

## Phase Morphologies of Vulcanized Chlorobutyl Rubber/Polyamide 12 Blends: The Breakup of Pre-crosslinked CIIR Phase

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**ABSTRACT:** Dynamic vulcanization to prepare blended thermoplastic vulcanizates (TPV) is a kind of complicated blending technology, where the breakup of the rubber phase happens accompanying with the crosslinking of rubber. In this study, we aim to investigate the effect of crosslinking on the breakup of chlorobutyl rubber (CIIR) phase in thermoplastic polyamide 12 (PA 12) matrix by purposely using pre-crosslinked CIIR with different crosslink degrees and plasticizer contents. Besides, the effect of blending conditions on the breakup of crosslinked CIIR phase was studied. The results show that a low crosslink degree, a high content of plasticizer, a low blending temperature and a moderate rotor speed of 70 rpm facilitate the breakup of pre-crosslinked CIIR in PA 12 matrix. This is ascribed to the decrease in the modulus of pre-crosslinked CIIR phase because of either a low crosslink degree or a high content of plasticizer, the increase in the molten viscosity of thermoplastic matrix because of a low blending temperature and a moderate rotor speed. It is indicated that the breakup of pre-crosslinked rubber is mainly dominated by the modulus of crosslinked rubber phase as well as the molten viscosity of thermoplastic matrix and shear stress. This study will provide guidance for the preparation of CIIR/PA TPV. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40765.

**KEYWORDS:** thermoplastic vulcanizates; pre-crosslinked; breakup; morphology

Received 16 August 2013; accepted 24 March 2014

DOI: 10.1002/app.40765

### INTRODUCTION

Thermoplastic vulcanizate (TPV) is an important class of green elastomer material and has been widely used in industrial applications because it combines the excellent resilience of ordinary vulcanized rubber, and the easy processibility and recyclability of thermoplastics. This material, consisted of about 20–40 wt % thermoplastic and about 60–80 wt % elastomer, is prepared by dynamic vulcanization during which the rubber is preferentially vulcanized under dynamic shear to generate 0.5 to 3.0  $\mu\text{m}$  cured rubber particles in thermoplastic matrix.<sup>1–8</sup> Since crosslinked rubber is unable to coalesce, rubber particles are dispersed in the thermoplastic matrix even at high rubber content. Nowadays, for environmental protection and resource saving, TPV products comprise the fastest growing rubber market. Among various TPVs, Polyamide (PA)/isobutylene-isoprene rubber (IIR) TPV has attracted much attention in recent years because both PA and IIR are well known for their barrier characteristics as homopolymers and successful blending of these polymers by dynamic vulcanization has produced thermoplastic barrier compositions for use in such applications as inner liner of tire

treads.<sup>9–13</sup> Due to the low shearing effect resulted from low molten viscosity of PA 12 as well as the poor compatibility between PA 12 and chlorobutyl rubber (CIIR), the CIIR/PA TPV is hard to be prepared and have not been industrialized till today.

The shape and size of the rubber phase in matrix have a significant effect on the mechanical property and processability of a TPV.<sup>8,14–17</sup> It has been reported that the decrease in the size of rubber phase leads to the significant increase in the ultimate tensile strength, and the elastic recovery of the TPV.<sup>18</sup> Therefore, it is of guiding significance to investigate how rubber particles form and develop in the molten thermoplastic matrix during dynamic vulcanization, to provide contributions to the understanding of the phase structure formation during dynamic vulcanization.

The breakup of rubber phase during the dynamic vulcanization has a significant effect on the final phase morphology of a TPV. The crosslink and breakup of rubber phase occur simultaneously

**Table I.** Compositions of (Pre-crosslinked) CIIRs

Content	ZnO (phr)	PK900 (phr)	PIBSA (phr)
Crosslink degree 1	0.5	0.25	0
Crosslink degree 2	2	1	0
Crosslink degree 3 (Plasticized 1)	4	2	0
Crosslink degree 4	6	3	0
Plasticized 2	4	2	20
Plasticized 3	4	2	40

during dynamic vulcanization, thus, it is quite complex. Therefore, we intend to separate the effect of blending from the actual chemical crosslinking aspect and focus on the breakup of the pre-crosslinked CIIR by purposely using pre-crosslinked CIIR with different crosslink degrees.<sup>17</sup> This article aims at addressing new information on phase structure formation during dynamic vulcanization of CIIR/PA 12.

