

Mechanical Properties of Dynamically Vulcanized Thermoplastic Polyurethane (TPU)/Polybutadiene Rubber (BR) Blends

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Abstract

To obtain thermoplastic polyurethane (TPU) with low hardness, dynamically vulcanized TPU/polybutadiene rubber (BR) (70/30) blends were prepared. The effect of dicumyl peroxide (DCP) content and stabilizers on the tensile strength and elongation at break of the dynamically vulcanized blends was examined. The tensile strength and elongation at break of the dynamically vulcanized blends decrease with increasing content of DCP. The addition of optimal content of stabilizer leads to the improvement of tensile strength and elongation at break of the blends. Also, the effect of sulfur cure systems and accelerators on the tensile strength and elongation of the blends was investigated. The tensile strength and elongation at break of all the dynamically vulcanized TPU/BR (70/30) blends using 1-step processing are not higher than those of simple TPU/BR (70/30) blends. However, the tensile strength and elongation of the dynamically vulcanized blends prepared at 8 min (mixing time) using 2-step processing are higher than those of the simple blends.

Keywords: dynamic vulcanization, blend, TPU, BR

1. Introduction

Thermoplastic elastomers (TPEs) are polymers that have similar properties of conventional rubbers at ambient temperature but they can be melted like a thermoplastic polymer at elevated temperature. They have an economic advantage over conventional rubber because they do not need slow and costly process of vulcanization. Another advantage of TPEs over conventional rubber is their recyclability, since conventional rubbers are irreversible cross-linked elastomers, they cannot be melted. Recycling becomes important because of increasing disposal costs and public concerns in environmental issues.

Because of these advantages, there have been many investigations to replace conventional rubbers with TPEs in many fields. Among TPEs, thermoplastic polyurethanes (TPUs) are used in many applications because of their excellent mechanical properties. TPUs are linear segmented copolymers with microphase-separated structures consisting of soft segments and hard segments. Immiscibility between soft segments and hard segments leads to microphase-separated structures. Hard segments act as physical cross-links, while soft segments induce the flexibility [1].

Low hardness (<70 Shore A) is preferred in many applications of TPUs [2]. However, TPUs have generally higher hardness than 70 (Shore A). To obtain low hardness, TPU can be mixed with polybutadiene rubber (BR). About 25% of the world's

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production of synthetic rubber is BR. 70% of total BR production is used in tire compounds and another 20% is used for modifying plastics. There are two kinds of blends: simple blends and dynamically vulcanized blends (TPVs). In a dynamic vulcanization method, the rubber phase is fully vulcanized under dynamic shear while maintaining the processing characteristics of thermoplastics [3-11]. Dynamically vulcanized polypropylene (PP)/ethylene-propylene-diene (EPDM) blends are the most important representatives of TPVs [7-9]. Thermoplastic characteristics of the TPVs are due to the network structures formed in small rubber particles dispersed in thermoplastic polymer matrix. Dynamically vulcanized blends have better physical properties than simple blends.

Even though there have been a lot of studies on simple blends between TPU and other polymers [12-20], there are few studies about the dynamically vulcanized TPU/elastomer blends [2,21]. Therefore, to obtain TPU with low hardness (< 70 Shore A), dynamically vulcanized TPU/BR (70/30 wt %) blends were prepared using dicumyl peroxide (DCP) or sulfur as a cross-linking agent in this study. The effect of DCP content, rotor speed and stabilizers on the tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends was examined. Also, the effect of sulfur cure systems and accelerators on the tensile strength and elongation at break of the blends was investigated. Finally, to decrease thermal degradation of BR and achieve the homogenous dispersion of DCP in BR, 2-step processing was used, and the influence of mixing time on their tensile strength and elongation at break of the blends was investigated.

2. Experimental

2.1. Materials

A commercial TPU, Neothane 5075P (Dongsung Highchem, Korea) and BR, KBR 01 (Kumho Polychemical, Korea) were used in this study. Hardness and specific gravity of TPU are 77 (Shore A) and 1.18, respectively. TPU is polyester-based TPU. Mooney viscosity (ML1+4 @ 100°C) and cis-1,4 content of BR are 55 and 96 wt%, respectively. DCP (Akzo Nobel, Netherlands) and sulfur (Saekwang Chem., Korea) were used as a cross-linking agent. Zinc oxide (ZnO) and stearic acid from LG Chem. (South Korea) were used as activators.

