

# Effect of the Processing Molding Temperature on the Crystalline Structure and Properties of Acrylonitrile-Butadiene Rubber/Trinylon Thermoplastic Vulcanizates

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**ABSTRACT:** The effect of the processing molding temperature on the properties and crystalline structure of acrylonitrile-butadiene rubber (NBR)/nylon 6,66,1010 (trinylon) thermoplastic vulcanizates (TPV) was studied. With decreasing molding temperature, the stress at 100% and elongation at break of TPV changed slightly, and the solvent resistance of TPV improved. The best conditions for processing molding were 170°C and 12 min. The crystalline structure of the nylon continuous phase in TPV was investigated by X-ray diffraction, polarized optical microscopy, and dif-

ferential scanning calorimetry. The results show that the crystalline structure of the nylon phase in TPV was more perfect/orderly and formed  $\alpha$ -crystalline structure at a processing molding temperature of 170°C. Therefore, the oil resistance of NBR/trinylon TPV clearly improved. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1374–1379, 2006

**Key words:** crystal structures; elastomers; mechanical properties; nylon; processing

## INTRODUCTION

Nylon 6,66,1010 (trinylon) is a semicrystal engineering plastic with a low melting temperature ( $T_m$ ). It has excellent chemical resistance and a high abrasion resistance.<sup>1</sup> NBR is a kind of rubber with good oil resistance. Therefore, NBR and trinylon were blended and *in situ* dynamically vulcanized to produce a new kind of TPV with good chemical resistance and resilience and processing properties.<sup>2–4</sup> As reported,<sup>5</sup> the chemical resistance and mechanical properties were influenced by the crystal structure of the nylon phase in TPV, which was related to the processing conditions. So the conditions of processing molding for TPV was an important factor influencing the properties of TPV.

In this article, the effects of the processing molding temperature on the properties of NBR/nylon TPV, differential scanning calorimetry (DSC) curves, and X-ray diffraction (XRD) data obtained from trinylon and NBR/trinylon TPV at various processing temperatures are discussed. The evidence for the formation of  $\alpha$ -crystalline structure in the trinylon continuous phase of TPV molded at 170°C are presented.

## EXPERIMENTAL

### Materials and recipe

Nylon 6,66,1010 (PSGN-170) was produced by Shanghai Sailulu Chemical Co., Ltd. (Shanghai, China); NBR (N220S) was produced by Japan JSR Co., Ltd. (Tokyo, Japan). The solvent used in the study was a 70/30 (v/v) mixture of gasoline 93<sup>#</sup> (produced by China Petroleum Chemical Corp., Beijing, China) and analysis-grade toluene (produced by Beijing Chemical Plant, Beijing, China). Other common additives, such as dicumyl peroxide (analysis grade), the antioxidant polymerized 2,2,4-trimethyl-1,2-dihydroquinoline resin (RD), and stearic acid, were produced in China.

The recipe of TPV was the following: NBR (70), trinylon (30), dicumyl peroxide (2.1), antioxidant RD (0.7), and stearic acid (1.1). The number after each item represents the loading amount (by weight) of each kind of materials. For example, in the blends of 70 g NBR and 30 g trinylon, 2.1 g dicumylperoxide, 0.7 g antioxidant RD and 1.1 g stearic acid were added.

### Preparation of the samples

#### Preparation of TPV

NBR compound with the components was blended with melting nylon on a twin roller at 170°C and *in situ* dynamic vulcanized for 6 min, and then, vulcanized NBR particles were dispersed into the nylon phase

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under shear force action. So, NBR/trinylon TPV was prepared.

#### Preparation of the samples

The TPV material was put into the mold, which was a frame (2.0 mm thick) on a flat press machine with a controlled temperature, and was heated under 2 MPa for 10 min and then under 15 MPa for 2 min. Then, the hot mold with the sample was transferred to a room-temperature press machine to cool under 15 MPa; this was the rapid cooling method. When the hot mold with the sample was cooled to follow the press machine cooling in nature, this was the slow cooling method. So, the TPV samples were made.

#### Measurements

The curing characteristic of the NBR/trinylon blend were measured with an oscillating disc rheometer (P355B2, Beijing Huanfeng Chemical Mechanical Plant, Beijing, China). Tensile tests were performed on dumbbell-shaped specimens according to ASTM D 412.

