

MORPHOLOGY DEPENDENCE OF CRYSTALLIZATION OF NATURAL RUBBER IN BLENDS

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Abstract Crystallization of natural rubber (NR) was investigated in different morphology for NR/styrene butadiene rubber (SBR) blend and NR/polystyrene-(*b*)-polyisoprene (SI)/polystyrene (PS) blend. A purified NR (PC-TE) was prepared from pale crape *via* transesterification. In the blends, PC-TE formed various morphologies; that is, matrix phase, island phase and continuous phase with a nano-scale, respectively, in dependence upon the ratio of the rubbers. The crystallization rate of the blends was also significantly associated with the morphology of the rubbers.

Keywords: Natural rubber; Crystallization; Morphology of natural rubber.

INTRODUCTION

Rapid crystallization is one of the unique characteristics of natural rubber (NR) and is caused by its molecular structure^[1]. Fundamental structure of NR molecules was proposed to consist of ω -terminal, two *trans*-1,4-isoprene units, long sequences about 1000–5000 of *cis*-1,4-isoprene units and α -terminal. The α -terminal is composed of phospholipids linking to fatty acids, which play an important role in branching structure of natural rubber. On the other hand, the ω -terminal of the rubber molecule in natural rubber was postulated to be a modified dimethylallyl group linking to a functional group, which is associated with proteins to form crosslinking junctions through intermolecular hydrogen bonding formation^[2]. The long sequences of *cis*-1,4-isoprene unit is one of the causes of the rapid crystallization. Furthermore it has been proved that the linked fatty acid ester in natural rubber might be an important factor as a nucleating agent in the nucleation of crystallization and the crystallization was promoted by interaction of the linked fatty acid ester with free fatty acid including saturated and unsaturated acid which were also contained in NR^[3, 4]. An ability of the rapid crystallization is closely related to superior mechanical properties of NR, such as green strength, tensile strength and tear strength and so forth^[5, 6].

NR is often used as an important component of blends in rubber industry to improve their mechanical properties because the natural rubber shows superior properties comparison with other synthesized rubbers, such as styrene butadiene rubber (SBR), butadiene rubber (BR), and so forth. However, in the previous work^[7], it was found that crystallization of NR may be delayed when NR was dispersed in immiscible rubbers. As the rate of isothermal crystallization was a strong function of number density of NR droplets in NR/SBR blends^[8], the depression of the crystallization might be attributed to a homogeneous nucleation by formation of significant larger number of NR droplets than number of active heterogeneities as Cormia *et al.* pointed out for polyethylene

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particles dispersed in an inert medium^[9]. These facts represent a possibility that NR in blends doesn't fully show capacity for the superior mechanical properties because of reduced crystallization ability. Our recent study revealed that NR droplets dispersed in SBR improved tear energy, but the improvement was cut down as tear rate was increased and this was attributed to a lack of the ability in the rapid crystallization of dispersed NR^[10].

The task is finding a method to give rapid crystallization of NR even in blends. Therefore we investigated the isothermal crystallization of NR in several kinds of blends, that had several characteristic morphologies in which NR formed dispersed phase, individual island phases and nanoscale continuous phase, in this study.

EXPERIMENTAL

NR used in this study was a commercially available pale crape. The rubber was purified by transesterification, a method in previous paper^[11] (denote transesterified pale crape as PC-TE). Styrene butadiene rubbers, Asaprene1204 (styrene contents = 25 wt%, vinyl contents in polybutadiene = 35.5 mol%, denoted as SBR) were supplied by Asahikasei corporation. Commercial grade of polystyrene-polyisoprene block-copolymer (SI) and polystyrene (PS) were also used. The SI, including 21.1 wt% of polystyrene-polyisoprene-polystyrene tri-block copolymer, and its molecular weight of polyisoprene part, polystyrene part and content of polystyrene were approximately 1.24×10^5 , 2.19×10^4 and 15 wt% respectively, was supplied by Nippon Zeon Co., Ltd. HIMER ST-95 (PS) was supplied by Sanyo Chemical Industries Ltd., which has a weight average molecular weight of 3.12×10^3 . SBR, SI and PS were used after precipitation in reagent grade methanol subsequently solved into reagent grade toluene. PC-TE was mixed with other polymers, such as SBR, PS and SI in the toluene. Two PC-TE/SBR blends (B1 and B2) were prepared by precipitation into the methanol from the corresponding toluene solutions. PC-TE/SI/PS blend (B3) was prepared by casting of the solution. All of the blends were dried under vacuum at 40 °C for more than 3 days before all measurements. Formulations of each blend used in this study are shown in Table 1.