The cohesive energy of rubber phase and the applied shear stress have a significant effect on the breakup of rubber phase in thermoplastic matrix. On one hand, the cohesive energy of rubber phase will be mainly affected by the crosslink degree, the addition of plasticizer and blending temperature. On the other hand, the shear stress applied on the rubber phase will be affected by the viscosity of thermoplastic phase, rotor speed and interfacial intension. Therefore, in this work, we mainly focus on the effects of crosslink degree, plasticizer and processing conditions on the breakup of pre-crosslinked CIIR phase in thermoplastic PA 12 in a Haake Rheometer (Rheomix OS) to provide guidance for the preparation of CIIR/PA 12 TPV. Polarized light optical microscope (PLM) was used to observe the phase morphologies of CIIR/PA 12 blends and a particle diameter distribution was obtained by the software of SEM image analysis (Nano Measurer System, 1.2.0).

**Table II.** Compositions and Processing Conditions of CIIR/PA 12 Blends

	Pre-crosslinked CIIR	Temperature (°C)	Rotor speed (rpm)
Blend 1	Crosslink degree 1	190	70
Blend 2	Crosslink degree 2	190	70
Blend 3	Crosslink degree 3	190	70
Blend 4	Crosslink degree 4	190	70
Blend 5	Plasticized 2	190	70
Blend 6	Plasticized 3	190	70
Blend 7	Crosslink degree 3	170	70
Blend 8	Crosslink degree 3	210	70
Blend 9	Crosslink degree 3	190	40
Blend 10	Crosslink degree 3	190	100

## EXPERIMENTAL

### Materials

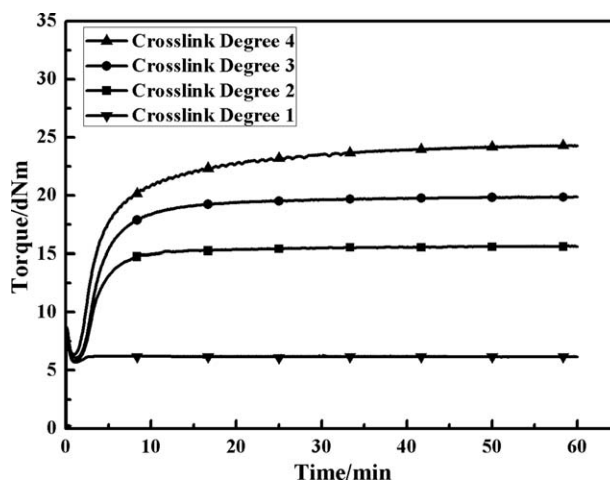
PA 12 was chosen from UBE (3030 JIX3) Japan with a melt flow index MFI = 5 g/10 min (190°C and 2.16 kg, XNR-400B melt flow rate instrument). The melting point is 180°C (Mettler-Toledo DSC1). Compared to other PA, PA 12 has a relatively low melting point, which allows a relatively low blending temperature. A relatively low melt flow index leads to a high viscosity of PA matrix when blending, which helps shearing.

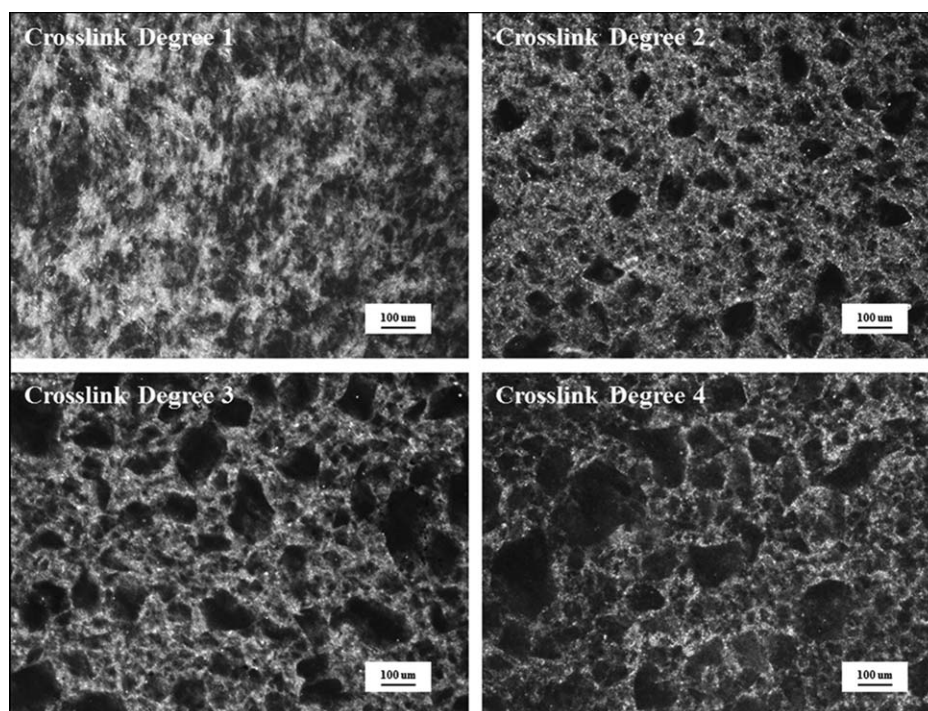
Experiments were carried out with a CIIR supplied by Exxon-Mobil Chemical (1066). The content of Cl is 1.25 wt % and the moony viscosity  $ML_{(1+8)} = 38 \pm 4$  at 125°C. Compared with butyl rubber and bromobutyl rubber, CIIR has a relatively high polarity due to the existence of Cl. A high polarity helps to improve the compatibility between polar PA and nonpolar butyl rubber.