For the oil resistance measurements, TPV samples were weighed ( $W_1$ ) and immersed in a mixed solution of gasoline and toluene (volume ratio = 70 : 30) at 40°C for 24 h, and the swollen samples were weighed ( $W_2$ ). The two corresponding volumes ( $V_1$  and  $V_2$ ) were calculated by the measurement of the density of TPV and its swelling sample. The mass/volume variation ratio of TPV samples were calculated by  $(W_2 - W_1)/W_1$  or  $(V_2 - V_1)/V_1$ .

Microscopy photographs were obtained with a PM-10AD polariscope made by Olympus Co., Ltd., Tokyo, Japan.

DSC measurements were carried out on a PerkinElmer DSC-7 (Wellesley, MA). The rate of temperature rise was 10°C/min in a nitrogen atmosphere.

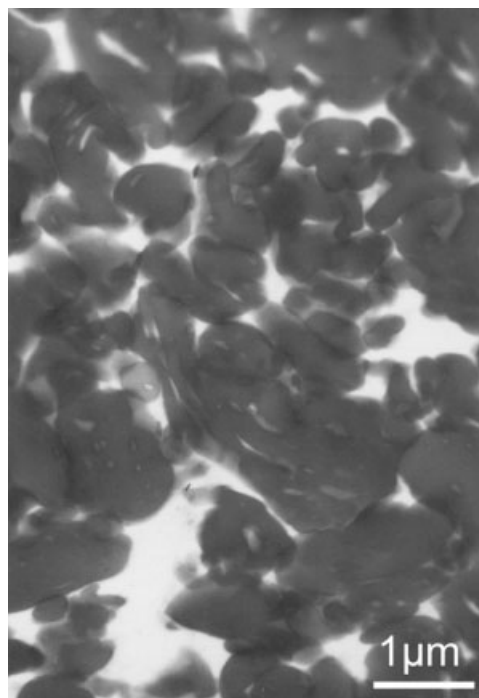
A transmission electron microscope (H-800, Hitachi Co., Ltd., Tokyo, Japan) operated at 200 kV was used to take pictures of the specimens, which were cut into ultrathin slices by microtomy at -100°C and stained with osmium tetroxide.

XRD scans curves were obtained at a scanning rate of 10°/min on an X-ray diffractometer (D/Max-IIIC, Rigaku Radial, Japan). XRD patterns with Cu K $\alpha$  radiation ( $\lambda = 0.1540$  nm) at 40 kV and 200 mA were recorded in the range  $2\theta = 5\text{--}40^\circ$ . The sample measured was a piece of TPV material with a frame 2.0 mm thick.

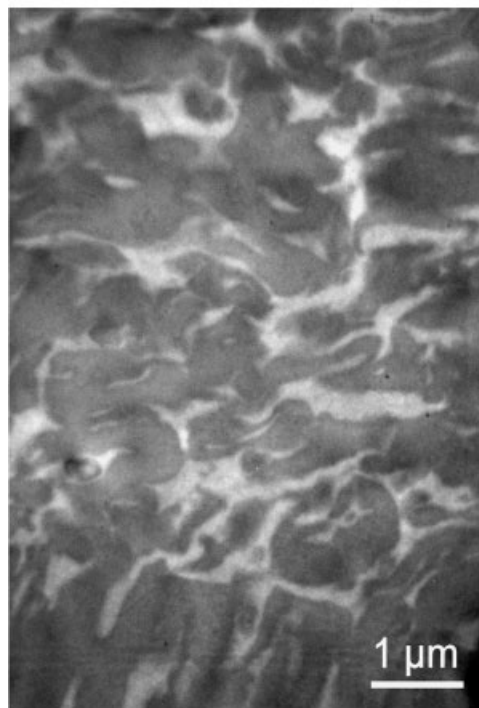
## RESULTS AND DISCUSSION

### Effect of the processing molding temperature on the morphology of TPV

As shown in Figure 1, NBR formed a dispersed phase with a spherical and strip shape, and nylon formed a