Table 1. Formulation of the samples

	B1	B2	B3	B4
PC-TE	30	70	24	
SBR	70	30		
SIS			56	80
PS			20	20

Molecular weight and molecular weight distribution of PC-TE were measured with a TOSOH HLC-8020 GPC system including columns with the exclusion limit of about 1×10^7 at a 40 °C with a THF flow rate of 1.0 mL/min. Content of fatty acid ester was determined by a Perkin Elmer System 2000 FTIR. Each rubber for FTIR measurements was cast on KBr disk with a 0.6 wt% chloroform solution. A calibration curve was obtained for a series of mixtures of methyl stearate and synthetic *cis*-1,4-polyisoprene. The content of the fatty acid ester groups per weight of the rubber was determined by the intensity ratio of peaks at 1739 cm^{-1} (C=O) to 1664 cm^{-1} (C=C).

Observation of morphology for the blends was investigated by using a transmission electron microscope (TEM), Hitachi H-800, at an accelerating voltage of 120 kV. The ultra thin sections of the blends used for the TEM observation were prepared by an ultra-microtome equipped with a cryo kit (Leica URTRA CUT UCT) at a temperature lower than glass transition temperature of the rubbers. The thin sections with the thickness of about 100 nm were stained with OsO₄.

Measurements of isothermal crystallization were carried out through dilatometry^[12, 13]. In the measurement, a dilatometer made of common Pyrex glass composed of a capillary of 1.0 mm in inner diameter and a reservoir was used. The NR and blended rubbers were sealed in the reservoirs of 6 mL, respectively. The mercury was then poured into an envelope of the sample. The dilatometer was annealed at 70 °C for 60 min in a water bath to indicate thermal history of the rubbers. The crystallization was then made at specified temperatures in a low temperature bath, in which a fluctuation of the temperature was ensured within ± 0.1 °C. Relative volume and

fluctuation of room temperature were recorded at pre-determined time intervals by a digital camera. The relative volume change was corrected by volume change of mercury caused by the fluctuation and translated to volume change of neat PC-TE.

RESULTS AND DISCUSSION

Molecular weight of PC-TE and the fatty acid ester content are shown in Table 2. A size exclusion chromatogram for PC-TE is shown in Fig. 1. It was found that the average molecular weight of PC-TE was decreased by transesterification corresponding to dissociation of the branching points in the rubber. FTIR spectrum of PC-TE is shown in Fig. 2. As an absorption peak for stretching vibration of C=O bond of carbonyl group at 1741 cm^{-1} was negligibly small compared with that of C=C bond of isoprene units at 1664 cm^{-1} . The ester content was below a detectable limit consisting with previous study^[14] and this suggested that the linked fatty acid ester and the free fatty acid were removed. Thus, it was confirmed that PC-TE was suitable to investigate the crystallization of NR in various morphologies without the effect of molecular branch points.

Table 2. Molecular weight and the fatty acid ester content of PC and PC-TE

	Molecular weight			Ester content (mmol/kg-rubber)
	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	
Pale crape (PC)	17.2	3.32	5.18	21
Transesterified PC (PC-TE)	13.0	2.99	4.35	0.0

