

# Investigation of Crystallization Behavior in Dynamically Vulcanized EPDM–Nylon Copolymer Blends

Hua Huang,<sup>1,2</sup> Xin Liu,<sup>1</sup> Takayuki Ikehara,<sup>2</sup> Toshio Nishi<sup>2</sup>

<sup>1</sup>School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

<sup>2</sup>Department of Applied Physics, School of Engineering, University of Tokyo, 7-3-1 Hongo Bunkyo-Ku, Tokyo, 113-8656, Japan

Received 28 August 2002; accepted 17 December 2002

**ABSTRACT:** A thermoplastic vulcanizate (TPV) of a ethylene–propylene–diene terpolymer (EPDM) and nylon copolymer (PA) was prepared by dynamic vulcanization. Maleic anhydride (MAH)–grafted EPDM (EPDM–*g*–MAH), MAH–grafted EPR (EPR–*g*–MAH), and chlorinated polyethylene (CPE) were used as compatibilizers. The effect of dynamic vulcanization and compatibilizer on the crystallization behavior of PA was investigated. Differential scanning calorimeter measurement results showed no pronounced shift in the crystallization temperature for PA in EPDM–PA TPV compared to that for PA in the neat state, whereas the crystallization temperature increased after adding compatibilizer. The decrease in the crystallinity of TPVs was a result of the crystallization occurring in confined spaces between rubber particles. The equilibrium melting temperature ( $T_m^0$ ) of the PA copolymer was measured and was determined to be 157°C. The isothermal crystallization kinetics of PA in the neat and TPV states also was investigated. The crystallization rate was highest in the compatibilized TPV and lowest in the neat PA, whereas it was intermediate in the uncompatibilized TPV unvulcanized blends.

Compared with unvulcanized EPDM–PA blends, the dynamic vulcanization process seemed to cause an obvious increase in the crystallization rate of the PA copolymer, especially when a suitable compatibilizer was used. This occurred because the dynamic vulcanization introduced fine crosslinked rubber particles that could act as heterogeneous nucleating centers. In addition, the use of a suitable compatibilizer permitted the formation of finely dispersed vulcanized rubber particles and therefore increased the density of the nucleating centers. The complex morphology of the blends was investigated by atomic force microscopy to evaluate the effect of compatibilizer on the size of the dispersed rubber particles. Compared with the morphology of TPVs with the same dosage of EPDM–*g*–MAH compatibilizer, the morphology of TPVs using EPR–*g*–MAH as compatibilizer showed much smaller dispersed rubber particles, which may have contributed to the higher crystallization rate. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 824–829, 2003

**Key words:** nylon copolymer; crystallization; dynamic vulcanization; compatibilizer

## INTRODUCTION

Dynamic vulcanization, the process of vulcanizing elastomer during melt-mixing with molten thermoplastic, is the best way to prepare thermoplastic vulcanizates (TPVs), which combine the excellent processing characteristics of thermoplastics with the elastic properties of elastomers. The elastic properties of TPVs are similar to the more conventional class of thermoplastic elastomers based on hard-segment and soft-segment block copolymers.<sup>1,2</sup> Dynamic vulcanization was first described by Gessler<sup>3</sup> in 1962 and then developed by Fisher<sup>4</sup> and Coran et al.<sup>5,6</sup> This technology has led to a significant number of new thermoplastic elastomeric products commercialized during the mid- to late 1980s.<sup>7</sup> Some thermoplastic elastomers

that were vulcanized through dynamic vulcanization have been commercialized with trade names such as Santoprene and Geolast.

A well-known commercial example of dynamically vulcanized thermoplastic-elastomer compositions are blends of polypropylene (PP) and ethylene–propylene–diene terpolymer rubber (EPDM).<sup>8</sup> These TPVs are prepared by first melt-mixing PP with EPDM, forming a cocontinuous phase morphology. Subsequently, a vulcanizing agent is added to crosslink the EPDM rubber phase, and the crosslinked rubber phase is sheared into small particles and then finely dispersed in the thermoplastic matrix. Research on the dynamic vulcanization of blends of EPDM elastomer with PE,<sup>8</sup> blends of nitrile elastomer with nylon,<sup>9</sup> and blends of chlorinated polyethylene rubber with nylon<sup>10</sup> have also been reported. However, few articles are available on dynamic vulcanization of EPDM–nylon blends. Ma et al. studied the structure and properties of EPDM–nylon copolymer high-performance elastomer<sup>11–12</sup>; however, the elastomer was prepared by static vulcanization.

