloxane linkages (Si–O–Si). In recent decades, the silane crosslinking of polyethylenes has been the subject of considerable research [7–14]. For example, Sen et al. [7–9] reported the grafting reaction kinetics, thermal properties which were studied by differential scanning calorimetry (DSC), dynamic mechanical properties which were studied by DMA, and structural parameters which were studied by X-ray diffraction analysis on silane grafting and moisture crosslinked polyethylene and ethylene–propylene rubber. Shieh et al. [10–12] investigated the silane grafting and crosslinking reactions of LDPE, HDPE and LLDPE. The silane crosslinking of polypropylene (PP) is much more complicated than for PE because PP is easily decomposed during the silane grafting process [15,16]. There are some papers concerning about the silane crosslinking of elastomers, e.g. EVA [17,18], EP [8] and EPDM [19]. In our previous work,

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we have investigated the flame retardation, thermal and crystallization behavior of silane crosslinked polyolefins [20–22].

Ethylene–octene copolymer (POE) is usually produced using a metallocene catalyst. It has fast mixing and better dispersion properties compared with the conventional elastomers, such as ethylene–propylene copolymer (EP) and ethylene–propylene-diene copolymer (EPDM) [23]. Some literatures about the graft and crosslinking of POE have been published, Wu et al. [24] studied the grafting of maleic anhydride (MAH) onto POE, and Liao and Wu [25] studied the peroxide crosslinking of POE. As for the silane crosslinking of POE, very few papers can be found in the literature. Sirisinha and Meksawat [26,27] studied the differences between peroxide crosslinked POE and vinyl trimethoxysilane (VTMS) crosslinked POE, in terms of processing and product mechanical and thermal properties, and also investigated the change in properties of silane water crosslinked POE after prolonged crosslinking time. In the present work, the influence of several factors on the silane grafting and crosslinking of POE were investigated in detail, and the silane grafting reaction of POE has been in situ monitored using DSC. A comparison of graft capability between VTMS- and VTES grafting POE was conducted. And the thermal stability of VTMS- and VTES grafted and crosslinked POE were also studied by TG method. Moreover, the apparent activation energies (E_a) of the VTES grafting POE reaction containing different DCP concentrations were calculated.

2. Experimental

2.1. Materials

POE used was Engage E8003 (Dow Chemical Co.). Vinyl trimethoxysilane (VTMS) and vinyl triethoxysilane (VTES) are standard laboratory reagents used as received. Dicumyl peroxide (DCP) was recrystallized using anhydrous ethanol.

2.2. Sample preparation

The POE pellets were premixed with VTMS (or VTES) and DCP. The mixture was kept immediately in a sealed bottle. The polymer was tumbledmixed for some time and allowed to stand overnight. And the mixture was mixed for 10 min at about 70 °C in a Brabender-like apparatus at 60 rpm. Then, the mixture was first compression molded into 1 mm thick sheets under a pressure of 10 MPa at a temperature between 150 °C and 210 °C for a given time to complete the silane grafting process. The grafted samples were finally immersed into water at 70 °C for some hours.

2.3. FTIR analysis

Samples for FTIR measurements were prepared by making films of the mixture in a hot press. Prior to the FTIR measurement, the films were immersed into excessive acetone for 12 h to remove unreacted silane and possible silane oligomers. The FTIR spectra were then recorded by using a Nicolet MAGNA-IR 750.

2.4. Differential scanning calorimetry

Grafting reacting of silane onto POE was performed during the heating-up at a heating rate of 20 °C/min under nitrogen using Pyris 1 DSC analyser. The grafting reaction was monitored in situ on DSC.

2.5. Melt flow index

The melt flow index (MFI) of the grafted POE was determined using SRZ-400C instrument. The condition of experiment is at 230 °C under a load of 20.16 kg. MFI is generally expressed in terms of the weight of extrudate in grams at 10 min intervals.

2.6. Gel content

Weighed samples of small pieces in a copper net were put into boiling xylene for 48 h. The extracted samples were washed using acetone, then dried to a constant weight in a vacuum oven. Then gel content is expressed in the percentage of the weight remaining.

2.7. Mechanical properties

The tensile strength and elongation at break were measured with a WD-20D Electronic Universal Testing Machine at the crosshead speed of 500 mm/min.

2.8. Thermogravimetric analysis

The thermogravimetric (TG) experiments were performed using analyzer (SHIMADZU, TA-50) in nitrogen atmosphere at a heating rate of 10 °C/min.

3. Results and discussion

3.1. FTIR characterization of the silane grafting reaction of POE

3.1.1. Effect of silane monomer

Fig. 1 presents FTIR spectra of the POE, VTMS grafted POE and VTES grafted POE. The peaks at 1193 and 1092 cm^{-1} in Fig. 1 curve B are assigned to Si–O–CH_3, whereas the peaks at 1167, 1105, 1082 and 958 cm^{-1} belong to absorption of Si–O–CH_2CH_3 (curve

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