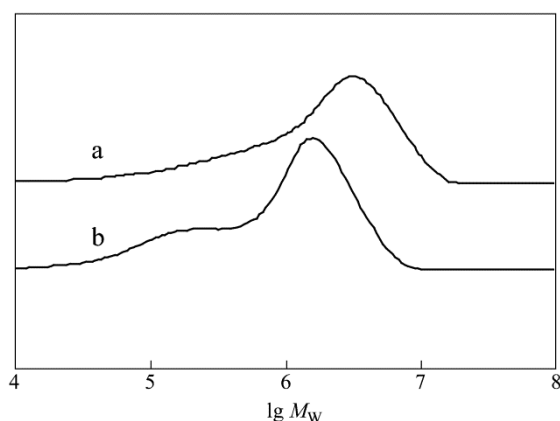


Fig. 1 Size exclusion chromatograms for (a) PC and (b) PC-TE

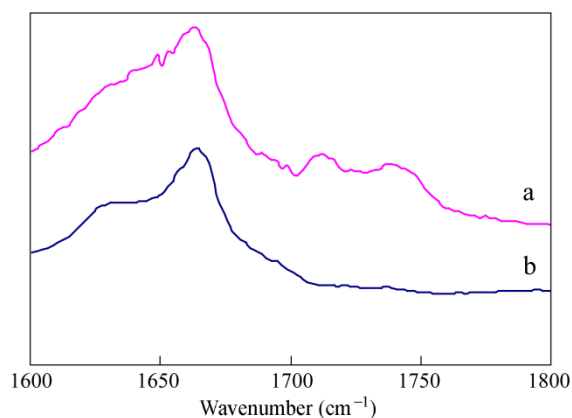


Fig. 2 FTIR spectrum for (a) PC and (b) PC-TE

The PI/PS blend is a typical immiscible polymer pair. In this case, the morphology is dependent only on the composition. For instance, island-matrix and *co*-continuous morphology appear with composition change of blend in micro-meter scale^[15] whereas island-matrix, cylinder, lamellar and gyroid morphology appear for block co-polymer in nano-scale^[16]. Figure 3 shows TEM photographs of PC-TE/SBR blends of which the weight ratio of PC-TE is 0.30 (B1) and 0.70 (B2). It was found that droplets of PC-TE with approximate size about $2\text{ }\mu\text{m}$ were clearly observed in the former, while PC-TE formed matrix phase in the latter. Figure 4 shows TEM photographs of SI/PS blend (B4; (a) and (b)) and PC-TE/SI/PS blend (B3; (c) and (d)). In the photographs (Figs. 4a and 4b) bright domains of a cylinder shape were the polystyrene phase, and the dark domains formed a continuous phase were polyisoprene. Same as above in Figs. 4(c) and 4(d), the dark domain was the polyisoprene phase in which PC-TE might be included and the bright domain was the polystyrene phase. The large circular particles in Fig. 4(d) are PC-TE and block-copolymer of SIS. The polyisoprene phase for B3 was still continuous but size of the polyisoprene matrix increased by addition of PC-TE. Furthermore, PC-TE formed the macro-separation phases, which were connected to the matrix, and the size was about 500 nm . As the total content of polystyrene and polyisoprene for B3 was almost similar to that for B4, the difference in the

morphology of both blends was attributed to difference in molecular weight between the polyisoprene block and PC-TE. PC-TE had still wide molecular weight distribution because branching points were cut through the transesterification. It was therefore inferred that the increase in the size of the matrix was caused by incorporation of the portion of PC-TE^[17].

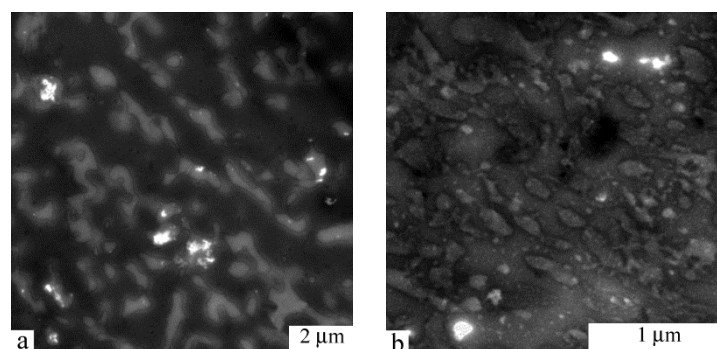


Fig. 3 TEM photographs of the PC-TE/SBR blend: (a) B1; PC-TE/SBR = 30/70 and (b) B2; PC-TE/SBR = 70/30