Additionally, 1,3-bis (citraconimidomethyl) benzene (PK 900) from Lanxess and Zinc Oxide (ZnO) were used as crosslink agents in CIIR. The assay of PK 900 is above 85%. In this article, PK 900 was used as an assistant crosslinker. Polyisobutylene Succinic Anhydride (PIBSA) T2007A is an effective compatibilizer in butyl rubber/PA system, but it was used as a plasticizer in CIIR in this study.

### Preparation of CIIR/PA 12 Blends

**Preparation of Pre-crosslinked CIIR.** First of all, concerning the composition of networks, such samples were made of CIIR, Stearic Acid (S.A.), crosslink agent ZnO, and assistant crosslinker PK 900, in addition, plasticizer PIBSA for some samples. The following protocol was used: first, the CIIR blends were homogeneously mixed together with all the materials needed including the curing system on an open mill at room temperature. Then the cure characteristics of CIIR blends were carried out on a sulfuration apparatus (Huanfeng Beihua Instrument P3555B2, China) at 190°C and curing curves of neat CIIRs were obtained. After the CIIR blends stored away from light and heat for 8 hours, all the samples were cured in a flat-panel curing press at 190°C and molded into 13.5 mm × 11.5 mm × 2 mm CIIR network. Likely stored for 16 hours, all the pre-crosslinked

**Figure 1.** Curing curve of CIIR blends with different crosslink degree.



**Figure 2.** Polarized light optical microscope (PLM) graphs of CIIR/PA 12 blends with different pre-crosslink degree.

CIIR samples were elaborately cut into homogenous  $2 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$  fragments, and then packaged and signed respectively and stored away from light and heat until further blending.

Just as shown in Table I, different pre-crosslink degrees were set by varying the amount of crosslink agent and different modulus of pre-crosslinked CIIR were set by varying the amount of introduced plasticizer PIBSA.

**The Mechanically Blending of Pre-crosslinked CIIR with PA 12.** Moreover, all the CIIR/PA 12 blends were mixed in a Haake Rheometer (Rheomix OS) at certain blending temperature and rotor speed until the torque behaved stabilized. The compositions of pre-crosslinked CIIR mixed, together with the different processing conditions in CIIR/PA 12 blends are shown in Table II and the blending ratio of CIIR to PA 12 is 65–35.

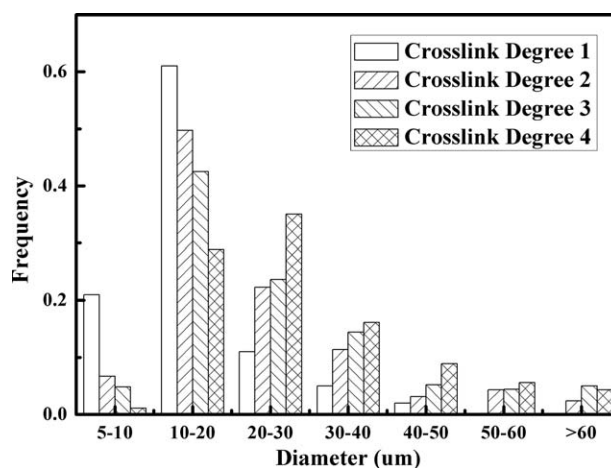
After blended elaborately, all the blends were molded in a flat-panel curing press at  $205^\circ\text{C}$  for 5 min into 1 mm thick samples after heated at the same temperature for 5 min, and then the mould together with the sample was moved to another flat-panel curing press and pressed at room temperature for 3 min, which makes the sample cooling down to keep the shape. Prior to introduced into the Haake Rheometer, PA 12 should be dried in an oven at  $80^\circ\text{C}$  for 12 hours in order to prevent the PA from hydrolysis. An antioxidant 1010 was introduced together with PA 12 to protect PA from oxidation when mixed. All the samples were package respectively and stored away from light and heat until further testing.

