

Toughening of polyamide 6 with β -nucleated thermoplastic vulcanizates based on polypropylene/ethylene–propylene–diene rubber grafted with maleic anhydride blends

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ABSTRACT

The toughening of polyamide 6 (PA 6) with β -nucleated thermoplastic vulcanizates (TPVs) based on polypropylene (PP)/ethylene–propylene–diene rubber grafted with maleic anhydride (EPDM-g-MAH) blends was studied. A series of TPVs without and with different dosage of β -nucleating agent (β -NA) were prepared and used to toughen PA 6 at the same proportion. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) measurements showed that β crystals of PP were effectively induced in the TPVs. The PA 6 blends toughened with β -nucleated TPVs (β -TPVs) exhibit significantly enhanced toughness, balanced mechanical properties and thermal properties compared with PA 6 toughened by TPV without β -NA or only by EPDM-g-MAH. Phase morphologies of the blends characterized by scanning electron microscopy (SEM) showed that better interfacial adhesion caused by the migration of β -NA from PP to PA 6/PP interface and PP/EPDM-g-MAH interface gives rise to more uniform dispersion and smaller size of the dispersed phase; moreover, the core–shell structure comprised of rubber particles enveloped by PP on the surface, brings about easier and stronger interference of the stress field of EPDM phase.

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1. Introduction

Polyamide 6 (PA 6) is a widely used engineering plastic with extensive usage and promising market prospect. However, its application is somewhat restricted by its brittleness at high strain rate, especially at low temperature. In order to improve the impact toughness of PA 6 and extend its application range, great attention has been paid to the toughening of PA 6 by incorporation of fine particles, particularly, particles of rubbers or elastomers [1–5]. For example, ethylene–propylene rubber (EPR) [3], ethylene–propylene–diene rubber (EPDM) [1], and acrylonitrile butadiene styrene resin (ABS) [2] have been introduced into PA 6 matrix to improve its impact strength. However, these toughening agents are usually resource-limited, and more expensive than general plastics. Furthermore, this traditional toughening strategy by rubbers or elastomers generally sacrifices the strength and rigidity of the polymer matrixes to some extent.

In recent years, to overcome the drawbacks caused by only incorporation of rubbers or elastomers, much work has been done on ternary systems, aiming at simultaneous reinforcing and toughening of the polymer matrixes [6–9]. Fu and co-workers [7] introduced both organoclay and ethylene–propylene–diene rubber

grafted with maleic anhydride (EPDM-g-MAH) into PA 6 to simultaneously improve the toughness and stiffness. Kusmono et al. [8] prepared PA 6/polypropylene (PP) (70/30 wt) blends containing organoclay and maleated styrene–ethylene–butylene–styrene (SEBS-g-MA) and found that the toughness and stiffness of the resultant material were improved simultaneously. Li et al. [9] studied the compatibilization and toughening of immiscible ternary blends of polyamide 6 (PA 6), propylene–ethylene copolymer (co-PP), and polystyrene (PS) and found that due to the formation of PP-g-(MAH-co-St), PP melt-grafted with styrene (St) and maleic anhydride (MAH) in melting process, the system was effectively compatibilized, resulting in uniform and fine dispersion of both the PP and PS phases in the PA 6 matrix and toughened multicomponent blends with balanced mechanical properties were achieved.

TPVs, or thermoplastic vulcanizates, are blends in which elastomers are vulcanized in situ during melt mixing with curing agent and thermoplastic components at high shear and elevated temperature. Dynamic cross-linking of EPDM during its melt mixing with iPP can improve the oil resistance, permanent set, ultimate mechanical properties, fatigue resistance, heat resistance and melt strength of the blend [10,11]. These enhanced properties of TPVs are attributed to the unique morphology that small and uniform crosslinked rubber particles finely distribute in the PP matrix. The resultant materials, TPVs, have been widely used in plastic

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industry [12]. It is generally known that β phase PP can be prepared with the help of selective β -nucleating agent and results in higher impact strength in comparison with the α -PP [13]. Recently, the development of β phase PP in TPVs based on PP/EPDM blends has been studied in our previous work [14–16]. We introduced β -nucleating agent (β -NA) into TPVs based on iPP/EPDM blends (β -TPVs) and found that the β -NA induced β phase of PP effectively in TPVs and with the increasing dosage of β -NA, the content of β phase in TPVs increased. By the essential work of fracture (EWF) approach, the specific essential work of fracture (w_e) was found to increase with increasing content of β phase, indicating that the presence of β phase could effectively enhance the fracture toughness of TPVs [14,15].

In this work, we introduced β -TPV in PA 6 for toughening. Considering the poor compatibility between interface of PA 6 and PP, an aryl amide nucleating agent, TMB-5, was used in our system, because there may exist an interaction or reaction of the amino group in TMB-5 and the hydroxyl group in PA 6 to a certain extent. Our focus is on the properties, microstructures and compatibility of PA 6/ β -TPVs blends to explain the toughening mechanism of this system, which was rarely reported before.

