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SC–CO_2-assisted rubber dispersion and dynamic vulcanization in blending of PP/EPDM thermoplastic olefin

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Abstract Supercritical CO_2 (SC–CO_2), as a green medium, was induced in the traditional way of preparing polypropylene/ethylene–propylene–diene terpolymer (EPDM) thermoplastic olefin (TPO) by dynamic vulcanization using a twin-screw extruder. The morphology observation suggested that the SC–CO_2 not only promoted the rubber dispersion, but also facilitated the rubber dynamic vulcanization; therefore, the crosslinked EPDM particles were more densely distributed in the TPOs prepared with SC–CO_2, and existed as a stronger viscoelastic phase restricting the mobility of polymer chains, increasing the complex viscosity and storage modulus and promoting the mechanical properties.

Introduction

Thermoplastic vulcanizates offer the performance of a thermoset rubber together with the good processibility and recyclability of thermoplastic materials [1]. In the continuous industrial production, dynamic vulcanization via the screw extruder is a commonly used method of obtaining polypropylene (PP)/ethylene–propylene–diene terpolymer (EPDM) thermoplastic olefin (TPO) [2]. In the PP/EPDM TPO, the uniform distribution of EPDM phase with small size morphology is the key to decide their better performance [1]. Unfortunately, PP and EPDM are thermodynamically immiscible, which results in poor interfacial adhesion and a phase-separated morphology, this consequently leads to poor mechanical properties [3–6].

Important functions of supercritical carbon dioxide (SC–CO_2) are the plasticization of the polymer and the change of polymer physical properties, such as the lowering of interfacial tension and a reduction of viscosity of the polymer melt [7, 8]. A great deal of attention has been given to the polymer processing with the aid of SC–CO_2 [9–13]. Elkovitch et al. [9] studied the blend of ethylene–methylacrylate copolymer and polystyrene and showed that the CO_2 altered the viscosity of each component in extrusion of their blend. Khan et al. [10] studied the effect of SC–CO_2 on the morphological features of blends of polycarbonate and a commercial thermoplastic elastomer. They found that the size distribution of the elastomer domains is effectively narrowed by the SC–CO_2 treatment. Some researchers investigated the acceleration effect of SC–CO_2 on the reactive extrusion and obtained some significant results [11–13]. Xue and Tzoganakis [11] carried out the research about reactive extrusion of maleic anhydride (MA) functionalized polyethylene and amine-terminated polyamide-6 in a twin-screw extruder with the injection of SC–CO_2. By measuring the amount of unreacted MA via FTIR, they found that the final MA conversion increased with the increase in CO_2 concentration.

In this study, a novel technology of SC–CO_2-assisted polymer blending, which combined with traditional crosslinking way of dynamic vulcanization, was developed. The effect of SC–CO_2 on the PP/EPDM dynamic vulcanization was evaluated, primarily based on the investigation of rheology, morphology, mechanical properties, and the relationships among them.

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Experimental

Materials and experimental equipment

The PP used was grade J501 manufactured by Sinopec Group Guangzhou Co., China. The EPDM used was grade 4045 manufactured by Mitsui Petrochemical Industries, Ltd. A sulfur system, which was used as vulcanization component during the dynamic vulcanization, was of laboratory grade and purchased from local suppliers. The equipment mainly included a co-rotating twin-screw extruder (35 mm diameter, 40 length-to-diameter ratio) and a CO_2 injection system (500D, ISCO). More details were described in previous papers [14, 15].

Sample preparation

A mixture containing PP, EPDM, and vulcanization component in a ratio of 80:20:2 by weight was fed to the extruder with the feed rate of 3 kg/h. The screw speed was set at 100 rpm. The flow rate of CO_2 was set to keep the CO_2 concentration to be 0, 1, and 2.5 wt% of the feed rate of the PP/EPDM mixture. At the position of about 38 times of screw diameter from the hopper, CO_2 was vented by vacuum pump. During the experiments, the CO_2 pressure in high-shearing section of extruder was kept about 9 MPa. The melt just at the die exit was immediately compression-molded into disks with a size of $\phi 25 \times 1$ mm^2. The extruded melt strands were pelletized after directly solidified in a water bath.

Characterization

Bohlin Gemini 200 Rheometer equipped with a parallel-plate fixture (25-mm diameter) was used in an oscillatory mode to conduct dynamic frequency sweep measurement at 170 °C. The above-said compression-molded disks were used as the test samples. The angular frequency (ω) ranged from 0.01 to 100 rad/s and the fixed strain was set at 5%. A Hitachi S-520 SEM was used to observe the phase morphology of blends, and the specimens were chosen from parts of extruded strands. Before morphological observation, the specimens were etched by xylene at room temperature for 4 h to remove the PP and non-crosslinked EPDM phase. Some pellets were injection molded into standard specimens for the mechanical property tests. The tensile tests were performed at a crosshead speed of 50 mm/min on a tensile tester (tensiTECH, USA). The Izod impact tests were conducted on an impact tester (ZWICK5331, German). Flexural tests were carried out at a crosshead speed of 20 mm/min on a flex tester (AG-1, Japan).