EPDM–nylon TPV is difficult to prepare because of the high interfacial energy between the two compo-

Correspondence to: H. Huang (huanghua@sjtu.edu.cn).

Contract grant sponsor: Ministry of Education, Science, Sports, Culture, and Technology, Japan, Grant-in-Aid for Scientific Research on Priority Areas; contract grant number: 413/13031012.

nents. By using a suitable compatibilizer and dynamic vulcanization, EPDM-nylon copolymer TPV was successfully developed, as described in our early work.<sup>13</sup> Different variables may affect the properties of EPDM-nylon blends: the ratio of EPDM to nylon, the volume fraction of compatibilizer, the molecular weight, the viscosity of EPDM and nylon, the composition and functionality of the compatibilizer, and the crystalline structure of these systems. This article focuses on the effect of dynamic vulcanization on the crystallization behavior of EPDM-nylon copolymer TPV and on the alteration of the crystallization behavior caused by the compatibilizer.

Atomic force microscopy (AFM) has been recognized as a powerful surface characterization technique and has been widely used to study the surface morphology of homopolymers,<sup>14-15</sup> block copolymers,<sup>16-18</sup> and polymer blends.<sup>19-24</sup> In this study AFM measurements were used to evaluate the effect of compatibilizer on the size of the dispersed rubber particles and on changes in the crystallization behavior of the PA copolymer matrix in TPVs.

## EXPERIMENTAL

### Materials

Ethylene-propylene-diene terpolymer EP4045 (ENB type), with a propylene content of 35.9 mol % and ML1+4 (100°C) = 42, came from Jilin Petroleum Chemical Co., Ltd. (Jilin, China). A copolymer of nylon 1010, nylon 6-6, and nylon 6 (70% nylon 1010, 20% nylon 6-6, 10% nylon 6) with a melting point of 150°C was produced by the Shanghai Celluloid Factory (Shanghai, China). EPR-g-MAH 1801 came from Exxon Co. Ltd. (Houston, TX). EPDM-g-MAH (grafting degree 1.0%) was synthesized in our own laboratory. Chlorinated polyethylene (CPE) with a chlorine content of 36% was from Jiangsu Dongtai Chemical Factory (Lianyungang, China). Zinc oxide (ZnO), stearic acid (SA), tetramethylthiuram disulfide (TMTD), *N,N'*-*m*-phenylene bismaleimide (HVA-2), dibenzothiazyl disulfide (MBTS), dicumyl peroxide (DCP), and sulfur were used as received.

### Preparation of EPDM-PA TPV

Prior to the melt-mixing operations, all materials were dried under vacuum at 80°C overnight. The preparation of EPDM-PA TPV was performed at 180°C and 80 rpm in a Haake Rheocord 90 batch mixer. After 1 min of melting the nylon-compatible blends in the mixer, EPDM was added. After 4 min had elapsed, curatives and curing coagents were added while mixing. Mixing was continued for 7 min after the last ingredient was added. The batch was dumped, cut into small pieces, and remixed for an additional 3 min to ensure homogeneity. The composition was then

compression-molded in a press at 180°C and cold-pressed to produce samples for testing.

The amounts of curatives and curing coagents per 100 parts of rubber used in all EPDM-PA TPVs were: 2 parts sulfur, 5 parts ZnO, 1 part TMTD, 0.5 parts MBTS, and 2 parts SA.

### Thermal analysis

The crystallization behavior of the TPVs was analyzed by a Perkin-Elmer DSC-7 in a nitrogen atmosphere. The samples (about 6 mg each) were first heated to 180°C, isothermalized for 5 min, and then cooled to 40°C at a rate of 5°C/min. The crystallization temperature ( $T_c$ ) and the enthalpy of crystallization ( $\Delta H$ ) were obtained from, respectively, the maximum and the area of the exothermic peaks.