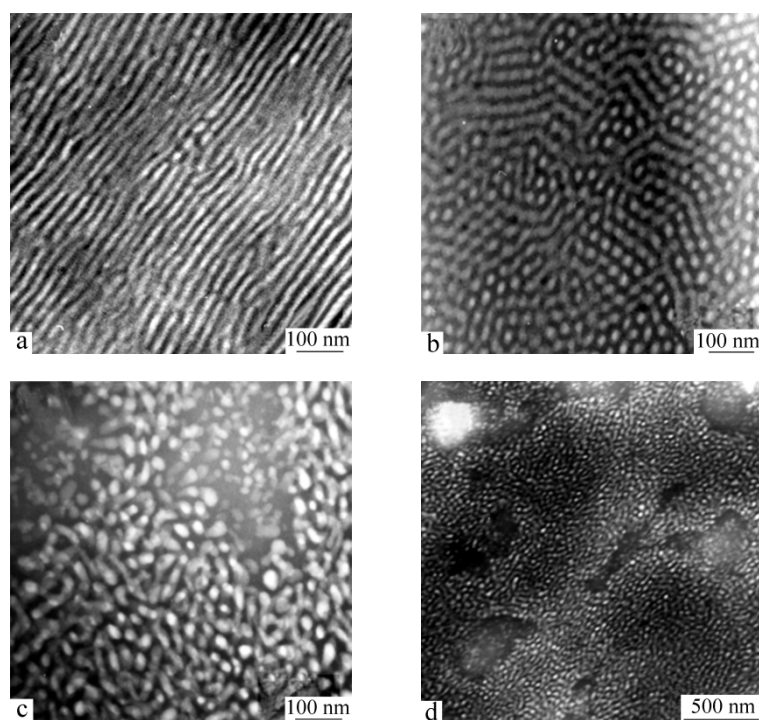


Fig. 4 TEM photographs of the various blends including SI: (a) B4; SI/PS = 80/20, parallel direction to PS cylinders, (b) B4; vertical direction to the cylinders, (c) B3; PC-TE/SI/PS = 24/56/20 and (d) a zoom out image of (c)

In order to overview the crystallization behavior of these blends, we measured volume depression of the blends at 248 K. The depressions are plotted as a function of time are shown in Fig. 5. The dispersed PC-TE in B1 showed fairly late crystallization in comparison with B2 in which PC-TE formed the matrix phase. This also may be attributed to lack of number of active heterogeneities in dispersed PC-TE islands corresponding to the previous work^[7, 8]. The curve for B2 was almost similar to that for PC-TE itself. This was easily understood because probability for nucleation in unit volume of PC-TE had to be the same in both states of the rubber.

Whereas the crystallization for B3 was faster contrary to general expectation that B3 had to represent later crystallization than B1 as a result of the size of PC-TE islands. As the total volume change observed in measured time for B3 was approximately equal to that of other blends or PC-TE itself, the volume depression for B3 might be mainly caused from blended PC-TE. Therefore the morphological difference between both blends, the PC-TE phase was independent or continuous, became the main concern. It was inferred that the morphological characteristics might affect the nucleation of the crystallization. Measurements of crystallization temperature of the blends dependence upon crystallization rate may support in order to consider the nucleation mechanism.

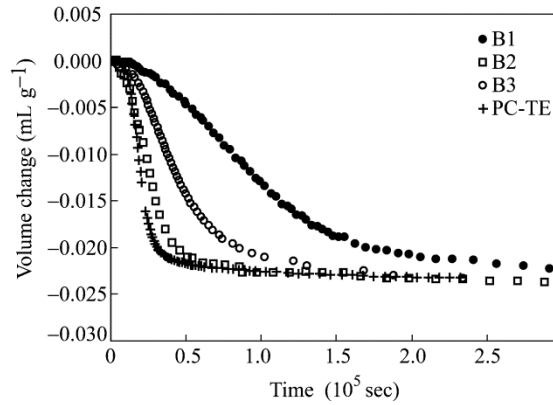


Fig. 5 Volume changes with isothermal crystallization measured for PC-TE and the blends at 248 K

The volume depression measured at various temperatures for each blends; that is, B1, B2 and B3 is plotted in Figs. 6, 7 and 8, respectively. Period required for crystallization of the blends was gradually increased as the temperature rose for the all blends. However, the decreasing rate of the blends was different and that for B1 was the biggest and for B2 was the smallest but the mutual relation among the blends was maintained as shown in Fig. 5. As an index of the crystallization rate $t_{0.5}^{-1}$, which was defined as the inverse of time corresponding to the half of the total volume depression, was calculated. The values of $t_{0.5}^{-1}$ for all the blends are plotted as a function of the crystallization temperature in Fig. 9. The maximum of $t_{0.5}^{-1}$ was at 248 K and 251 K for B1 and B2; it might be at about 248 K for B3. Assuming the crystal linear growth rate is identical, the crystallization half time is related to interfacial free energy for nucleating through Eqs. (1) and (2) according to a crystallization kinetic theory^[18, 19].

$$\ln t_{0.5}^{-1} = - \frac{\{1 + (n-1)b\} \kappa T_m^{\circ 2}}{nT(\Delta T)^2} \quad (1)$$

$$\kappa = \frac{32\sigma_e \sigma_u^2}{k(\Delta H_v)^2} \quad (2)$$

where T_m° , σ_e , σ_u , k and Δh_v are equilibrium melting temperature, the fold surface free energy, side surface free energy, Boltzmann's constant and the enthalpy of fusion, respectively. The n is the exponent which represents the course of the isothermal crystallization as the equation, $1-X(t) = \exp(Kt^n)$, here $X(t)$ is crystallinity. The parameter b is defined as a ratio of interfacial free energy to form a critical nucleation for the heterogeneous nucleation to that for the homogeneous nucleation. Thus, we can estimate degree of tendency for the nucleation type that is the heterogeneous nucleation or the homogeneous one by evaluation the value of b .