Results and discussion

Rheology

As can be directly seen from Fig. 1, the η^*, G', and G'' of PP/EPDM TPO prepared with SC–CO_2 are higher than those prepared without SC–CO_2, and the increase in η^*, G', and G'' is significant with adding 1 wt% CO_2, but a further increase in the CO_2 concentration up to 2.5 wt% does not increase the η^*, G', and G' much. The maximum increase in η^* is 29% at the lowest ω for PP/EPDM TPO prepared with 2.5 wt% SC–CO_2 and the increment keeps reducing with the increase in ω. The increment for G'' is less than that for G' when CO_2 is added, meaning that the SC–CO_2 has a more significant effect on the elastic behavior than the viscous behavior of PP/EPDM TPO. The maximum increases in G' and G'' are 42 and 25% at the lowest ω, respectively, for PP/EPDM TPO prepared with 2.5 wt% SC–CO_2. These rheological behaviors suggest that the presence of SC–CO_2 changes the final morphology of PP/EPDM TPO.

Morphology

Because the PP and non-crosslinked EPDM phase at the surface layer were removed by xylene, the grey or white particles left on the surfaces shown in Fig. 2 are crosslinked EPDM. As can be clearly seen, the injection of SC–CO_2 leads to the size reduction and distribution uniformity improvement of crosslinked EPDM phases. More significantly, the particle number is increased and particle distribution is denser for PP/EPDM TPO prepared with SC–CO_2 than that without SC–CO_2. This may deduce that, during the dynamic vulcanization, the lubricating effect of SC–CO_2 not only promoted the rubber dispersion, but also

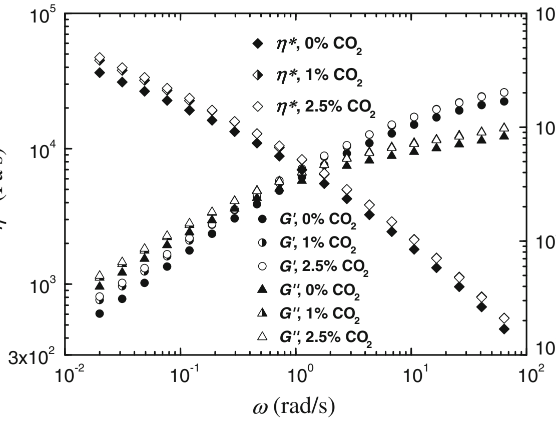

Fig. 1 Complex viscosity η^*, storage modulus G', and loss modulus G'' as a function of frequency ω at 170 °C for PP/EPDM TPOs prepared with different concentrations of SC–CO_2

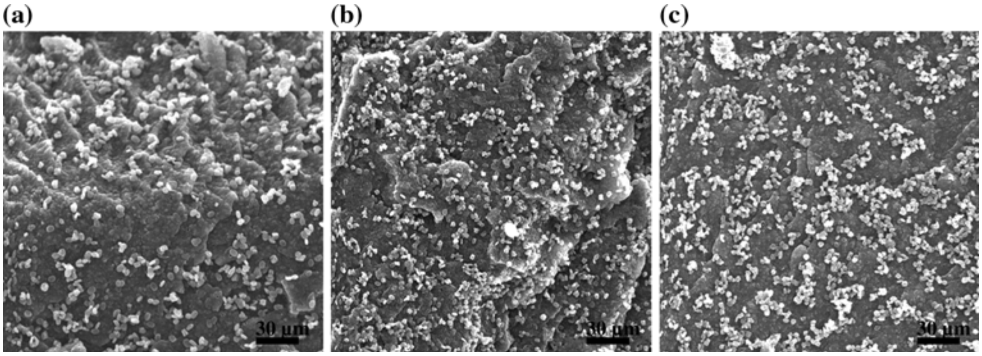

Fig. 2 SEM micrographs for PP/EPDM TPOs prepared with **a** 0 wt% SC–CO_2, **b** 1 wt% SC–CO_2, and **c** 2.5 wt% SC–CO_2

helps to change the conformation of rubber chains or reorientate the chain configuration, which facilitates the contact of reactive unsaturated double bonds with sulfur and promote their crosslinking. Similar phenomenon was also reported by Xue and Tzoganakis [11], who attributed this to the enhancement of the segmental chain mobility when dissolving the CO_2 into polymer melt.