Dibenzothiazyl disulfide (MBTS), N-tert-butyl-2-benzothiazole sulfenamide (TBBS), and N-cyclohexyl-2-benzothiazole sulfenamide (CBS) from Lanxess (Germany) and tetramethylthiurammonosulfide (TMTM) from Akrochem Co. (USA) were used as accelerators. 2, 6-di-tert-butyl-4-methylphenol (BHT) from Songwon Industrial Co. (South Korea) and 4,4'-bis(α,α -dimethylbenzyl) diphenylamine (Naugard 445) from Chemtura Co. (USA) were used as stabilizers.

2.2. Preparation of Dynamically Vulcanized TPU/BR (70/30) Blends Using DCP as a Cross-linking Agent

Dynamically vulcanized TPU/BR (70/30) blends using DCP as a cross-linking agent were prepared by two methods (Fig. 1). For the first method, TPU and BR were melt-mixed with or without a stabilizer in an internal mixer PBV-03 (Irie Shokai Ltd., Japan) at 160 °C and a rotor speed of 20 or 60 rpm for 5 min. And then DCP was introduced into the Haake internal mixer. Mixing was continued for another 5 min. After the compounding, the dynamically vulcanized TPU/BR (70/30) blends were put in a mold, and the samples for various measurements were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 160 °C for 1 min. Uncross-linked TPU/BR (70/30) blends were prepared using the same method without DCP.

For the second method, 2-step processing was used. To decrease thermal degradation and achieve the homogenous dispersion of DCP in BR, at 1st step, BR and DCP were mixed in the kneader at lower temperature (90 °C) for 10 min. At 2nd step, TPU

was firstly melted at 160 °C for 2 min followed by the addition of premixed BR and DCP. Rotor speed was fixed at 60 rpm. Mixing was continued for different mixing time. After the compounding, the dynamically vulcanized TPU/BR (70/30) blends were put in a mold, and the samples for various measurements were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 160 °C for 1 min.