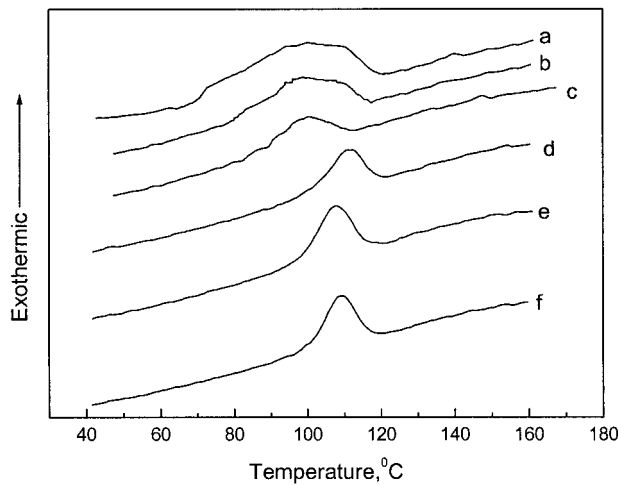
For studies of crystallization kinetics of PA in blends, a two-step procedure was applied. The samples were annealed at 180°C for 10 min and then cooled at a rate of 80°C/min to the preset crystallization temperature of PA. The crystallization heat was recorded in terms of time required until crystallization was completed or until any heat liberated was too small to be detected.

### AFM analysis

AFM images were acquired at RT in noncontact mode using a JEOL JSPM-4210. The cantilevers (OMCL-AC160TS-C2, Olympus) had a spring constant of 36-66 Nm<sup>-1</sup> and a resonance frequency of 283-347 kHz. To get an ultrasurface, the specimen was cut with a diamond knife at -100°C.

## RESULTS AND DISCUSSION

Thermal analysis of the EPDM-PA thermoplastic vulcanizates for different compatibilizers was done using differential scanning calorimetry (DSC). The cooling curves for the neat nylon copolymer and EPDM-PA TPVs with or without compatibilizer are shown in Figure 1. The crystallization temperature ( $T_c$ ) and the enthalpy of crystallization ( $\Delta H$ ) of the PA phase for the different blend compositions are given in Table I. The wide crystallization peak of neat PA may be a result of the copolymer nature of nylon 1010, nylon 6-6, and nylon 6 (70% nylon 1010, 20% nylon 6-6, 10% nylon 6). Unvulcanized EPDM-PA blends showed almost the same crystallization behavior as neat PA, except the enthalpy of crystallization was a little lower, which may be because PA was the dispersed phase in the unvulcanized EPDM-PP blends. The crystallization peak became narrower for EPDM-PA TPVs, possibly because the rubber particles introduced may have acted as heterogeneous nucleating centers. This tended to result in the rapid crystallization of the main part (nylon 1010) of the PA copoly-

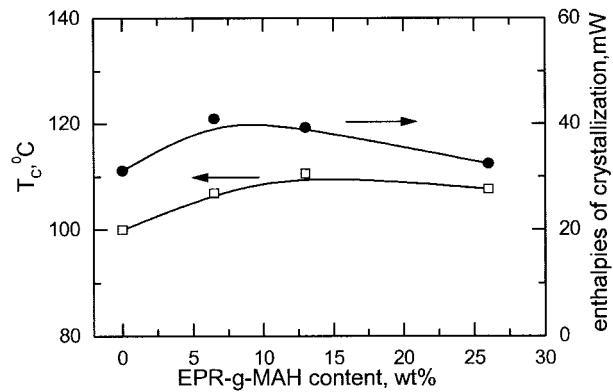


**Figure 1** DSC cooling traces (cooling rate of  $-5^{\circ}\text{C}/\text{min}$ ): (a) PA, (b) EPDM-PA (65:35), (c) EPDM/EPR-g-MAH/PA (52:13:35), (d) EPDM/EPDM-g-MAH/PA (52:13:35), (e) EPDM-CPE-PA (52:13:35).