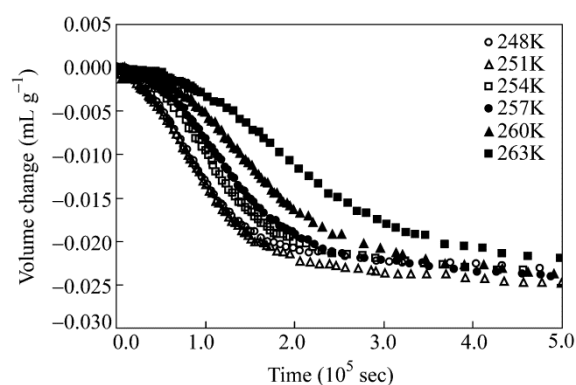


Fig. 6 Volume changes with isothermal crystallization measured for PC-TE/SBR = 30/70 blend (B1) at various temperatures

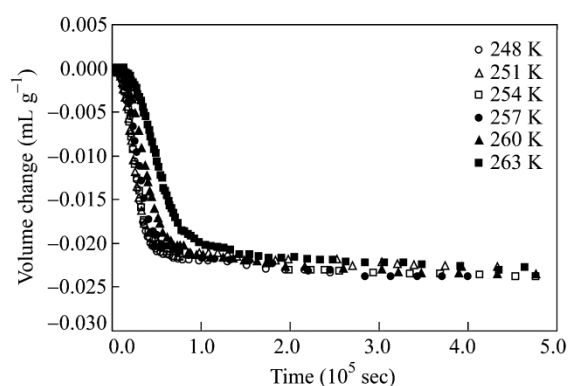


Fig. 7 Volume changes with isothermal crystallization measured for PC-TE/SBR = 70/30 blend (B2) at various temperatures

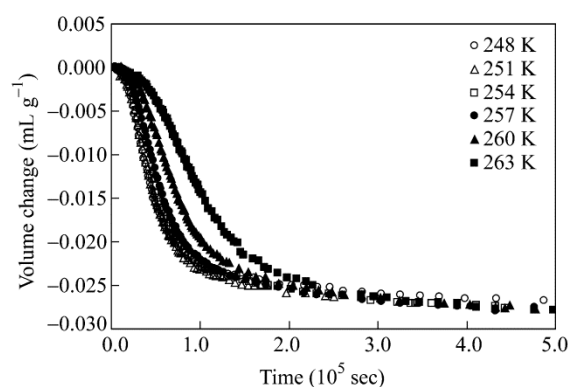


Fig. 8 Volume changes with isothermal crystallization measured for PC-TE/SI/PS = 24/56/20 blend (B3) at various temperatures

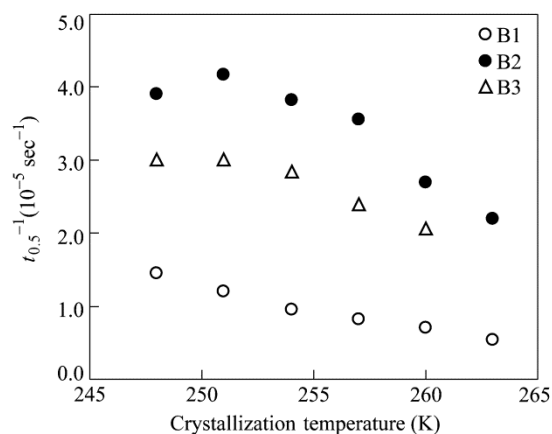


Fig. 9 Crystallization temperature dependence of the crystallization rate ($t_{0.5}^{-1}$) for the blends