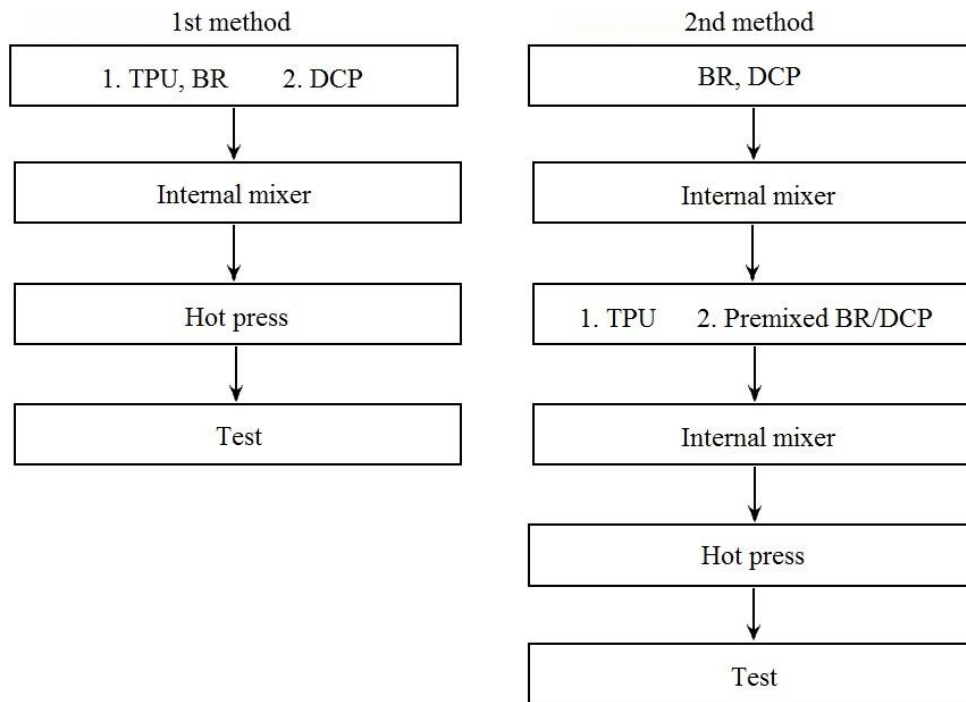


Fig. 1 Flow chart of the fabrication using DCP as a cross-linking agent

2.3. Preparation of Dynamically Vulcanized TPU/BR (70/30) Blends Using Sulfur as a Cross-linking Agent

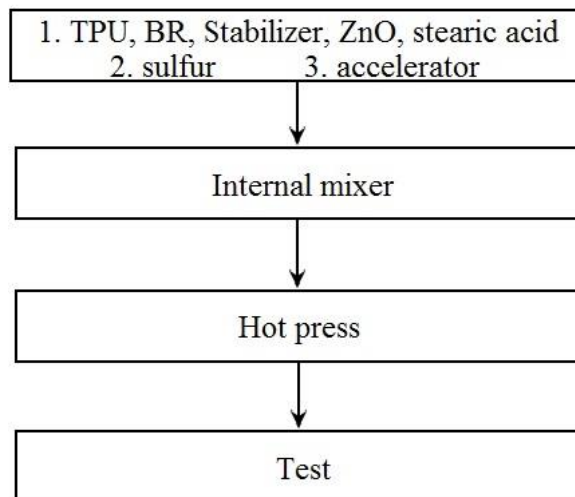


Fig. 2 Flow chart of the fabrication using sulfur as a cross-linking agent

TPU and BR were melt-mixed with a stabilizer, ZnO and stearic acid in an internal mixer PBV-03 (Irie Shokai Ltd., Japan) at 160 °C and a rotor speed of 60 rpm for 5 min (Fig. 2). And then sulfur was added, and mixing was continued for another 2 min. Finally, accelerator was introduced and mixing was continued for another 3 min. The formulations of dynamically vulcanized TPU/BR (70/30) blends are described in Table 1. After the compounding, the TPU/BR blends were put in a mold, and the samples for various measurements were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 160 °C for 1 min.

Table 1 Formulations of the compounds

| Materials | Sample notation | | | | | | | |
|-----------|-----------------|-----|-----|-----|-----|-----|-----|-----|
| | A | B | C | D | E | F | G | H |
| TPU | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| BR | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Stearic | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| ZnO | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| BHT | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Sulfur | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| MBTS | 0.2 | 3.5 | | | | | | |
| TMTM | | | 0.2 | 3.5 | | | | |
| TBBS | | | | | 0.2 | 3.5 | | |
| CBS | | | | | | | 0.2 | 3.5 |

unit: phr (parts per hundred rubber)

2.4. Testing

A Universal Testing Machine (Model 4466, Instron Co., USA) was used to obtain the tensile properties of the samples at room temperature. The crosshead speed was 500 mm/min. All measurements were performed for five replicates of dumbbell-type specimens with thickness 0.8 mm and averaged to get the final result. Hardness was measured with an Asker durometer (Shore A type, Kobunshi keiki Co., JAPAN).

The morphology of TPU, dynamically vulcanized TPU/BR (70/30) and simple TPU/BR (70/30) blends was investigated with field emission Scanning Electron Microscope (SEM, Hitachi S-4200, JAPAN). TPU and the TPU/BR (70/30) blends were cryogenically fractured in liquid nitrogen and etched with xylene at 130 °C to extract uncross-linked BR and dried for about 12 hrs at 100 °C under vacuum.

3. Results and Discussions

Fig. 3 and 4 show the effect of DCP content on the tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends, respectively. DCP was used as a cross-linking agent. The tensile strength and elongation at break of the dynamically vulcanized TPU/BR (70/30) blends decreased with increasing content of DCP. The decrease of tensile strength and elongation at break is due to the thermal degradation of BR which could be accelerated by DCP [22]. With addition of lower content of DCP (0.1 phr), the tensile strength and elongation at break of the TPU/BR (70/30) blends prepared using 60 rpm is higher than those of the TPU/BR (70/30) blends prepared using 20 rpm. High rotor speed results in high shear stress. High shear stress leads to better dispersion of BR in TPU matrix.

