Effect of silane curing conditions on properties of the metallocene-based polyethylene-octene copolymers compound

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Abstract

A compound was prepared from crosslinking of blend from two type of metallocene-based polyethylene-octene copolymers by different octene content through a two-step silane grafting method (Sioplas process) in a twin-screw extruder. The silane grafted compound was used as wire and cable coatings. The curing condition and specimen preparation method (injection molding and/ or extrusion) were factors influenced the hot-set test results at 200 °C. The results of tensile and elongation studies showed a maximum value of 9 MPa for tensile strenght and 397 % for elongation-at-break after 6 h curing.

Keywords: Sioplas process, blend, silane grafting, curing condition

Introduction

Polyethylene copolymers are usually crosslinked to ensure that they maintain their stability and mechanical properties above the melting point of their crystalline phase [1, 2]. In industry, the crosslinking process is generally performed by using peroxide or silane compounds, and sometimes through electron beam crosslinking processes [1, 3, 4]. The crosslinking using silane grafting reagents is one of the most common methods for improving the properties of Polyethylene copolymers [5, 6]. Easy processing, low capital investment and favorable properties of processed materials are the advantages of using silane crosslinking method [3, 4, 6, 7]. The Monosil and Sioplas processes are two of the major technologies in the manufacturing of silane crosslinked materials. At low temperatures, the rate-determining step of the cross-linking reactions is water diffusion, rather than the hydrolysis and the subsequent condensation reactions of the silyl trimethoxy groups. However, at high temperatures and high degrees of silane grafting in the samples, the chemical reactions dominate in the crosslinking process [3]. Hot set tests (duration of 15 min, at temperature of 200°C, and under definite static load) are carried out on cross-linked samples to evaluate and quantify the cross-link density [8].

In this work, the crosslinking of a blend of comprising metallocene-based polyethylene-octene copolymers by different octene content was carried out using the Sioplas process, which represents a two-step silane crosslinking process.

Experimental/Theoretical

Materials

EOC and LLDPE were purchased from SK Global Chemical Co., Ltd, (South Korea) and Amirkabir Petrochemical Co., (Iran), respectively. Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate), Irganox 1010 antioxidant, was supplied by BASF Co., Germany. Vinyl trimethoxysilane (VTMS) was purchased from RUI Chemical (China). Dibutyltin dilaurate (DBTDL), the catalyst, was supplied by Merck (South Korea). Dicumyl peroxide and benzoyl peroxide, the initiators, were supplied by Coin AKZO Nobel Co., (Netherlands) and Arkema (France), respectively.

Preparation of Sample

The silane grafting of EOC/LLDPE blend was performed in a co-rotating twin-screw extruder with twelve heating/ cooling zones (Model CTE 65, COPERION Co. Germany). A temperature profile of 170-210 °C were applied. A

Table 1. Effect of curing conditions on results of the hot set test at 200 °C.

Curing temperature (°C)	Curing time (h)	Results	
85	8 h	Extension <175 %	Set < 15 %
		-24.85	31.05
		-26.50	28.85
		-29.45	26.05
100	Shelf life at 200 °C (min)		
	2 h	3:26	
	4 h	4:28	
	6 h	3:56	

Table 2. Hot-set test results for specimens with different shapes.

Specimen type	Gel content (%)	Hot-set test at 200 °C	
		Extention < 175 %	Set < 15 %
Cable	74.0	154	2.25
	78.2	146	0.25
dumbbell-shaped	75.6	29.6	-23.9
	75.0	29.6	-27.2

constant silane and peroxide concentration of 5 wt% and 0.13 wt% was used, respectively. In the next step, a blend of the silane grafted compound (~95 parts) and the catalyst masterbatch (~5 parts) was shaped as wire and cable coatings. For extrusion coating of a cable using the prepared silane grafted compound, an extruder with seven heating/cooling zones was used at a production speed of 10 m/min under a temperature profile of 170-220 °C from the feed zone to the die zone. The specimens (sheets) with different thicknesses were cured under the same conditions in a water bath operated at 85 °C for 4-6 h per 1 mm sheet thickness.

Results and Discussion

Hot-set test at 200 °C

Effect of curing conditions

The results of hot-set test at 200 °C at different curing conditions are shown in Table 1. As seen, the morphology of specimens is affected by the curing conditions. The hot-test was not confirmed because of possible degradation of the polymer as a result of curing.

Effect of processing type

The hot-set test at 200 °C was performed on the specimens prepared by injection molding and extrusion processes (Table 2). Differences in the obtained results can be attributed to the difference in the shape of the test specimens prepared. The pressure in extrusion process typically is 5000 Psi (35 MPa) which is less than that in injection molding process [9]. Due to high pressure of injection, the test specimens prepared by injection molding process is more compressed than those prepared by extrusion process. It may state that more compressed specimens have higher stress resistance.

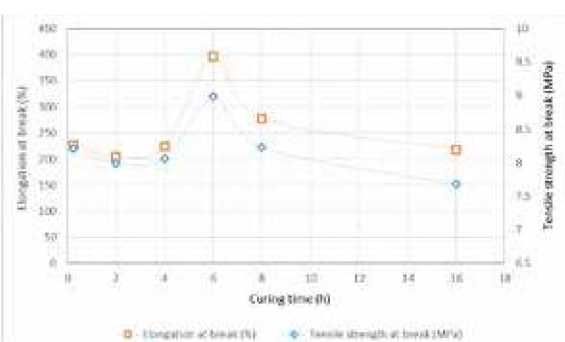

Fig. 1. Effect of curing time on the elongation-at-break and tensile strength of the crosslinked compound.

Effect of curing time on mechanical properties of the crosslinked compound

The tensile strength-at-break and elongation-at-break versus curing time are shown in Fig. 1. As seen, the highest amount of tensile strength and elongation are obtained after 6 h of curing time. The loss in the mechanical properties is probably due to the polymer degradation occurred after curing. The curing conditions can improve the direction of the polymer chains, thereby reducing the tensile strength [10].

Conclusion

Crosslinking of EOC/LLDPE blend was carried out using the two-step Sioplas process in a twin-screw extruder. The blend of the silane-grafted compound (~95 parts) and the catalyst masterbatch (~5 parts) was used to make coatings for wire and cable. The curing conditions and the type of specimen were factors influenced the hot-set test results at 200 °C. Study of tensile strength and elongation-at-break of the crosslinked compound showed a maximum value of 9 MPa and 397 % after 6 h curing time, respectively.

Acknowledgments

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