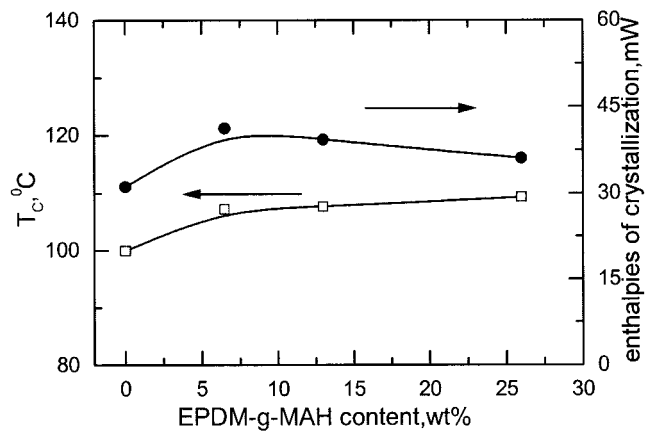
mer, which may have suppressed the crystallization of the other parts. The EPDM-PA TPVs had almost the same  $T_c$  as neat PA, whereas the  $T_c$  of the EPDM-PA-compatibilizer TPVs was about  $8^{\circ}\text{C}$ – $10^{\circ}\text{C}$  higher. This phenomenon can be ascribed to the addition of compatibilizer helping to form a fine dispersion of the crosslinked rubber particles, which could subsequently act as heterogeneous nucleating centers for PA crystallization. Moreover, for the EPDM-PA-compatibilizer TPVs, the  $T_c$  increased and finally arrived at a constant value with increasing compatibilizer content (as shown in Fig. 2). The enthalpy of crystallization of the PA phase in the TPVs was less than that in the neat PA. The reason for this decrease in crystallinity could be the crystallization in confined spaces between rubber particles. Figure 2 shows that the enthalpy of crystallization of the PA phase went through a maximum value at a compatibilizer content of 20% on rubber when either EPR-g-MAH or EPDM-g-MAH was used as compatibilizer. The addition of compatibilizer may reduce the particle size of the dispersed rubber phase, which is beneficial for the nucleating of PA, but at the same time introduce the compatibilization reaction between compatibilizer and PA, which restricts the growth of crystalline PA. There-

**TABLE I**  
Crystallization Temperature and Enthalpies of Crystallization of PA Phase

	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta H_{PA}$ (mW)
PA	99.8	41.2
EPDM/PA (unvulcanized) (65:35)	99.9	39.4
EPDM/PA (65:35)	99.9	31.1
EPDM/EPR-g-MAH/PA (52:13:35)	110.5	39.1
EPDM/EPDM-g-MAH/PA (52:13:35)	107.5	39.1
EPDM/CPE/PA (52:13:35)	108.7	36.0



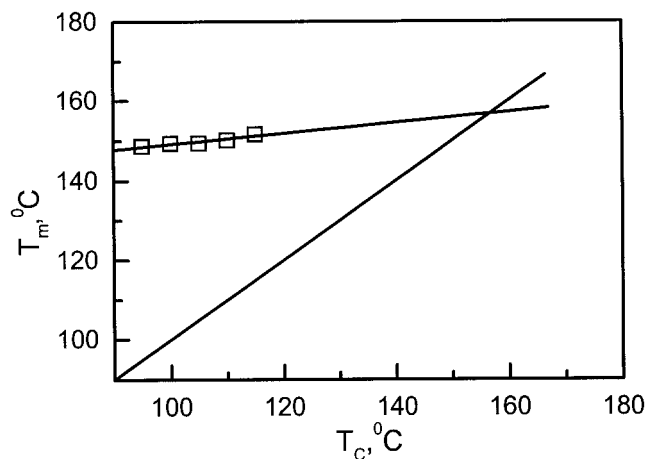
(a)



(b)

**Figure 2** Effect of compatibilizer content on  $T_c$  and enthalpies of crystallization in EPDM-PA TPVs (EPDM+compatibilizer/PA: 65:35).

fore, the enthalpy of crystallization of the PA phase went through a maximum with increasing compatibilizer content.



