

# Synthesis and Properties of Nano Carboxylic Acrylonitrile Butadiene Rubber Latex Toughened Phenolic Resin

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**ABSTRACT:** Nano carboxylic acrylonitrile butadiene rubber latex-toughened-phenolic resins (XNBRL-PF) were prepared by *in situ* polymerization in this work. The influence of nano XNBRL on the microstructure and physical properties of modified PF resin was investigated. Impact test testified that the impact strength of XNBRL-PF was remarkably improved compared to pure PF and as the content of XNBRL increased to 10 wt %, the impact strength of the XNBRL-PF kept increasing. Scanning electron microscope analysis of the fracture surface of the XNBRL-PF indicated that the XNBRL were uniformly dispersed in the PF matrix, with diame-

ters ranging from 200 to 400 nm. The results of Fourier transform infrared spectroscopy proved that chemical reaction occurred between XNBRL and PF matrix, which can greatly improve the interface interaction between rubber particles and PF matrix. Thermogravimetric analysis test showed that the incorporation of XNBRL can improve the thermostability of PF at low temperatures. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1079–1084, 2012

**Key words:** phenolic resin; toughness; XNBRL; crazing; shear band

## INTRODUCTION

As phenolic resins enter their second century of existence, they have continued being used as coatings, adhesives, composites, and foams<sup>1–4</sup> as a result of their excellent flame resistance, heat resistance, insulativity, dimensional stability, and chemical resistance. They are equally important as a resin matrix for fiber reinforced composites used in critical high performance areas such as aircraft interiors/panels, tunnel materials, offshore oilfield grating, deluge pipe, and fire safe components. However, the inherent brittleness and the cure shrinkage are the major drawbacks that hinder the widespread applications

of phenolic resins. For most applications, they are modified by the inclusion of fibers such as glass fibers,<sup>5</sup> carbon nanotubes and carbon fibers,<sup>6</sup> inorganic nanoparticles such as alumina,<sup>7</sup> silver<sup>8</sup> and silica,<sup>9</sup> or rubber to improve the toughness of the final products.

Rubber-toughened phenolic resin is the most common toughening system. Rubbers such as nature rubber,<sup>10</sup> nitrile rubber,<sup>11–13</sup> and styrene-butadiene rubber<sup>14</sup> are widely used. While among them nitrile rubber is the most established and commercially exploited choice to improve toughness of the cured phenolic resin because its solubility parameter is the closest to phenolic resin ( $\delta = 10.5$ ), so they have good compatibility. The nitrile rubber component in the system imparts elasticity and resilience, which helps to improve mechanical performance by absorbing energy. The role of rubber in the blend is to modify deformational behavior. The interactions between the nitrile rubber and phenolic resin at the interfacial zone have a dominant effect on the mechanical properties of the blend. Nowadays, nitrile rubber-toughened phenolic resin is prepared by physical mixing in common, and the most common method is to mix rubber and phenolic resin in the mixing machine, but it is not only labor intensive and time-consuming, but also limited in rubber dispersion. In the high temperature conditions, its

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impact strength is low, and the durability is not good. Another way to make rubber-toughened phenolic resin is solution blending. First rubber and phenolic resin are dissolved in the cosolvent, then remove the solvent by evaporation, and get the product. However, this method requires a long time, and the cost is relatively high. Moreover, it will produce large quantities of volatile gases, which may pollute the environment.

In this article, a new method was used to prepare rubber toughened PF. Nano XNBRL was added into the PF reaction system in the process of novolac's polymerization, and powerful shear force was adopted to improve the homogeneous dispersion of rubber particles in the PF matrix. In the process of polymerization, the functional group ( $-\text{COOH}$ ) of XNBRL react with  $-\text{CH}_2\text{OH}$  of PF, which further improve the dispersion of the rubber particles and the interface interaction between rubber particles and PF matrix. Details of the research results will be discussed in this article.

## EXPERIMENTAL

### Materials

Materials used in the study were novolac PF synthesized in our laboratory with phenol (99%) and formaldehyde (99%) monomers obtained from Beijing Chemical Factory, China. Oxalic acid (99%), a catalyst agent, was supplied by Beijing YiLi Fine Chemical Company, China. Hexamethylenetetramine (HMTA), a curing agent, was supplied by Beijing Yili Fine Chemical Company, China. Nano carboxylic acrylonitrile butadiene rubber latex (XNBRL) whose particle size is 169.2 nm, a toughening agent, was supplied by Shandong Zibo Qilong Chemical Company, China. Sodium hydroxide (NaOH), a neutralizing agent, was supplied by Beijing Chemical Factory, China. Silicon oil, an antifoaming agent, was supplied by Beijing Lianhua Fine Chemical Company, China.