However, with addition of higher content of DCP (0.3 and 0.5 phr), the tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends prepared at 20 rpm are higher than those of dynamically vulcanized TPU/BR (70/30) blends prepared at 60 rpm. This could be due the dominant effect of thermal degradation of BR on tensile strength and elongation at break for higher content of DCP and higher rotor speed. Generally, the processing parameters during the dynamic vulcanization are known to be very important for the mechanical properties of dynamically vulcanized PP/EPDM blends [7]. In this study, the effect of peroxide concentration is the most important parameter. Since BR has the double bonds in the polymer backbones, thermal degradation could be accelerated by DCP and high rotor speed [22]. To melt TPU, high temperature (160 °C) should be used. Therefore, dynamically vulcanized TPU/BR (70/30) blends using this formulation and method cannot obtain higher tensile strength and elongation at break than those of simple TPU/BR (70/30) blends.

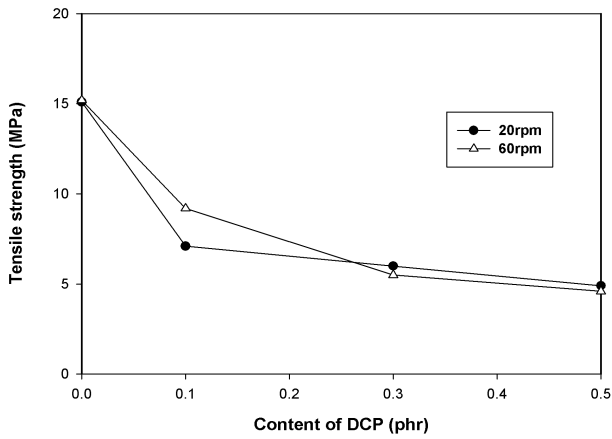


Fig. 3 Effect of DCP content on the tensile strength of dynamically vulcanized TPU/BR (70/30) blends

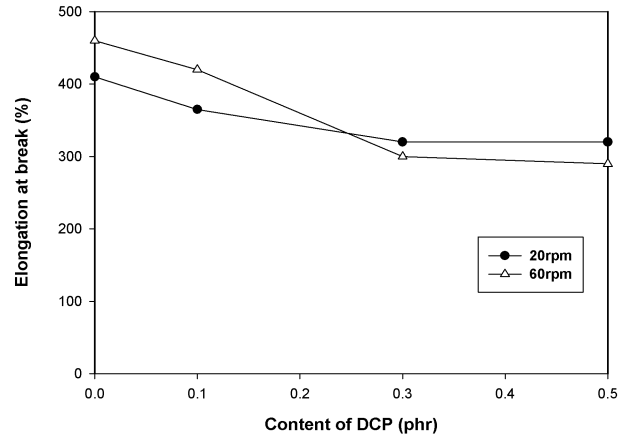


Fig. 4 Effect of DCP content on the elongation at break of dynamically vulcanized TPU/BR (70/30) blends

To decrease thermal degradation, stabilizers were added to dynamically vulcanized TPU/BR (70/30) blends. The content of DCP was fixed at 0.1 phr. The rotor speed was fixed at 60 rpm. Figs. 5 and 6 show the effect of stabilizer content on the tensile strength and elongation at break of the TPU/BR (70/30) blends, respectively. With increasing content of BHT, tensile strength and elongation at break increase and reach a maximum value at 1 phr. After that, tensile strength and elongation at break decrease with increasing content of BHT. With increasing content of Naugard 445, tensile strength and elongation at break increase and reach a maximum value at 1 phr. After that, there is nearly no change in tensile strength and elongation at break with increasing content of Naugard 445. At 1 phr of stabilizers, tensile strength and elongation at break of the TPU/BR (70/30) blends with BHT are higher than those of the TPU/BR (70/30) blends with Naugard 445.