Mechanical properties

Table 1 shows that, except the elongation at break, the mechanical properties of PP/EPDM TPO prepared with 2.5 wt% SC–CO_2 are the highest, followed by those prepared with 1 wt% SC–CO_2. The elongation at break decreases with increasing SC–CO_2 concentration. The increments of the tensile strength, flexural modulus, maximum strength, and impact strength for PP/EPDM TPO prepared with 2.5 wt% SC–CO_2 are 5.9, 10.5, 13.1, and 6.5%, respectively, when comparing with those without SC–CO_2.

Relationship of rheology, morphology, and mechanical properties

The dynamic rheological measurement is an indirect method to probe the morphologies of polymer blends and provides fundamental insights about their viscoelastic properties. Figure 1 shows that the complex viscosity η^* of PP/EPDM TPO increases with the increase in SC–CO_2 concentration. This may be attributed to the morphology change of EPDM phase in PP matrix, because as can be seen from Fig. 3, the SC–CO_2 has no effect on the rheology of pure PP, which suggests that the morphology of pure PP is not changed. Actually, morphological observation in Fig. 2 shows that the crosslinked EPDM particles distribute more uniformly and densely with the aid of SC–CO_2, which act as a rigid structure to restrict the mobility of polymer chains. So the further confinement of polymer chains increases the complex viscosity and dynamic moduli. In addition, because EPDM crosslinking is promoted for TPO prepared with SC–CO_2, more and denser

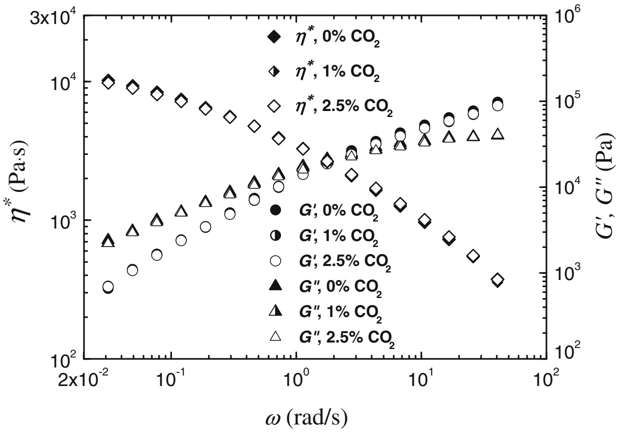

Fig. 3 Complex viscosity η^*, storage modulus G', and loss modulus G'' as a function of frequency ω at 170 °C for PP extruded under different concentrations of SC–CO_2

Table 1 Mechanical properties of PP/EPDM TPOs prepared with different concentrations of SC–CO_2

CO_2 concentration (wt%)	Tensile properties		Flexural properties		Izod impact strength (kJ/m^2)
	Tensile strength (MPa)	Elongation at break (%)	Flexural modulus (MPa)	Maximum flexural strength (MPa)	
0	22.0 ± 1.1	169 ± 21	1037 ± 39	42.6 ± 0.5	6.2 ± 0.2
1	22.2 ± 0.3	161 ± 13	1091 ± 22	43.5 ± 0.3	6.4 ± 0.3
2.5	23.3 ± 1.2	160 ± 16	1173 ± 24	47.1 ± 0.6	6.6 ± 0.2

crosslinked EPDM makes the TPO exhibit stronger elastic response than the viscous response, this is the reason for the increment of G' is more than that of G'' when CO_2 is added.

Mechanical properties of polymer blend are directly related with its morphology. In the deformation under an external force, the crosslinked EPDM acting as rigid structure not only restricts the mobility of the polymer chains to change conformations and promotes the elastic recovery of deformed chains, but also helps to transfer the stress and reduces the stress concentration, which leads to the increase in fracture initiation energy. Therefore, tensile, flexural, and impact strengths increase with more and denser distributed crosslinked EPDM in TPO prepared with higher SC–CO_2 concentration.

Conclusion

A SC–CO_2-assisted polymer extrusion setup was used to prepare the PP/EPDM 80/20 TPO by dynamic vulcanization. The dynamic rheology and morphology of the PP/EPDM TPO were characterized using oscillation-mode rheological test and SEM, respectively. Rheological test results showed that the complex viscosity and dynamic moduli significantly increased for the PP/EPDM TPO prepared with the 1 wt% SC–CO_2, but a further increase in the CO_2 concentration up to 2.5 wt% did not increase the complex viscosity and dynamic moduli much. The SEM results indicated that the addition of SC–CO_2 enhanced the degree of dynamic vulcanization, and led to the size reduction and distribution uniformity improvement of crosslinked EPDM phases. The mechanical measurements showed that the better mechanical properties were obtained for TPOs prepared under the inducing of SC–CO_2 in the dynamic vulcanization in extrusion. And the increments of the tensile strength, flexural modulus, maximum strength, and impact strength for PP/EPDM TPO prepared with 2.5 wt% SC–CO_2 were 5.9, 10.5, 13.1, and 6.5%, respectively.

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