#### Polarized Light Optical Microscope (PLM)

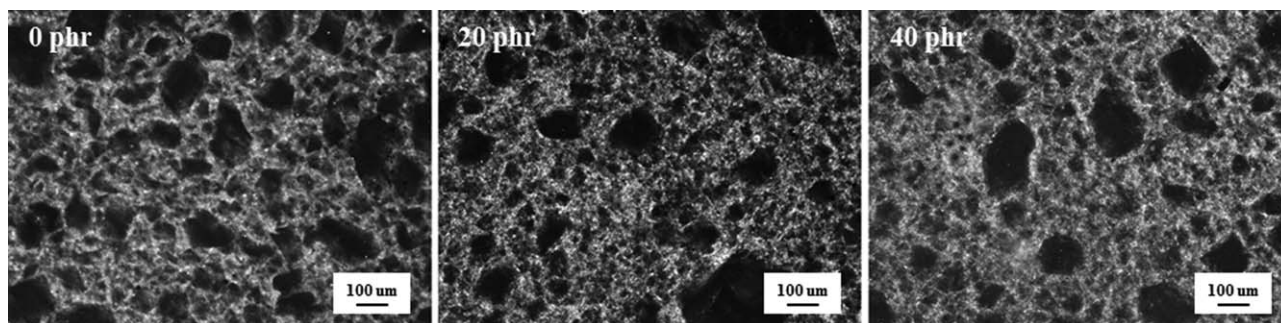
A PLM (ZEISS Axioskop 40) was used to observe the size of dispersed pre-crosslinked CIIR of these blends. The thin film

samples of pre-crosslinked CIIR and PA 12 blends were firstly maintained at  $205^\circ\text{C}$  for 2 min, and then cooled down to room temperature. PA 12 crystallized during the cooling process. The continuous PA 12 phase shows bright on the PLM graph due to the crystallization, whereas the dispersed CIIR is dark on the PLM graph. The image area we chose comprises almost the whole sample and the scale bar was added on the image.

The diameter analysis was calculated by the software of SEM image analysis (Nano Measurer System, 1.2.0). The diameter of every dispersed rubber particle in a chosen representative area of the PLM graph was measured for three times. Subsequently, a particle diameter distribution was summarized and the error is  $<5\%$ .



**Figure 3.** A particle diameter distribution statistics of CIIR/PA 12 blends with different pre-crosslink degree.



**Figure 4.** Polarized light optical microscope (PLM) graphs of CIIR/PA 12 blends with different amount of plasticizer (PIBSA) in pre-crosslinked CIIR.

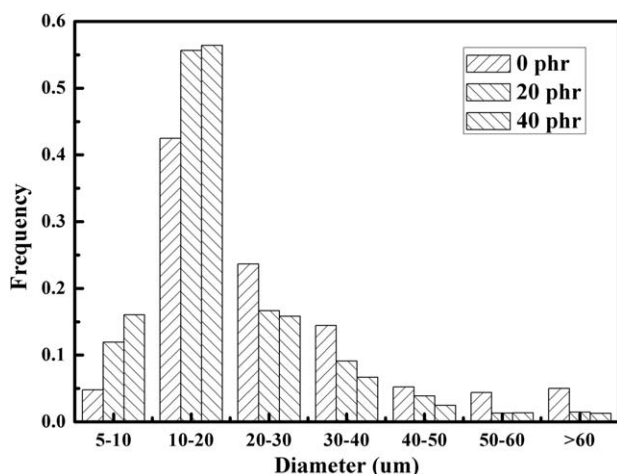
## RESULTS AND DISCUSSION

### Effect of Pre-crosslink Degree on the Phase Morphologies of CIIR/PA 12 Blends

To investigate the effect of pre-crosslink degree on the phase morphologies of CIIR/PA 12 blends, different amounts of curing agents ZnO/PK 900—0.5 phr/0.25 phr, 2 phr/1 phr, 4 phr/2 phr, 6 phr/3 phr—are used to prepare pre-crosslinked CIIR samples with different crosslink degrees. Figure 1 shows the curing curve of CIIR blends with different crosslink degrees. The torque difference ( $\Delta M$ ) between the maximum and the minimum in the curing curve indicates the crosslink degree of CIIR. The higher  $\Delta M$  means the higher crosslink degree of CIIR.