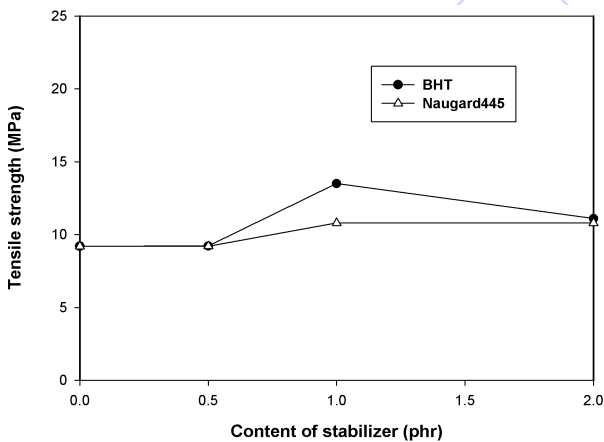


Fig. 5 Effect of stabilizer content on the tensile strength of dynamically vulcanized TPU/BR (70/30) blends

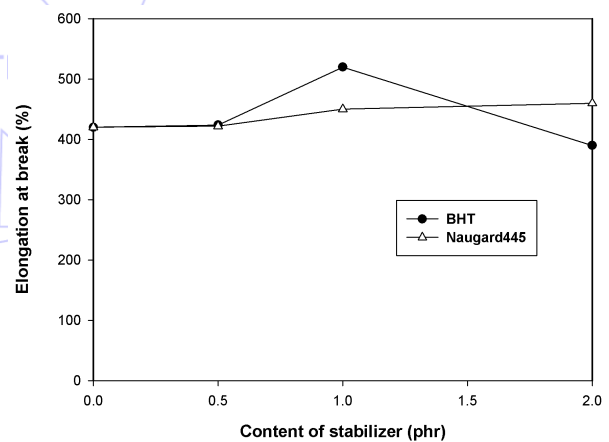


Fig. 6 Effect of stabilizer content on the elongation at break of dynamically vulcanized TPU/BR (70/30) blends

To investigate the effect of sulfur vulcanization on tensile strength and elongation at break of the TPU/BR (70/30) blends, sulfur and various accelerators were used to prepare dynamically vulcanized TPU/BR (70/30) blends. Table 1 shows the formulations of dynamically vulcanized TPU/BR (70/30) blends using sulfur as a cross-linking agent. Because the mechanical properties of vulcanized rubbers are significantly dependent on the sulfur/accelerators systems, a conventional vulcanization (CV) and efficient vulcanization (EV) systems were prepared. EV and CV systems have high and low accelerator-sulfur ratios, respectively. Sample A, C, E, and G were CV systems, and B, D, F, and H systems were EV systems.

Table 2 shows tensile strength and elongation at break of the TPU/BR (70/30) blends. The tensile strength and elongation at break of CV systems are higher than those of EV systems. Especially, tensile strength of CV systems is much higher than that of EV systems. It was known that the tensile strength and elongation at break of CV systems are higher than those of EV

systems [23]. When the sulfur was used as a cross-linking agent at high temperature in this study, high temperature causes a strong odor of sulfur. Tensile strength of all the dynamically vulcanized TPU/BR (70/30) in Table 2 is lower than that of simple TPU/BR (70/30) blends in Fig. 1. This indicates that thermal degradation is still a problem in this formulation.

Table 2 Tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends using sulfur

| Tensile properties | Sample notation | | | | | | | |
|-------------------------|-----------------|-----|------|-----|------|-----|------|-----|
| | A | B | C | D | E | F | G | H |
| Tensile strength (MPa) | 11.4 | 8.2 | 12.4 | 7.6 | 13.8 | 7.4 | 11.8 | 2.8 |
| Elongation at break (%) | 508 | 497 | 530 | 485 | 526 | 525 | 528 | 157 |

The tensile strength and elongation at break of all the dynamically vulcanized TPU/BR (70/30) blends (Fig. 3-6 and Table 2) are not higher than those of simple TPU/BR (70/30) blends. This is due to thermal degradation of BR which could be accelerated by DCP or sulfur. Because of a strong odor, sulfur was not used as a cross-linking agent for further investigations in this study. Since melting temperature of TPU is high, high temperature should be used even though high temperature and DCP lead to the thermal degradation of BR.