**Figure 3**  $T_m$  versus  $T_c$  for PA copolymer.

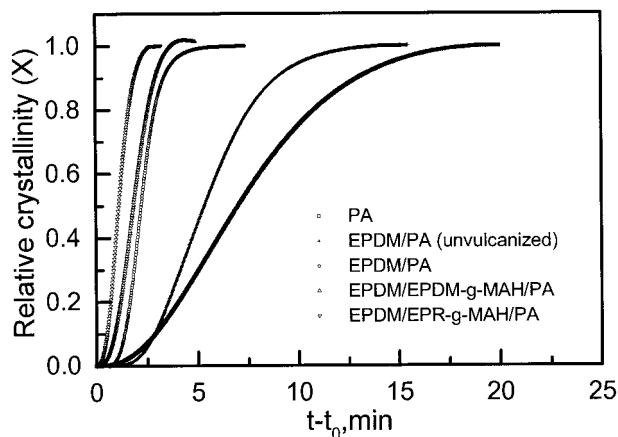


Figure 4 Normalized crystallinity versus time for PA copolymer at  $T_c = 100^\circ\text{C}$ .

As nothing in the literature has mentioned the equilibrium melting temperature ( $T_m^0$ ) of PA copolymer, the melting temperature ( $T_m$ ) of PA copolymer crystallized at different crystallization temperatures was measured in this study, which is plotted in Figure 3. By extrapolation, the  $T_m^0$  of the PA copolymer was determined to be  $157^\circ\text{C}$ . Thus, to ensure suitable undercooling, an isothermal crystallization temperature in the range of  $100^\circ\text{C}$ – $108^\circ\text{C}$  was chosen for the study of the crystallization kinetics.

Normalized degrees of crystallinity,  $X$ , determined under isothermal condition is plotted versus time for  $T_c = 100^\circ\text{C}$  in Figure 4. Quantity  $t_0$  denotes the induction period, which was determined experimentally and defined as the time after which the first deviation of the DSC trace from the baseline could be detected in an isothermal crystallization experiment. As can be seen, the nucleation induction time of PA copolymer in TPVs was obviously shortened more than that of neat PA. This may be because of the heterogeneous nucleating effect introduced by the crosslinked rubber particles. Figure 4 shows that the crystallization kinetics of the PA copolymer follow the Avrami equation:

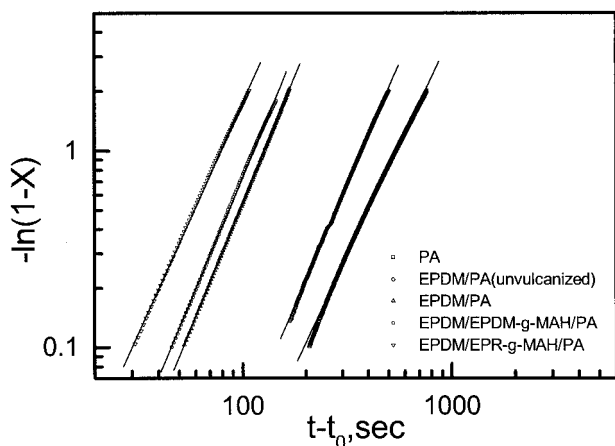


Figure 5 Avrami plots for PA copolymer at  $T_c = 100^\circ\text{C}$ .

TABLE II  
Averages of Avrami Exponents in the Indicated Range of Crystallization Temperatures

Sample	$T_c$ ( $^\circ\text{C}$ )	$n$	$-\lg K$
PA	100	2.2	6.12
	102		6.17
	104		6.23
	106		6.28
	108		6.36
EPDM/PA (unvulcanized) (65:35)	100	2.3	5.76
	102		5.88
	104		5.96
	106		6.07
	108		6.17
EPDM/PA (65:35)	100	2.5	5.43
	102		5.58
	104		5.66
	106		5.84
	108		5.97
EPDM/EPDM-g-MAH/PA (52:13:35)	100	2.5	5.22
	102		5.28
	104		5.35
	106		5.46
	108		5.59
EPDM/EPR-g-MAH/PA (52:13:35)	100	2.4	4.50
	102		4.71
	104		4.82
	106		5.05
	108		5.21

$$X(t) = 1 - \exp[-K(t - t_0)^n]$$

where  $X(t)$ , normalized crystallinity, is the ratio of the peak areas,  $a(t)/a(\infty)$ , or the ratio of degree of crystallinity at time  $t$  to the final degree of crystallinity; and  $K$  and  $n$  are the overall rate constant and the Avrami exponent, respectively. Selected examples for Avrami plots are given in Figure 5. The linear relationship could be seen up to a high degree of conversion, which allowed the estimation of quantities  $K$  and  $n$ . Values for the overall rate constant,  $K$ , and the Avrami exponent,  $n$ , at different crystallization temperatures are listed in Table II. The Avrami exponent was 2.2 for neat PA copolymer and 2.3 for PA in unvulcanized