The PLM graphs of blend 1 to blend 4 with different pre-crosslink degrees are shown in Figure 2. It can be seen that the dark particles, which stand for broken up pre-crosslinked CIIR particles, have irregular shapes and wide distributions. A particle diameter distribution was summarized to study the effect of crosslink degree on the phase morphologies of CIIR/PA 12 blends, and the result is showed in Figure 3.

The diameter of the pre-crosslinked CIIR dispersed phase even with very low crosslink degree in blend 1 ranges from 5 to 50  $\mu\text{m}$ , much larger than 0.5 to 2  $\mu\text{m}$  of rubber particles in commercial ethylene-propylene-diene terpolymer (EPDM)/polypropylene (PP) TPV reported in literatures.<sup>2,19</sup> More than 90%

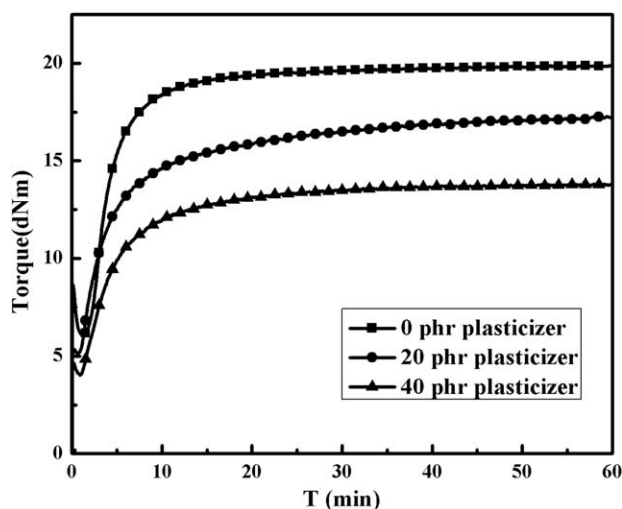


**Figure 5.** A particle diameter distribution statistics of CIIR/PA 12 blends with different amount of plasticizer (PIBSA) in pre-crosslinked CIIR.

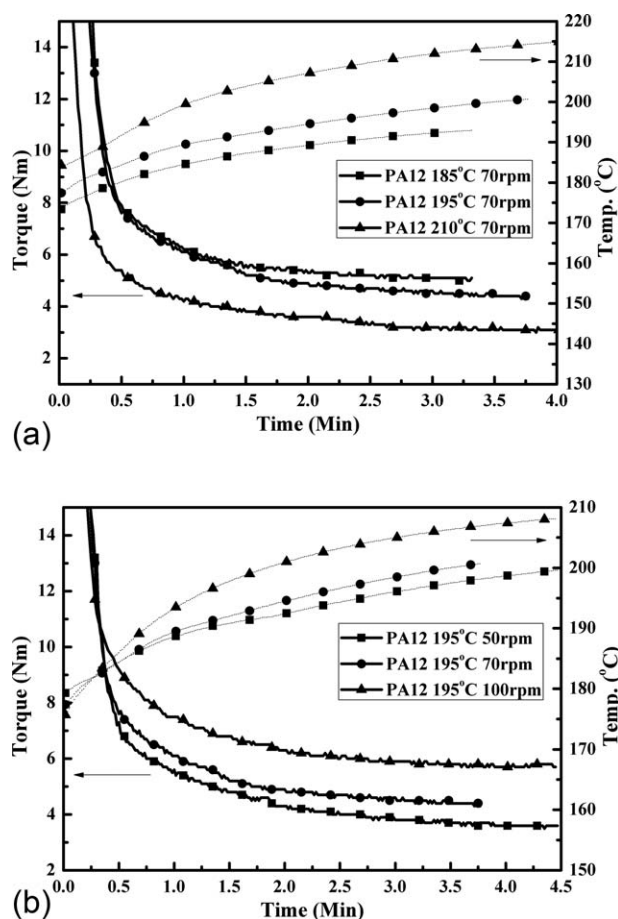
particles of blend 1 (lowest pre-crosslink degree) range from 5 to 30  $\mu\text{m}$  and over 80% of the particles in blend 2 to blend 4 (pre-crosslink degree from low to high) have diameters of 5 to 40  $\mu\text{m}$ . When the diameter ranges from 5 to 20  $\mu\text{m}$ , the lower the crosslink degree of pre-crosslinked CIIR is, the more the small particles are. However, there are more large particles in the blend with high pre-crosslink degree of CIIR than that with low pre-crosslink degree when the diameter ranges from 20 to 40  $\mu\text{m}$ . The result indicates that the increase of crosslink degree has an adverse effect on the breakup of pre-crosslinked CIIR in PA 12. The reason is that the modulus of pre-crosslinked CIIR increases with the increase of the crosslink degree, which is a disadvantage for the breakup of pre-crosslinked CIIR in PA 12. In a word, a low crosslink degree facilitates the breakup of pre-crosslinked CIIR in PA 12. This result also agrees well with previous work, which reported that the breakup of rubber phase occurs at the early stage of dynamic vulcanization when the crosslink degree is low.<sup>7,17,20</sup>