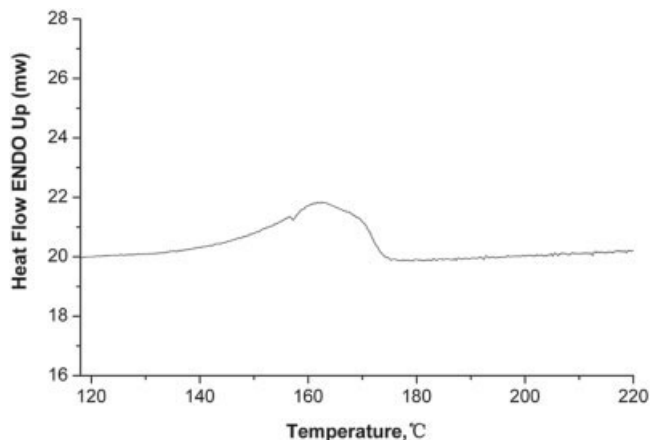
(a)



(b)

**Figure 1** Morphologies of NBR/trinylon TPV samples (a) dynamic vulcanized at 170°C and (b) TPV sample dynamic vulcanized at 170°C and then molded at 180°C.

continuous phase in TPV. After TPV was molded at 180°C, its morphology showed no significant difference, and some of the particle shape of the NBR dispersed phase only changed to a similar ellipse from a



**Figure 2** DSC curves of trinylon at a heating rate of 10°C/min.

sphere. This showed that the molding processing did not change the morphology of TPV.

#### Effect of the processing molding temperature on the properties

As shown in Figure 2, the melting zone of trinylon was from 153.7 to 176.5°C. In this study, the range of molding processing temperatures was chosen from 170 to 185°C.

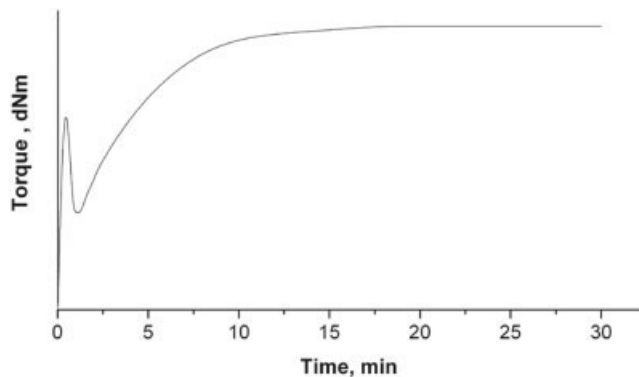
The effects of the processing molding temperature on the properties of TPV are shown in Table I. The stress at 100% and the elongation at break of TPV changed slightly with increasing molding temperature, and the tensile strength of TPV molded at 175°C was the biggest. This shows that the equitable matching of the deformation ability of the nylon continuous phase and the NBR disperse phase could give TPV good mechanical properties.

As also shown in Table I, the mass and volume swelling ratios of the samples in the solvent mixture decreased with decreasing molding temperature in the range of 170–185°C. The solvent mixture resis-

**TABLE I**  
Effect of the Molding Temperature on the Properties of the TPV Samples

	Molding temperature (°C)			
	170	175	180	185
Stress at 100% (MPa)	8.7	9.3	8.5	8.0
Tensile strength (MPa)	20.9	23.9	21.5	21.9
Elongation at break (%)	312	310	300	308
Permanent set (%)	18	22	22	20
After swelling in a mixture of gasoline and toluene				
Mass swelling ratio (%)	19.0	23.5	27.4	27.6
Volume swelling ratio (%)	24.1	28.4	32.5	33.8

All samples were cooled by the rapid cooling method.