Figure 10 shows a plot of logarithmic $t_{0.5}^{-1}$ versus $T^{-1}\Delta T^{-2}$. For the three blends, the results showed that linear line was respectively given. The linear line for B2 and B3 were mutually parallel, but the slope of the line for B1 was somewhat bigger than the others. The parameter b was estimated from the slope of the line if the value of T_m^0 and the exponent n were given. We estimated the exponent n from the data for the isothermal crystallization shown in Figs. 6, 7 and 8. The exponent values for the blends are shown with the value for PC-TE

itself in Fig. 11. The values for each blend were almost the same; that is, there was independence upon the crystallization temperature. The averaged values of the component n for the blends from 248 K to 260 K were applied to the above estimation and the n values were 1.7, 2.7 and 3.0 for B1, B2 and B3 respectively. The exponent value for B1, it is consistent with the value for our previous result of NR/SBR blend^[10], may be suggested that the system has rather high tendency of homogeneous nucleation in finely dispersed rubber droplets. On the other hand, the value for B2 and B3 may be implied to the heterogeneous nucleation. We also used the value of T_m^0 which was recently measured for transesterified NR by a direct observation method with a polarized light microscope^[20]. The resulted values of the parameter b for the each blend were $3.2 \times 10^1 \kappa$, $1.7 \times 10^1 \kappa$ and $1.4 \times 10^1 \kappa$ for B1, B2 and B3 respectively. The value of the parameter b for B3 was almost similar to that for B2 and about 56% less than the value for B1. This may represent that the interfacial free energy to form the critical nucleation in B3, in which PC-TE was finely dispersed in the matrix, was similar to the value for the heterogeneous nucleation as for B1. Following reason was so far inferred that the heterogeneous nucleation could occur due to the formation of continuous PC-TE phase as shown in the TEM photographs.

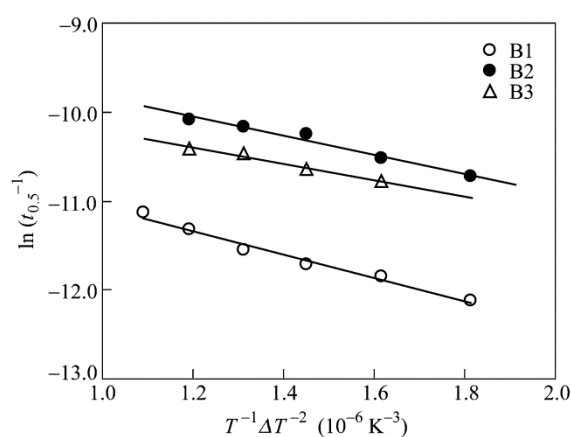


Fig. 10 A plot of $\ln(t_{0.5}^{-1})$ versus $T^{-1}\Delta T^{-2}$ for the blends

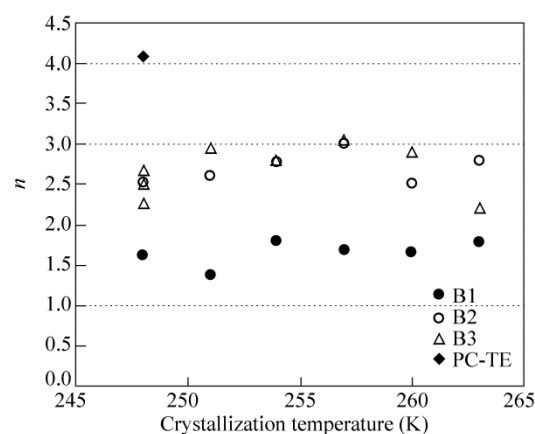


Fig. 11 A plot of exponent n values versus crystallization temperature for the blends

The fast crystallization of NR in the nanoscale-dispersed and continuous phases under isothermal conditions was found in this study. This showed a possibility to enhance the ability of rapid strain induced crystallization of the blended NR with other elastomers in order to improve the mechanical properties, such as tensile strength, tear strength and so forth, even at rapid deformation rate of the rubbers.

CONCLUSIONS

Measurements of the isothermal crystallization in the various morphologies for the NR blends at various temperatures was investigated. The rapid crystallization of NR was observed for blend when the continuous phase was formed in the blend as shown in PC-TE/SBR = 70:30 blend (B2). In contrast, when NR was dispersed as island phase (B2) in blend, the crystallization of the blend was very low. In the case of the NR/SI/PS blend (B3), the rubber was dispersed into nano-scale islands but they were connected with each other through a matrix comprising of the rubber. It showed an intermediate crystallization rate. This may be attributed to the homogeneous nucleation from the result of the interfacial free energy of the nucleation.

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