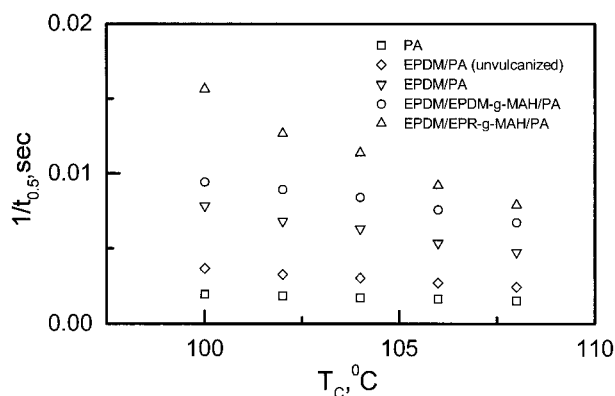
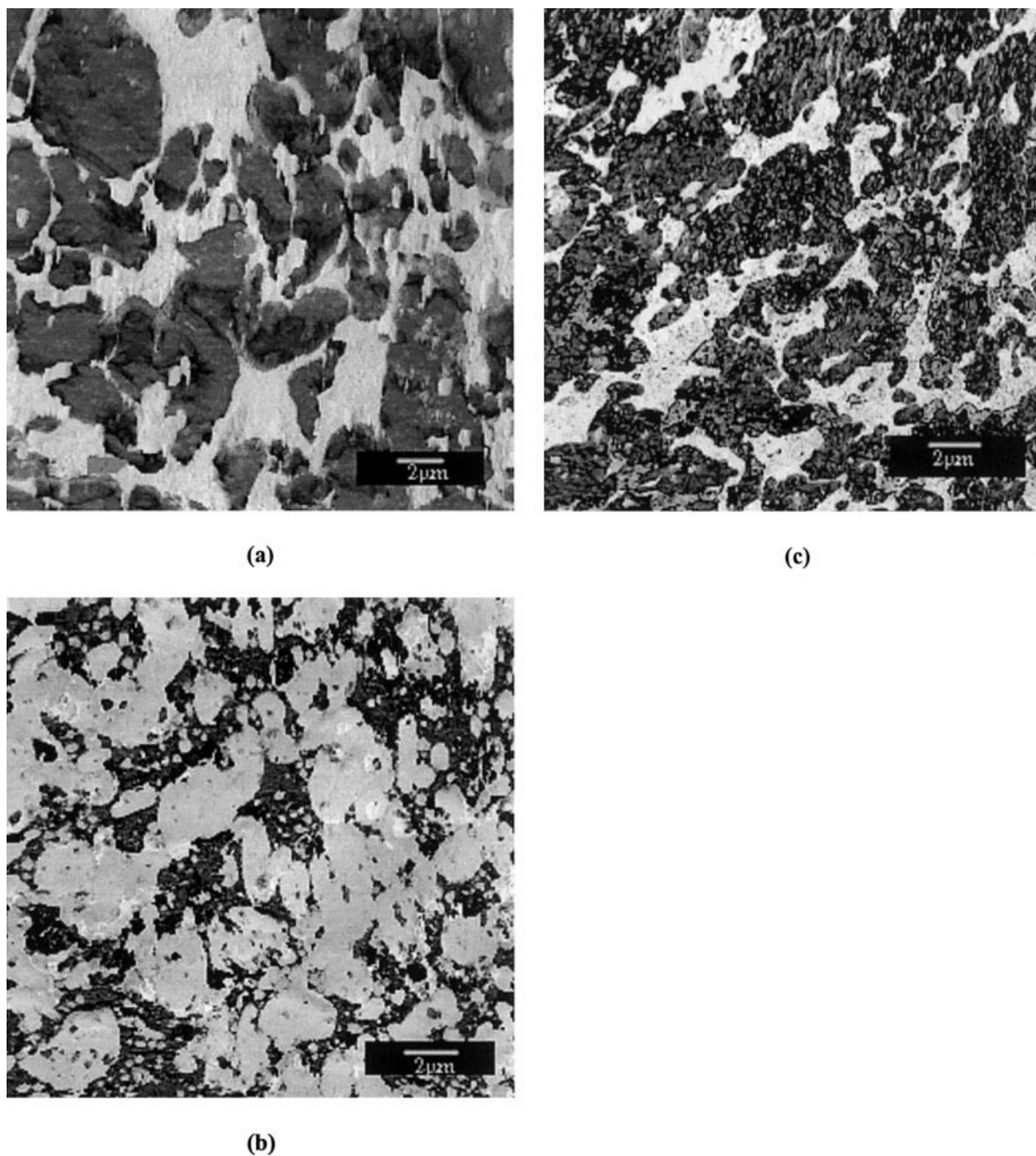


