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Material properties

Ternary blends based on poly (ethylene-naphthalate)/glass fibers/nitrile rubber: Preparation, properties and effect of dynamic vulcanization

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ABSTRACT

This work studied the possibility of utilizing nitrile rubber (NBR) to modify the impact properties of poly (ethylene-naphthalate) (PEN). The PEN/NBR ratio used changed from 100/0 to 60/40. At the same time, glass fibers (GF), 40% weight of the PEN component, were used to reinforce the blends to compensate for the loss of mechanical properties of PEN by incorporation of NBR. The results showed that the impact strength of the PEN/GF/NBR blend (PEN/NBR = 60/40) was increased up to 27.6J/m, nearly 5 times higher than that of the neat PEN. Meanwhile, the tensile strength and flexural strength were still maintained at as high as 66.1 MPa and 98.2 MPa, respectively. Dynamic vulcanization further improved the mechanical properties of the PEN/GF/NBR blends, which provided routes to the design of new PEN/elastomer blends. Other properties of the PEN/GF/NBR blends were also investigated in terms of morphology of fractured surface, dynamic mechanical behavior, thermal stability and crystallization, by scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively.

1. Introduction

Polymer blending is an attractive alternative for producing new polymeric materials with desirable properties without having to synthesize a totally new material. Other advantages of polymer blending are versatility, simplicity and relatively low cost. Numerous published articles related to blends of polyesters are available in the open literature. Examples are blends of poly(ethylene 2,6-naphthalate) (PEN) and poly(-butylene 2,6-naphthalate) (PBN) [1]; poly(ethylene terephthalate) (PET) and poly(butylenes terephthalate) (PBT) [2]; PET and PEN [3]; poly(trimethylene terephthalate) (PTT) and PET [4]; PTT and PBT [5]; and PTT and PEN [6].

Poly (ethylene-naphthalate) (PEN) is widely viewed as a new generation of polyester. It is first commercialized by Teijin Co. (Japan) nearly three decades ago. Since then, many investigations on PEN film applications and crystallization characteristics have been attempted. PEN has a rigid rod backbone structure, which enhances stiffness and improves gas barrier characteristics [7]. It has a similar molecule-structure to PET, but is more rigid [8,9]. This special molecular-structure gives PEN many excellent properties, such as high tensile strength, excellent barrier properties and good resistance to high temperatures, but it is brittle with poor impact resistance [10–13].

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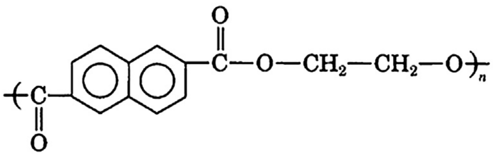

Blending PEN with various elastomers is an effective way to improve the poor impact strength of PEN. However, up to now, most of the reports about PEN are focused on the crystallization behavior and physical properties, and the work on PEN blends is largely limited to its blends with PET [3] or PTT [6]. Information about PEN/elastomer blends is still missing.

An approach to further improve the performance of blends is to develop dynamically vulcanized blends [14,15]. During dynamic vulcanization, the rubber is vulcanized in the presence of the molten thermoplastic under shear forces. Since the crosslinked rubber is unable to coalesce, dynamic vulcanization results in a fine dispersion in the thermoplastic matrix even at high rubber content [16,17]. The dynamic vulcanization technique may be useful in PEN/elastomer blends to offer better mechanical properties.

In the present work, considering the ester group of PEN, we selected nitrile rubber (NBR) as the dispersed component to blend with PEN. At the same time, we used glass fibers (GF) to reinforce the PEN/NBR blend in order to compensate for the loss of mechanical properties of PEN by adding NBR. The preparation processing, morphology, dynamic mechanical properties, mechanical properties and thermal properties of the resultant blends were investigated through mixing torque, scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), mechanical properties tests, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. The effect of dynamic vulcanization on the mechanical properties of the PEN/NBR blends was also studied.

2. Experimental

2.1. Materials

PEN pellets, with an intrinsic viscosity of 0.56 dL/g, were supplied by Teijin Co. Ltd. Nitrile butadiene rubber (KNB 35LM) was commercially manufactured by Korea Kumho Petrochemical Co., Ltd., Korea. Irganox 1010, antioxidant, was of industrial grade and obtained on the open market. Commercially available chopped strand glass fibers (GF) with average diameter 13 μm, and Young's modulus 72 GPa, was purchased from Yancheng Xinhui, China. P-tert-butyl phenol-formaldehyde resin (phenolic resin 2402) was purchased from Qingdao Chemical Co., Ltd., China. Stannous chloride, used as active agent, was obtained on the open market.

2.2. Composition and sample preparation

The compositions for PEN/GF/NBR blends are presented in Table 1.

The blends were prepared in an internal mixer with two rotors (Haake 400P) by melt mixing of the components at 290 °C and 90 rpm for about 15 min. All samples were prepared following the same procedure: PEN pellets with 40wt% GF were first mixed. Then, a uniform mixture of PEN/GF and Irganox 1010 was blended in the internal mixer for 8 minutes. After reaching a stable torque, NBR was added and mixing was continued until the final stable torque was reached. For the dynamically vulcanized blends, the previous step of preparation was the same as for the unvulcanized blends as above, followed by the addition of phenolic resin 2402 and stannous chloride to crosslink the NBR phase. Finally, the blends were removed from the internal mixer and cooled to room temperature, followed by chopping into small granules. The specimens for mechanical testing were prepared with an injection molding machine (TTI-160F, Welltec Machinery & Equipment Co. Ltd., China). The nozzle temperature was maintained at 300 °C, and the injection pressure was 40 MPa. The process is illustrated in Fig. 1.

2.3. Mechanical properties measurements

Standard tensile tests were carried out using a universal testing instrument (Shimadzu AG-1, 10 kN, Japan), and test speed was kept at 50 mm/min according to GB/T 1040-92 standard. The flexural strength was also measured using the same instrument at a speed of 20 mm/min according to GB 9341-88 standard. The notched Izod impact strength were tested through an impact test machine (ZWICK5331, Germany, Zwick/Roell), according to GB/T 1843-96 standard. All the tests were conducted at room temperature. The average value was calculated for at least 5 test specimens.

2.4. Morphology

A Nova Nano SEM 430 (FEI Company) was used to observe the phase morphology of the blends. Before morphological observation, the surface of samples was coated with a thin layer of gold to prevent electrostatic charge build-up during observation.

2.5. Dynamic mechanical analysis (DMA)

The dynamic mechanical behavior of the blends was determined using a dynamic mechanical analyzer (DMA242C NETZSCH, Germany) in 3-point bending mode at 1 Hz and with a heating rate of 5 °C/min. The

Table 1
Formulations of the prepared samples (weight ratio).

Coding	PEN	NBR	GF	Phenolic resin 2402	Stannous chloride	Antioxidizer1010
PEN/GF	100	0	40	0	0	0.2
B91	90	10	36	0	0	0.2
B82	80	20	32	0	0	0.2
B73	70	30	28	0	0	0.2
B64	60	40	24	0	0	0.2
D82	80	20	32	1	0.1	0.2