### Effect of Plasticizer (PIBSA) on the Phase Morphologies of CIIR/PA 12 Blends

Moreover, the effect of plasticizer PIBSA on the breakup of pre-crosslinked CIIR in melt PA 12 was investigated as plasticizing is an effective way to decrease the modulus of pre-crosslinked



**Figure 6.** Curing curve of CIIR blends with different amount of plasticizer (PIBSA) in CIIR.



**Figure 7.** The effect of (a) processing temperature and (b) rotor speed on the torque of PA 12 in Haake rheometer.

CIIR. Figure 4 shows the PLM graphs of CIIR/PA 12 blends with different amounts of plasticizer (PIBSA). It can be seen that the shapes of the dispersed pre-crosslinked CIIR particles, which is dark on the PLM pictures, are irregular and the diameters of particles ranges from 5 to 250  $\mu\text{m}$ .

A particle diameter distribution was summarized to study the effect of plasticizer (PIBSA) on the phase morphologies of CIIR/PA 12 blends, and the result is shown in Figure 5. The diameters of more than 85% particles in blend 3, blend 5, and blend 6 (plasticized with 0 phr, 20 phr, and 40 phr PIBSA, respectively) are in the range of 5 to 40  $\mu\text{m}$ . When the

diameters of particles range from 5 to 20  $\mu\text{m}$ , the proportion of particles increases as the amount of plasticizer increases. However, the proportion of particles decreases as the plasticizer increases when the diameters of particles are in the range of 20 to 40  $\mu\text{m}$ . The result indicates that the increase of PIBSA facilitates the breakup of pre-crosslinked CIIR in PA 12.

Figure 6 shows the curing curve of CIIR blends with different amounts of PIBSA. In the curing curve, the shear modulus is proportional to the torque value.<sup>21</sup> Thus, the modulus of pre-crosslinked CIIR decreases as the amount of PIBSA increases and this makes the rubber easy to be broken up. In a word, a high content of plasticizer (PIBSA) facilitates the breakup of pre-crosslinked CIIR in PA 12.

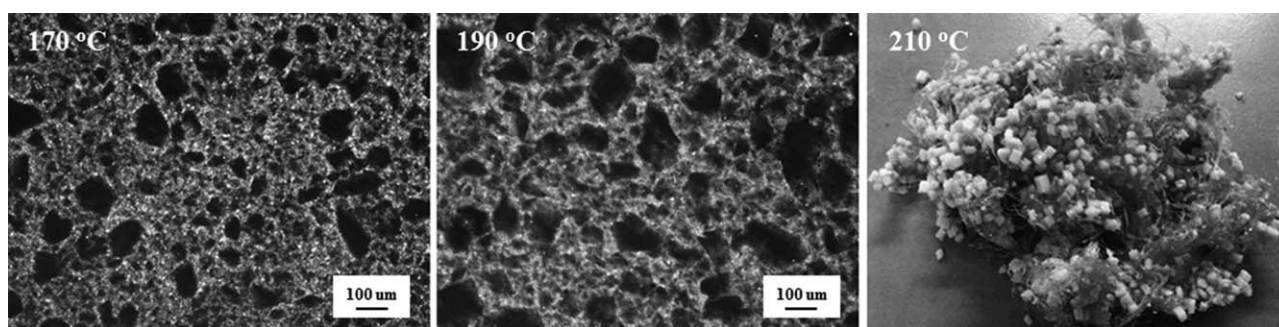
#### Effect of Blending Temperature and Rotor Speed on the Phase Morphologies of CIIR/PA 12 Blends

In addition, the effect of blending temperature and rotor speed in the Haake rheometer on the breakup of pre-crosslinked CIIR in melt PA 12 was studied. The viscosity of PA 12 is sensitive to temperature and rotor speed, as shown in Figure 7. The viscosity of PA 12 decreases sharply just after the PA melts as the temperature rises because PA 12 is a typical kind of crystalline polymer. However, a low viscosity of PA 12 matrix makes it difficult for PA 12 to transfer shear stress to rubber, and subsequently makes the breakup of pre-crosslinked CIIR harder than a high viscosity of PA 12. Additionally, as shown in Figure 7(b), the increase in rotor speed leads to the increase in shear heat which increases the temperature and shear thinning of the PA 12. Both of them decrease the viscosity of PA 12.