### Preparation of novolac phenolic resin

The novolac phenolic prepolymer was synthesized in a three-neck flask equipped with a thermometer, a reflux condenser and a stirrer. The reagents, 300 g phenolic (3.19 mol), 6 g Polysorbate (Tween 80), and 160 g formalin (37 wt % water solution, 1.97 mol), were fed into the three-neck flask reactor. The reaction was catalyzed by 1.5 g oxalic acid and proceeded at 85°C for 60 min in the reactor. Then 52 g formalin (0.64 mol) and 0.9 g oxalic acid were replenished to the system, proceeding at 90°C for another 90 min. At the end of the reaction, a calculated amount (1.80 g) of NaOH was

dispersed in 10 mL of water and added to neutralize the oxalic acid catalyst. After cooling the system to 70°C, calculated amounts of XNBRL (0, 2, 4, 6, 8, and 10 wt %, respectively) which were dispersed in an equivalent amount of water, were dropwise added into the system. It was then strongly stirred for another 30 min. The mixture was dehydrated at a Gauge pressure of  $-0.1$  MPa until the temperature reached 160°C.

### Gel permeation chromatography (GPC)

The molecular weights and distribution of XNBRL-PFs were estimated with GPC 515-2410 System (Water), with polystyrene as the standard and with a refractive index detector, and the sample was eluted with anhydrous tetrahydrofuran (THF).

### Flowability

The flowability of XNBRL-PFs was characterized by flowing length. The experiment was performed on a heated glass plate according to ISO 8619. The viscosity of XNBRL-PFs was measured by a tone plate viscometer (mode CPA2000, Shanghai Jiehu Instruments), and the testing temperature was 170°C.

### Thermogravimetric analysis (TGA)

The heat decomposition temperature ( $T_d$ ) was measured by thermogravimetric analysis with a TGA Q500 thermal analyzer at a heating rate of 10°C/min from 20 to 800°C in an atmosphere of nitrogen.

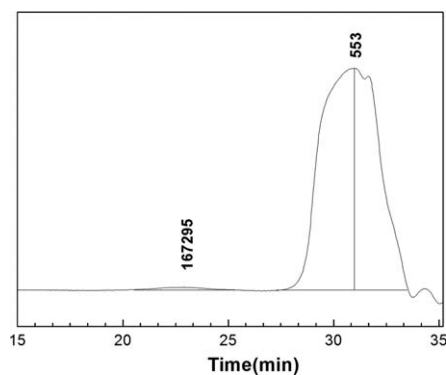
### Fourier transform infrared spectroscopy (FTIR)

The possible chemical reaction between XNBRL and PF was examined by attenuated total reflection (ATR)-FTIR. The experiments were done in a Nicolet NEXUS FTIR spectrometer with a microscope attachment at a resolution of  $2\text{ cm}^{-1}$ .

Three kinds of samples were prepared for testing, sample 1 being pure PF; sample 2 being dry XNBRL, and sample 3 being the purified XNBRL-PF. To prepare sample 3, the XNBRL-PF was first washed with ethanol to remove PF, and then the undissolved materials were thrown into THF. After 24 h of dissolution, ethanol was added to the solution and the purified XNBRL-PF was precipitated out.

### The test of SEM

The morphology of fracture surface of the samples was examined with a FEI XL-30 field emission environment scanning electronic microscope (SEM). Samples were sputter coated with a thin gold layer under vacuum situation.