2. Experimental procedures

2.1. Materials

The following materials were used in this study. PA 6 (trade-mark M2800) with a MFR of 11.0 g/10 min was supplied by Guangdong Xinhui Meida Nylon Co. Ltd. iPP, with the trademark T30S, a resin with a melt flow rate of 2.3 g/10 min was purchased from Lanzhou Petrochemical Company, PR China. EPDM grafted with maleic anhydride at a ratio of about 2% (trademark MB01) and a melt rate of 2.3 g/10 min, was obtained from Haimen Borun Engineering Plastics Company, PR China. β -nucleating agent used was TMB-5, a patented substituted aromatic amide compound (the chemical structure provided by the supplier is shown in Fig. 1), purchased from Fine Chemicals Department of Shanxi province Institute of Chemical Industry, PR China, with the melting point of 197.8 °C. Phenolic resin (PF) with the trade mark TXL-201, used as curing agent, was obtained from Yuantai Biochemistry industry Company, PR China.

2.2. Sample preparation

2.2.1. Preparation of TPV grafted with maleic anhydride (TPV-g-MAH)

The compositions of the TPV-g-MAH prepared are listed in Table 1 and the detailed preparation procedure is as follows. The melt reactive blending process for preparing TPV-g-MAH samples was carried out in an SHJ-20 co-rotating twin-screw extruder with a screw diameter of 25 mm, a length/diameter ratio of 23, and a temperature profile of 175, 185, 190, and 185 °C from the feeding zone to the die. PP, EPDM, PF, and β -NA at the preset proportions were simply mixed first and added to the twin-screw extruder. Then the extrudate was pelletized. After drying to remove the attached moisture during extrusion at 60 °C, and for the crystalline structure characterization of the TPVs, a certain amount of the dried pellets

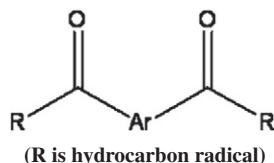


Fig. 1. Chemical structure of the β -nucleating agent, TMB-5.

Table 1
Composition of the TPVs studied in this work.

Code	PP (wt%)	EPDM (wt%)	β -nucleating agent (β -NA) (wt%)	Phenolic resin (PF) (wt%)
TPV0	50	50	0	2
TPV1	50	50	0.1	2
TPV3	50	50	0.3	2
TPV5	50	50	0.5	2
TPV10	50	50	1.0	2

were injected into dumbbell tensile samples and rectangular impact samples on a PS40E5ASE precise injection-molding machine with a temperature profile of 180 °C, 200 °C, 220 °C and 215 °C from the feeding zone to the nozzle, and an injection and molding pressure of 30 MPa. Then the samples were heat pressed for 10 min in a compression mold machine (XLB-D 400 × 400 × 2) into 0.5-mm-thick sheets, with a temperature of 200 °C and a pressure of 10 MPa. The compression-molded sheets were then cooled to room temperature under pressure.

2.2.2. Preparation of PA 6/TPV-g-MAH

Firstly PA 6 was dried in a vacuum oven at 100 °C for at least 12 h. PA 6 and the prepared TPVs pellets (PA 6:TPV = 80:20 wt%) were mixed and melt blended in the same extruder, with a temperature profile of 190 °C, 230 °C, 240 °C and 235 °C from the hopper to die. The extrudate was then pelletized. After drying in a vacuum oven at 100 °C for at least 12 h, the pellets were injection molded into dumb-bell tensile samples and impact samples on PS40E5ASE precise injection molding machine, with a temperature profile of 275 °C, 270 °C, 255 °C and 250 °C from the feeding zone to the nozzle. Both the injection and molding pressure were 37.4 MPa. For comparison, pure PA 6 and EPDM-g-MAH toughened PA 6 (PA 6:EPDM-g-MAH = 80:20 wt%) blends were extruded and injection molded under the same processing conditions.

For the sake of clarity, the samples were designated as follows:

- PA6 (pure PA6);
- PA/E (PA 6 toughened with 20 wt% EPDM-g-MAH);
- PA0 (PA 6 toughened with 20 wt%TPV0);
- PA1 (PA 6 toughened with 20 wt% TPV1);
- PA3 (PA 6 toughened with 20 wt% TPV3);
- PA5 (PA 6 toughened with 20 wt% TPV5);
- PA10 (PA 6 toughened with 20 wt% TPV10).

2.3. Tests

2.3.1. Mechanical testing

The tensile test was performed on an AGS-J universal material testing machine (Shimadzu Instrument, Japan) according to ASTM D638-10 [17] and the crosshead speed was 50 mm/min. The flexural test was performed on the same universal material testing machine according to ASTM D-790 [18]. Notched Izod impact strength was obtained by using a UJ-40 impact testing machine, according to ASTM D-256 [19]. All the specimens were tested at ambient temperature (about 23 °C). At least five samples were used for each measurement, and the average values were reported.

2.3.2. Differential scanning calorimetry (DSC)

The melting behaviors of the TPVs were studied by a TA Q20 differential scanning calorimeter. The samples, of about 5 mg, were heated to 200 °C at a rate of 10/min and held at 200 °C for 5 min to eliminate the influence of thermal history. Afterward, the samples were cooled to 40 °C at a rate of 10 °C/min, and then heated again to 200 °C at a heating rate of 10 °C/min. The temperature and heat flow scales were calibrated using high-purity indium

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