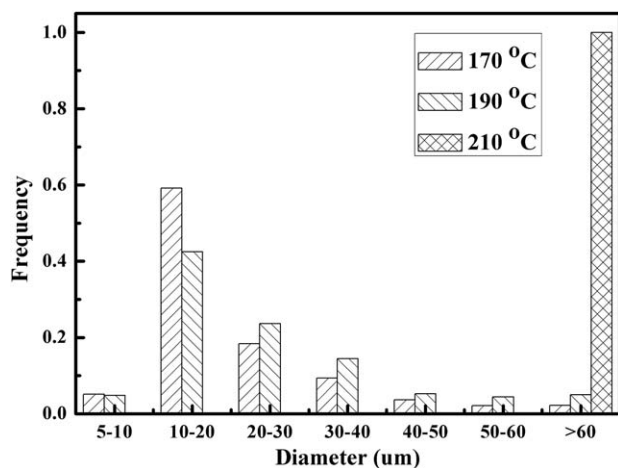
#### Effect of Blending Temperature on the Phase Morphologies of CIIR/PA 12 Blends.

The PLM graphs of CIIR/PA 12 blends with different blending temperatures are shown in Figure 8. It can be seen that in those samples whose temperature was lower than 210°C, the dark particles, which stand for broken up pre-crosslinked CIIR particles, have irregular shapes and different diameters in the range of 5 to 250  $\mu\text{m}$ . However, the pre-crosslinked CIIR fragments are rarely broken up after blended with PA 12 in the Haake rheometer at 210°C. The reason is that a high temperature leads to a sharp decrease in viscosity of PA 12 in which condition the PA 12 matrix cannot transfer enough shear stress to break up any pre-crosslinked CIIR fragments.

A particle diameter distribution was summarized to study the effect of blending temperature on the phase morphologies of CIIR/PA 12 blends, and the result is shown in Figure 9. The



**Figure 8.** Polarized light optical microscope (PLM) graphs of CIIR/PA 12 blends with different processing temperatures in Haake rheometer.



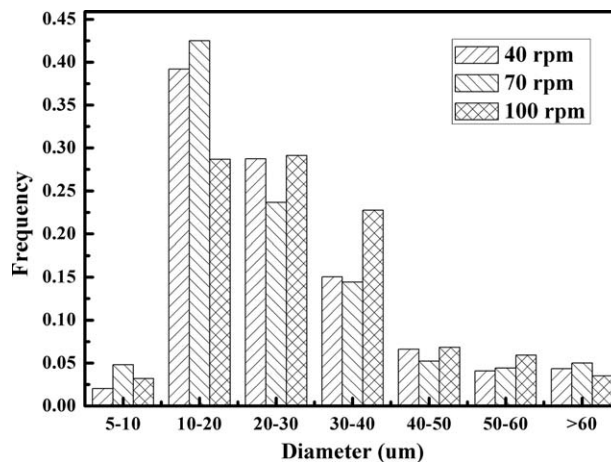
**Figure 9.** A particle diameter distribution statistics of CIIR/PA 12 blends with different processing temperatures in Haake rheometer.

diameters of 85% particles in blend 7 (170°C) and blend 3 (190°C) range from 10 to 40 µm. As the blending temperature increases, the number of particles with diameters in the range of 10 to 20 µm decreases while that of 20 to 40 µm increases. The result indicates that the increase in blending temperature has an adverse effect on the breakup of pre-crosslinked CIIR in PA 12. The reason is that the viscosity of PA 12 decreases as the blending temperature increases and this is a disadvantage for the pre-crosslinked rubber to be broken up. In a word, a low blending temperature facilitates the breakup of pre-crosslinked CIIR in PA 12.

**Effect of Rotor Speed on the Phase Morphologies of CIIR/PA 12 Blends.** The PLM graphs of CIIR/PA 12 blends with different rotor speeds are shown in Figure 10. It can be seen that the dispersed pre-crosslinked CIIR, which shows dark on the PLM graphs, have irregular shapes and different diameters ranging from 5 to 250 µm.