Figure 6 Plots of crystallization rate  $t_{0.5}^{-1}$  versus  $T_c$  for neat PA and TPVs.



**Figure 7** AFM image of EPDM-PA TPVs: (a) EPDM-PA (65:35), (b) EPDM/EPDM-*g*-MAH/PA (52:13:35), (c) EPDM/EPR-*g*-MAH/PA (52:13:35).

blends, whereas it was about 2.5 for PA in TPVs and did not change significantly whether or not compatibilizer was added. The overall rate constants for PA copolymer were highest in neat PA copolymer and were reduced in unvulcanized blends and TPVs.

The inversion of half-time of crystallization,  $t_{0.5^{-1}}$ , was used to evaluate the crystallization rate. The values of  $t_{0.5}$  were estimated from the area of the crystallization peak at the respective crystallization temperature,  $T_c$ . The values of  $t_{0.5^{-1}}$ , which is a function of

crystallization temperature, are shown in Figure 6. It can be seen that the crystallization rate was highest in compatibilized TPV and lowest in neat PA, whereas it was intermediate in uncompatibilized TPV and the unvulcanized EPDM-PA blends. It seems that the dynamic vulcanization process obviously could increase the crystallization rate for PA copolymer, compared with unvulcanized EPDM-PA blends, especially when a suitable compatibilizer was used. This is because the dynamic vulcanization introduced fine

crosslinked rubber particles that could act as heterogeneous nucleating centers, which may have gone into the PA matrix, causing the increase in the nucleating rate. For unvulcanized EPDM-PA blends, PA copolymer was the island phase dispersed in the unvulcanized rubber matrix, which restricted the growing process of PA crystallites, thus resulting in a lower crystallization rate compared with PA in TPVs. If EPDM-PA, an immiscible polymer blend, was without compatibilizer, it was difficult to disperse the rubber phase in the PA matrix during dynamic vulcanization, and so the crosslinked rubber particles were large [as shown in Fig. 7(a)]. Using EPDM-g-MAH or EPR-g-MAH as compatibilizer, the corresponding succinic anhydride groups could react readily with the terminal amine group of the PA copolymer, leading to an *in situ*-formed graft copolymer. The copolymer acted as a macromolecular surfactant, and its presence during mixing permitted the formation of very small droplets of the elastomer that later, during dynamic vulcanization, became very small particles of vulcanized rubber. These finely dispersed vulcanized rubber particles increased the density of the nucleating centers and thus increased the nucleating rate. On the other hand, the compatibilization reaction restricted the mobility of the PA copolymer chains and decreased the crystal growing rate. However, Figure 6 indicates that in this case the nucleating rate was the main influencing factor and that the crystallization rate increased by adding compatibilizer. Compared with the morphology of TPVs with the same dose of EPDM-g-MAH compatibilizer [Fig. 7(b)], the morphology of TPVs using EPR-g-MAH as compatibilizer showed much smaller dispersed rubber particles [Fig. 7(c)], which may have contributed to the higher crystallization rate, as shown in Figure 6.