**Figure 3** Curing curve of NBR/trinylon blends at 170°C.

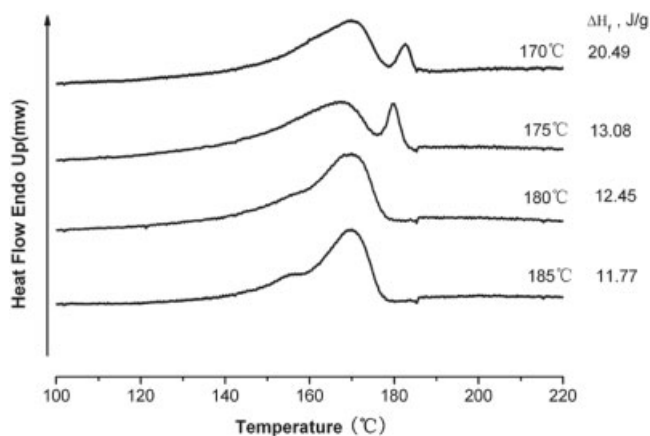
tance of nylon was much better than that of NBR (the mass and volume swelling ratios of the NBR vulcanizate in the solvent mixture measured in our laboratory were 42.4 and 51.4%, respectively, and those of nylon were 0.5 and 0.6%, respectively). Because dynamic vulcanized processing gave the NBR phase an optimum curing degree (Fig. 3), the effect of the NBR phase molded again at high temperature on the improvement of the solvent resistance of TPV did not have to be thought out. This shows that the molding temperature only influenced the crystal structure of the trinylon phase in TPV and then made TPV behave with different solvent resistance.

#### Crystal structure of the trinylon phase in TPV

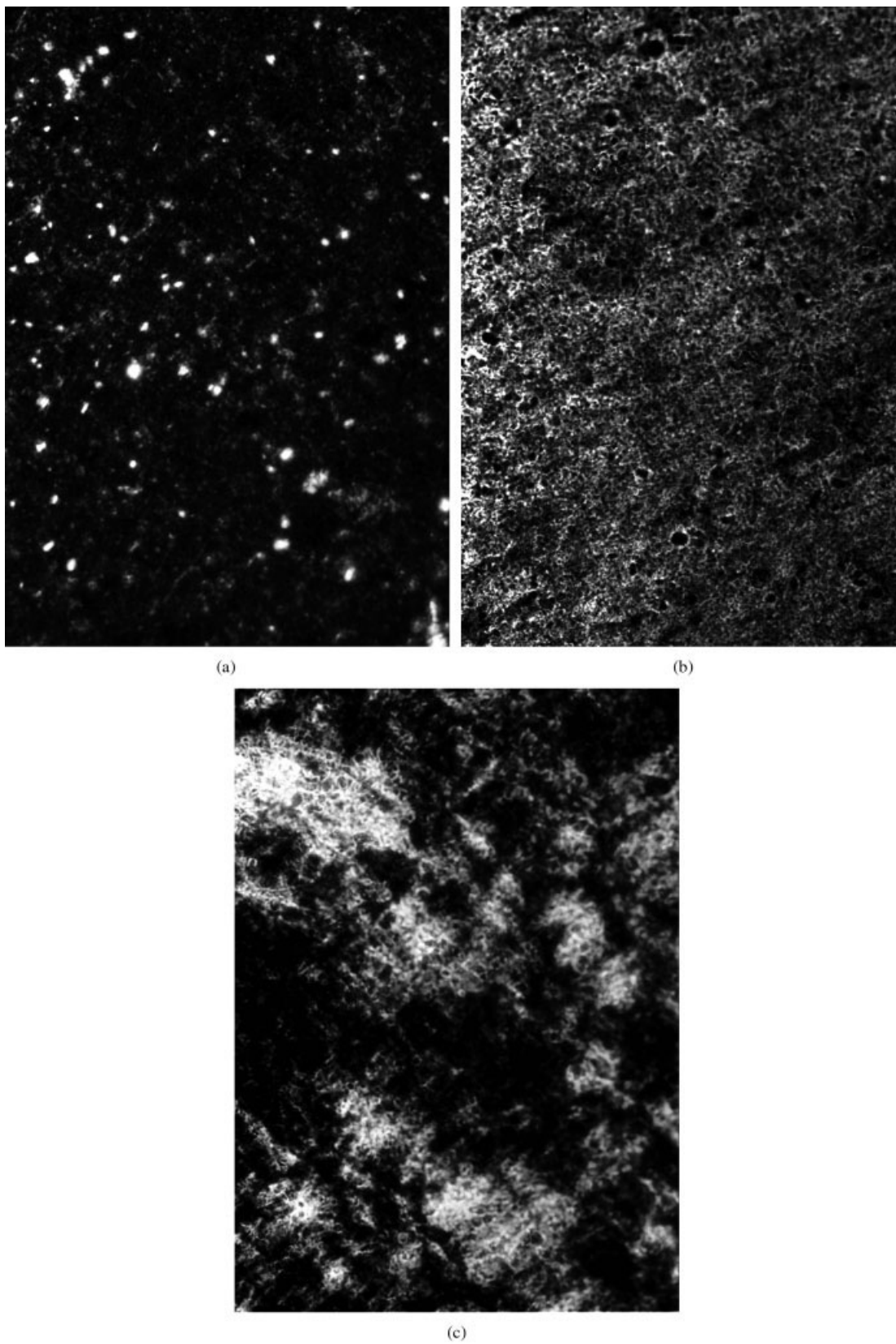
##### Dsc curves

The DSC curves of TPV at different molding temperatures are shown in Figure 3.