A particle diameter distribution was summarized to study the effect of rotor speed on the phase morphologies of CIIR/PA 12 blends, and the result is shown in Figure 11. More than 85% particles in blend 9 (40 rpm), blend 3 (70 rpm), and blend 10 (100 rpm) have diameters of 10 to 40 µm and these particles reflect the effect of rotor speed.

As the rotor speed increases from 40 to 70 rpm, the number of particles in the range of 10 to 20 µm increases while that of



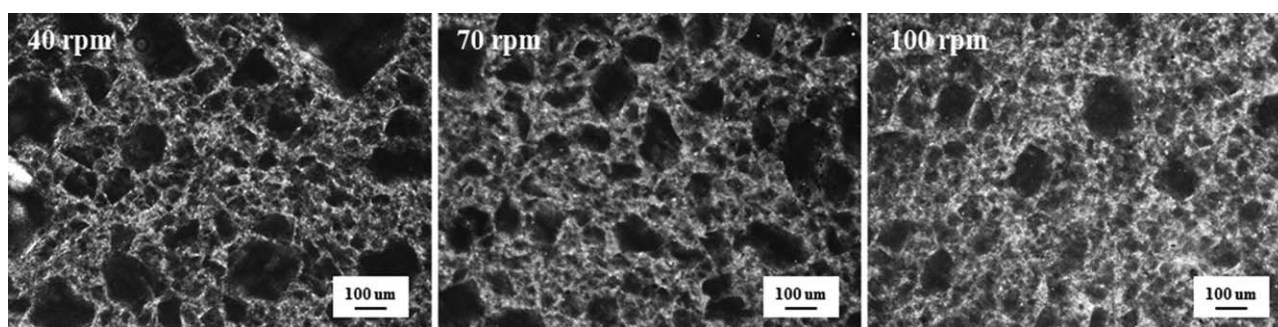
**Figure 11.** A particle diameter distribution statistics of CIIR/PA 12 blends with different rotor speeds in Haake rheometer.

20 to 40 µm decreases. However, the trend behaves unexpectedly opposite: the number of particles in the range of 10 to 20 µm decreases while that of 20 to 40 µm increases as the rotor speed increases from 70 to 100 rpm. The result indicates that a rotor speed of 70 rpm is a moderate mixing rate leading to a better morphology compared with 40 rpm and 100 rpm.

Generally, the shear stress which facilitates the breakup of rubber in PA 12 matrix increases as the rotor speed increases. However, when the rotor speed increases, the shear heat and shear thinning of PA 12 decrease the viscosity of PA 12, and thus have an adverse effect on the breakup of rubber. According to the result gained from the diameter distribution, increasing shear stress dominates when the rotor speed increases from 40 to 70 rpm, and this facilitates the breakup of rubber in PA 12 matrix. However, when the rotor speed increases from 70 to 100 rpm, the increasing shear heat and shear thinning of PA 12 dominates and this have an adverse effect on the breakup of rubber. In a word, 70 rpm is a more moderate rotor speed than 40 rpm and 100 rpm to break up the pre-crosslinked CIIR in PA 12.

## CONCLUSIONS

The effect of pre-crosslink degree, plasticizer (PIBSA), blending temperature and rotor speed on the phase morphologies of CIIR/PA 12 blends in a Haake Rheometer was investigated. These factors have significant effects on the modulus of rubber



**Figure 10.** Polarized light optical microscope (PLM) graphs of CIIR/PA 12 blends with different rotor speeds in Haake rheometer.

phase as well as the molten viscosity of PA 12 matrix, and thus play important influence on the breakup of pre-crosslinked CIIR. The results show that a low crosslink degree, a high content of plasticizer, a low blending temperature and a moderate rotor speed of 70 rpm facilitate the breakup of pre-crosslinked CIIR in PA 12 matrix. We can conclude that the breakup of crosslinked rubber phase as well as the molten viscosity of thermoplastic matrix. The diameter of the pre-crosslinked CIIR dispersed phase even with very low pre-crosslink degree mainly ranges from 5 to 30  $\mu\text{m}$ , much larger than 0.5 to 2  $\mu\text{m}$  of rubber particles in commercial EPDM/PP TPV reported in literatures. This is mainly due to the low shearing effect resulted from very low molten viscosity of PA 12 as well as the poor compatibility between PA 12 and CIIR. It seems that it is harder to prepare CIIR/PA TPV than EPDM/PP TPV.

#### ACKNOWLEDGMENTS

We would like to acknowledge the National Basic Research Program of China (Grant No. 2011CB606003) for financial support, and the financial supports of the National Natural Science Foundation of China under Grant No. 51221002 are also gratefully acknowledged.

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