## CONCLUSIONS

A thermoplastic vulcanizate (TPV) of ethylene-propylene-diene terpolymer (EPDM) and nylon copolymer (PA) was prepared by dynamic vulcanization. The effect of dynamic vulcanization and compatibilizer on the crystallization behavior of PA was discussed. No pronounced shift in crystallization temperature was observed for PA in EPDM-PA TPV compared to that of PA in the neat state, whereas the crystallization temperature increased after adding compatibilizer. The decrease of crystallinity in TPVs resulted from crystallization between the rubber particles in confined spaces. The crystallization rate was highest in compatibilized TPV and lowest in neat PA, whereas it was intermediate in uncompatibilized TPV and unvulcanized blends. It seems the dynamic vulcanization process obviously could increase the crys-

tallization rate of the PA copolymer, compared with that of unvulcanized EPDM-PA blends, especially when a suitable compatibilizer was used. The reason for this was that the dynamic vulcanization introduced fine crosslinked rubber particles that could act as heterogeneous nucleating centers. And the use of a suitable compatibilizer permitted the formation of finely dispersed vulcanized rubber particles and therefore increased the density of the nucleating centers. The complex morphology of the blends was investigated by atomic force microscopy (AFM) to evaluate the effect of compatibilizer on the size of dispersed rubber particles. Compared with the morphology of TPVs with the same dosage of EPDM-g-MAH compatibilizer, the morphology of TPVs using EPR-g-MAH as compatibilizer showed much smaller dispersed rubber particles, which may have contributed to the higher crystallization rate.

We are grateful to Ms. Haruna Horikawa of Bridgestone Corp. for the ultrasurface preparation for our AFM studies.

## References

1. Kresge, E. N. *J Appl Polym Sci* 1984, 39, 37.
2. Coran, A. Y. In *Thermoplastic Elastomers*; Legge, N. R.; Holden, H. E.; Schroeder, H. E., Eds.; Hanser Publishers: Munich, 1987.
3. Gessler, A. M.; Haslett, W. H. U.S. Pat. 3,037,954 (1962).
4. Fisher, W. K. U.S. Pat. 3,758,643 (1973).
5. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1980, 53(1), 141.
6. Coran, A. Y.; Patel, R. P.; Williams, D. *Rubber Chem Technol* 1982, 55(1), 116.
7. Abdou-Sabet, S.; Fath, M. A. U.S. Pat. 4,311,628 (1982).
8. Coran, A. Y. In *Thermoplastic Elastomers Based on Elastomer/Thermoplastic Blends Dynamically Vulcanized*; Al-Malaika, S., Ed.; Blackie Academic and Professional: London, 1997; p 349.
9. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1980, 53(4), 781.
10. Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1983, 56(2), 211.
11. Ma, J.; Feng, Y. X.; Xu, J.; Xiong, M. L.; Zhu, Y. J.; Zhang, L. Q. *Polymer* 2002, 43, 937.
12. Ma, J.; Feng, Y. X.; Lei, C. C. *Acta Polym Sin* 2000, 6, 727.
13. Huang, H.; Yang, J. L.; Liu, X.; Zhang, Y. X. *Eur Polym J* 2002, 38, 857.
14. Li, L.; Chan, C. M.; Li, J. X.; Ng, K. M.; Yeung, K. L.; Weng, L. T. *Macromolecules* 1999, 32, 8240.
15. Magonov, S. N.; Elings, V.; Papkov, V. S. *Polymer* 1997, 38, 297.
16. Stocker, W.; Beckmann, J.; Stadler, R.; Rabe, J. P. *Macromolecules* 1996, 29, 7502.
17. Dijk, M. A.; Van Den Berg, R. *Macromolecules* 1995, 28, 6773.
18. McLean, R. S.; Sauer, B. B. *Macromolecules* 1997, 30, 8314.
19. Raraf, R. F. *Macromolecules* 1993, 26, 3623.
20. Kajiyama, T.; Tanaka, K.; Ohki, I.; Ge, S. R.; Yoon, J. S.; Takahara, A. *Macromolecules* 1994, 27, 7932.
21. Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* 1996, 29, 3232.
22. Chen, S. A.; Lee, H. T. *Macromolecules* 1995, 28, 2858.
23. Krausch, G.; Hipp, M.; Boltau, M.; Marti, O.; Mlynek, J. *Macromolecules* 1995, 28, 260.
24. Walheim, S.; Boltau, M.; Mlynek, J.; Krausch, G.; Steiner, U. *Macromolecules* 1997, 30, 4995.