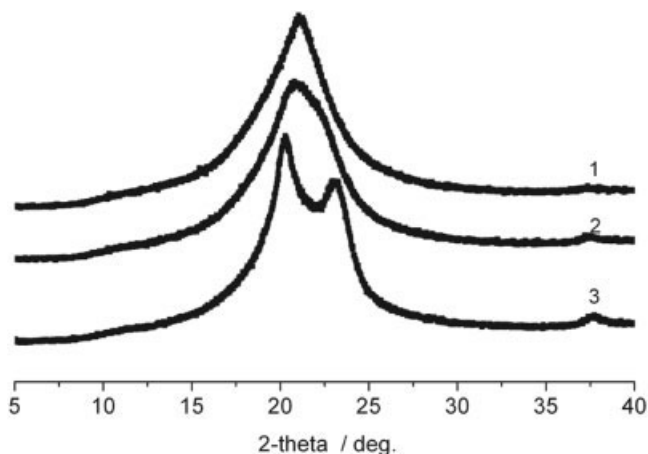
As is shown in Figure 4, there were two endothermic peaks in the curves of TPV samples molded at 170 and 175°C. The temperature scope for the high-temperature melting peak went beyond the melting zone



**Figure 4** DSC curves of TPV samples at different molding temperatures (rapid cooling method).



**Figure 5** Photographs of the polarization microscopy of TPV at different molding temperatures: (a) 180, (b) 175, and (c) 170°C.



**Figure 6** XRD scan of nylon: nylon molded at (1) 185 and (2) 170°C by the rapid cooling method and (3) 170°C by the slow cooling method.

of pure trinylon. The enthalpy ( $\Delta H_f$ ) of the sample molded at 170°C was bigger than that at 175°C. When the molding temperatures were 180 and 185°C, the DSC curve of TPV sample had only one endothermic peak. This shows that the crystalline structure of TPV was influenced by the molding temperature. The two peaks of the DSC curve for the TPV sample molded at 170 and 175°C also suggested that there were two crystalline forms in the trinylon phase.<sup>1</sup> When the molding temperature was above 180°C, the nylon melted and was then rapidly cooled, and the nylon phase transformed from an amorphous state to a semi-crystalline state. The crystalline structure of the nylon continuous phase in TPV was not perfect, and the solvent could permeate through TPV easily. When the molding temperature for TPV was 170°C, which was below  $T_m$  of trinylon, there were still some nucleus or imperfect crystalline structure in the trinylon phase. When rapidly cooled, some polymer chains piled up around them or stacked more tightly, so the crystalline structure became more perfect.<sup>3</sup>  $\Delta H_f$  and heat of fusion increased with decreasing processing temperature. In conclusion, the reason the oil resistance was improved was that the crystalline structure of the nylon phase was more perfect and the crystal degree was higher when molding temperature chosen was close to  $T_m$  of nylon.

#### Effect of the molding temperature on the crystal morphology of TPV

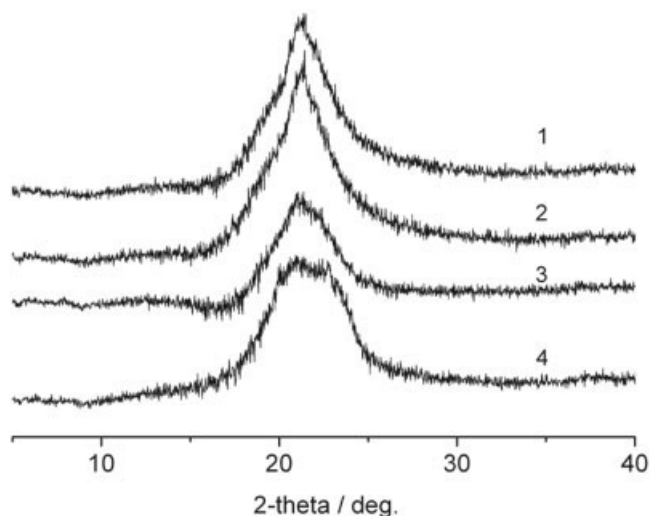
Figure 5 shows three polarized optical pictures of TPV samples molded at 170, 175, and 180°C. There are only a few dots in Figure 5(a), but the district of light in Figure 5(b,c) were connected, and that in Figure 5(c) is most intense. This figure indicates further that the crystal structure of the trinylon continuous phase in