Therefore, the exposure time of BR to high temperature should be optimized. For this purpose, 2-step processing was investigated. To decrease thermal degradation of BR and achieve the homogenous dispersion of DCP in BR, at 1st step, BR and DCP were mixed in the kneader at lower temperature (90 °C) for 10 min. At 2nd step, TPU was firstly melted at 160 °C for 2 min followed by the addition of premixed BR and DCP. Mixing was continued for different mixing time. Too short mixing time leads to the poor dispersion of BR in the TPU matrix, and too long mixing time leads to the thermal degradation of BR.

Fig. 7 and 8 show the effect of mixing time on the tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends prepared using 2-step processing, respectively. With increasing mixing time at 2nd step, tensile strength and elongation at break of the TPU/BR (70/30) blends initially increased and reached a maximum value at 8 min. And then they decreased with further increase of mixing time. The decrease could be due to the thermal degradation of BR. This result indicates that the optimization of mixing time at 2nd step is very important for dynamically vulcanized TPU/BR (70/30) blends. Tensile strength and elongation of dynamically vulcanized TPU/BR (70/30) blends prepared at 8 min (mixing time) were higher than those of simple TPU/BR (70/30) blend observed in Fig. 1. The hardness of dynamically vulcanized TPU/BR (70/30) blends prepared at 8 min (mixing time) is 65 (Shore A). Therefore, using 2-step processing, thermal degradation of BR was minimized with the homogeneous dispersion of DCP in BR at optimal mixing time, leading to the increase of tensile strength and elongation at break.

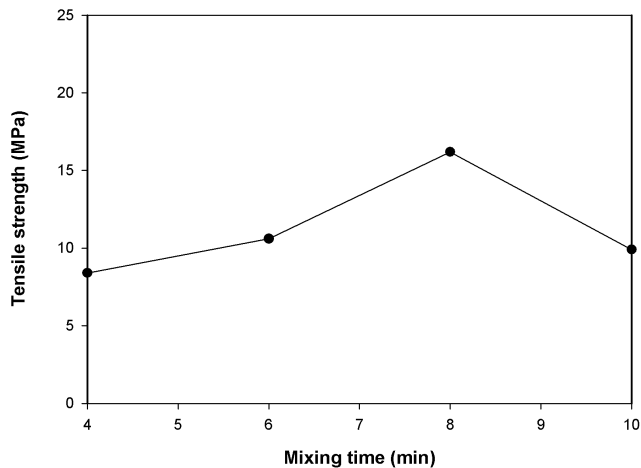


Fig. 7 Effect of mixing time on the tensile strength of dynamically vulcanized TPU/BR (70/30) blends prepared using 2-step processing

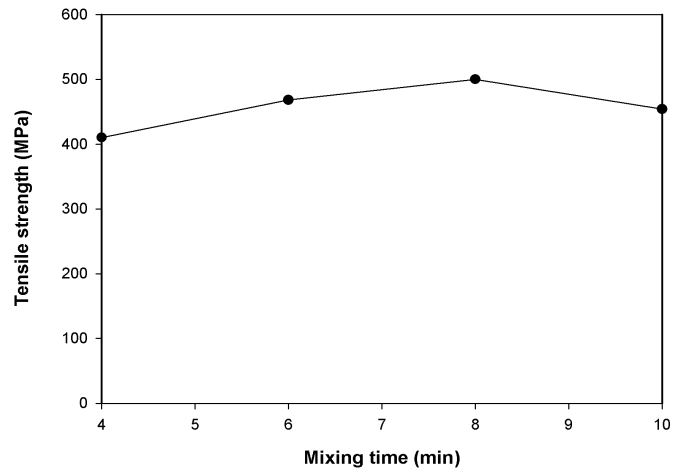


Fig. 8 Effect of mixing time on the elongation at break of dynamically vulcanized TPU/BR (70/30) blends prepared using 2-step processing

In order to confirm that BR is cross-linked during dynamic vulcanization, the morphologies of TPU, simple TPU/BR (70/30) and dynamically vulcanized TPU/BR (70/30) blends are investigated with SEM. Fig. 9 shows the SEM images of cross-sections of TPU etched by hot xylene. The extracted portion is not observed in Fig. 9. This result indicates that TPU is not dissolved in hot xylene. Fig. 10 shows simple TPU/BR (70/30) blend etched by hot xylene. The dark portions represent the uncross-linked BR phase extracted out by hot xylene. Fig. 9 shows the SEM images of cross-sections of dynamically vulcanized TPU/BR (70/30) blend etched by hot xylene. The dark portions extracted out by hot xylene are not observed in Fig. 11. This result indicates the fully cross-linked BR phase for dynamically vulcanized TPU/BR (70/30) blends.