the TPV sample molded at 170°C was more perfect/orderly and that the solvent resistance was improved obviously.

#### XRD analysis

The three profile-fitted XRD scans of the trinylon samples molded at 170 and 180°C, respectively, and cooled in different conditions are shown in Figure 6. The XRD scans of the trinylon phase in TPV were obtained after the NBR curve was subtracted from the TPV curve.

The scans in Figure 6 reflect the substantial changes in the structure as the trinylon was heated to different temperatures in the molder and then cooled to room temperature at different speeds. The XRD data for trinylon molded at 170°C and slowly cooled to room temperature [Fig. 6(3)] showed a pair of peaks at  $2\theta = 20.3$  and  $23.2^\circ$  and were labeled  $\alpha_1$  and  $\alpha_2$ , respectively. This shows that trinylon had crystallized in the  $\alpha$ -crystalline structure with triclinic structure, whereas nylon molded at 185°C and cooled rapidly [the scan of trinylon; Fig. 6(1)] showed a strong peak at  $2\theta = 21^\circ$ . This indicates that crystalline structure for trinylon had changed, and an  $\gamma$ -crystalline form with pseudohexagonal structure was formed. The results show that the trinylon also exhibited Bill transition behavior similar to nylon 6,6.<sup>5,6</sup> There was a wide crystalline reflection connected at  $20.8$ – $22.5^\circ$  in the XRD pattern of the nylon sample molded at 170°C and cooled rapidly. This shows that the pattern consisted of  $\alpha$ - and  $\gamma$ -crystalline peaks and some amorphous peak because of the three-block structure of nylon. According to a previous report,<sup>7</sup> the chains of the  $\alpha$ -crystalline form arrange closer than those of the



**Figure 7** XRD scans of the nylon phase in TPV samples molded at (1) 185, (2) 180, (3) 175, and (4) 170°C by the rapid cooling method.

$\gamma$ -crystalline form.  $T_m$  of the  $\alpha$ -crystalline form was higher.

If Figure 7 is compared with Figure 6, one can see that the trinylon phase in TPV underwent a structural transition similar to that of pure trinylon at different molding temperatures and cooling speeds. The XRD scans of the TPV samples molded at 185 and 180°C with the rapid cooling method showed the patterns of the  $\gamma$ -crystalline form. The XRD scans of TPV samples molded at 175 and 170°C showed the coexistence of the  $\gamma$ - and  $\alpha$ -crystalline forms. The XRD result was consistent with the DSC result in which the sample molded at 170°C and cooled rapidly behaved characteristically of the  $\alpha$ -crystalline form.

In summary, a low molding temperature allowed the trinylon molecular chains to stack orderly and easily to produce the  $\alpha$ -crystalline form. Therefore, molding at 170°C was more fit for NBR/trinylon TPV to ensure that TPV had a high temperature resistance and good solvent resistance.

### CONCLUSIONS

1. The stress at 100% and elongation at break of TPV decreased slightly with increasing molding

temperature (170°C~185°C), and the tensile strength of TPV molded at 175°C was the biggest. The solvent resistance of the TPV sample molded at 170°C was improved markedly.

2. Trinylon molded at different temperatures and cooled at different speeds could form  $\alpha$ - and  $\gamma$ -crystalline structures. This showed a typical Bill transition.
3. Processing molding at 170°C made the crystalline structure of the trinylon phase in TPV more perfect/orderly, and some chains formed  $\alpha$ -crystalline phase. This was the natural reason that the high temperature resistance and solvent resistance of NBR/trinylon TPV were improved.

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