Fig. 9 SEM images of cross-sections of TPU etched by hot xylene

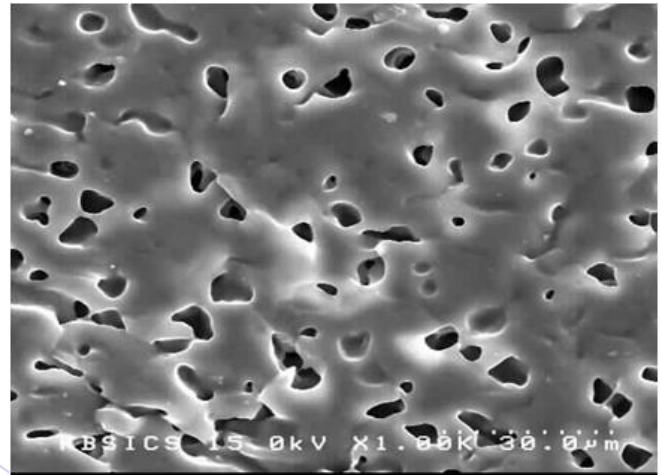


Fig. 10 SEM images of cross-sections of simple TPU/BR (70/30) blend etched by hot xylene

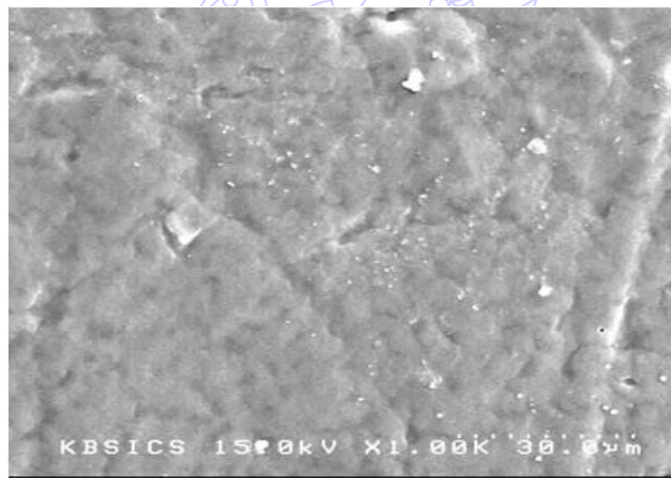


Fig. 11 SEM images of cross-sections of dynamically vulcanized TPU/BR (70/30) blend etched by hot xylene

4. Conclusions

When DCP was used as a cross-linking agent, tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends decrease with increasing content of DCP. The decrease of tensile strength and elongation at break is due to the thermal degradation of BR which could be accelerated by the presence of DCP. In this case, the effect of peroxide concentration is the most important parameter. The addition of optimal content of stabilizer leads to the improvement of tensile strength and elongation at break of dynamically vulcanized TPU/BR (70/30) blends. However, still tensile strength of the dynamically vulcanized TPU/BR (70/30) blends is lower than that of the simple TPU/BR (70/30) BR blends. When sulfur was used as a cross-linking agent, still tensile strength of the dynamically vulcanized TPU/BR (70/30) blends is lower than that of the simple TPU/BR (70/30) blends.

Two-step processing using DCP as a cross-linking agent was employed in order to decrease thermal degradation of BR and achieve the homogenous dispersion of DCP in BR. Tensile strength and elongation of the dynamically vulcanized TPU/BR (70/30) blends prepared at 8 min (mixing time) are higher than those of the simple TPU/BR (70/30) blends. The hardness of dynamically vulcanized TPU/BR (70/30) blends prepared at 8 min (mixing time) is 65 (Shore A).

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