**Figure 1** Molecular weight and distribution of XNBRL-PF.

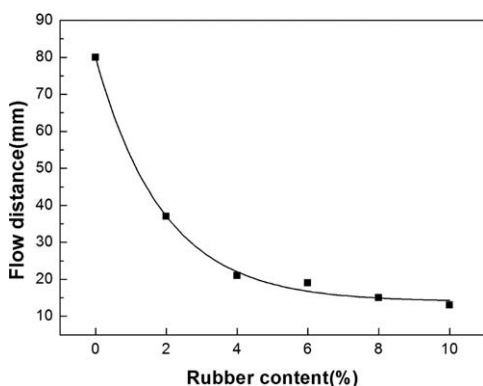
### Mechanical property measurements

#### Preparation of specimens

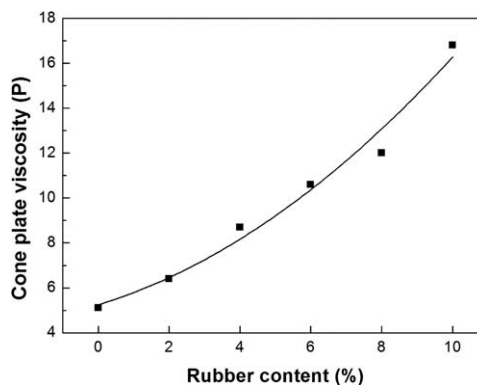
The phenolic resin powder was mixed with 10% hexamethylenetetramine. Threw the mixtures into a mold with dimensions of  $80 \times 10 \times 4$  mm, then put it into a press molding machine (mode SLY-812A, Dongguan Blue Eagle Jewelry Machinery factory) for curing. The curing process consisted of four stages. The first one was preheating stages, whose pressure was 2–3 MPa, and temperature was  $110^\circ\text{C}$ . This stage cost about 15–30 min. The second phase was the heating stage, at which the pressure slowly rose to 12 MPa, and the temperature rose to  $170^\circ\text{C}$ . That cost about 30 min. After that, the pressure and temperature of the system were maintained for about 10min. Then the system was left to cool down naturally to  $60^\circ\text{C}$ , while the pressure was kept at 12 MPa. After curing, the specimens were removed from the molds.

#### Izod Impact strength

To characterize the mechanical behavior, especially the toughness, of the specimens, IZOD test was carried out in this work. This test was performed on a



**Figure 2** Flow distance of phenolic resin as a function of rubber content.



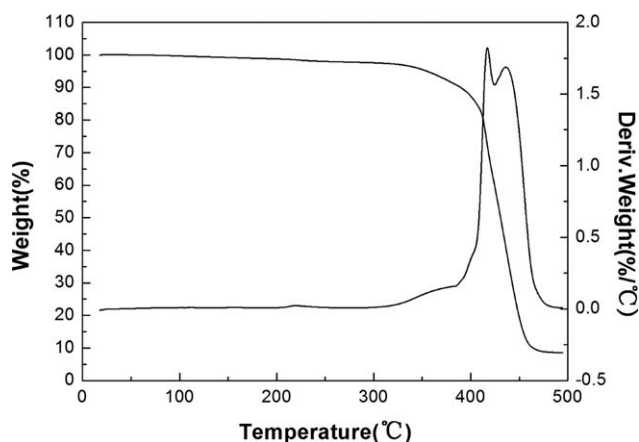
**Figure 3** Cone plate viscosity of phenolic resin as a function of rubber content.

GT-7045-1 impact machine (GOTECH testing machines) according to testing standard ISO180. Each sample was tested up to five specimens.

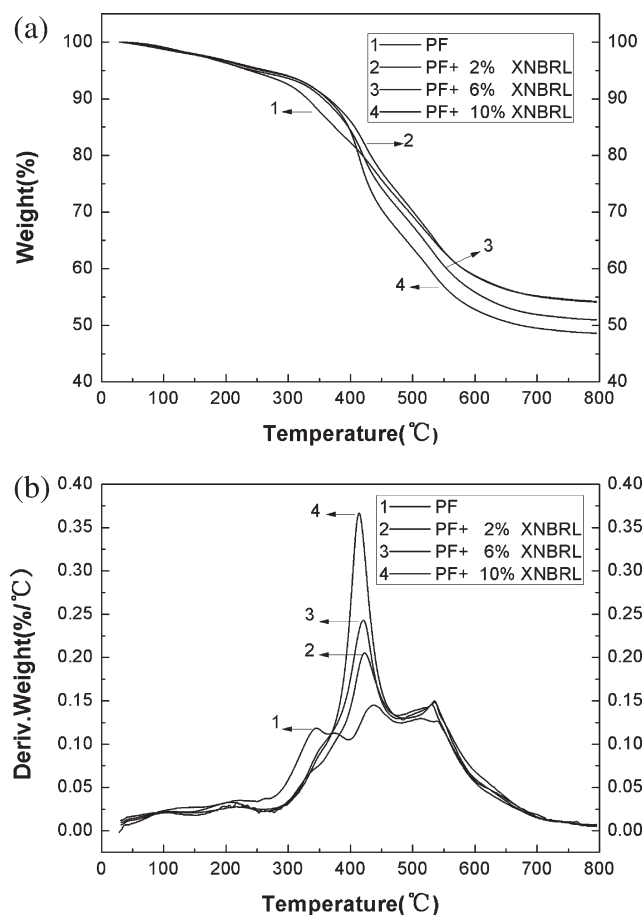
## RESULTS AND DISCUSSION

The elution profile in GPC for XNBRL-PF is shown in Figure 1. The molecular weights were estimated from GPC using polystyrene standards. The band at long retention time corresponds to PF, whose molecular weight is about 553 g/mol. In addition, the small peak at short retention time arises from XNBRL-graft-PF, whose molecular weight is evaluated as 167,295 g/mol. It should be noted that the molecular weight of pure XNBRL is about 30,534 g/mol. And the increase of molecular weight indicates that XNBRL may graft to the PF.

Figures 2 and 3 show the effect on the flowing length (Fig. 2) and the viscosity (Fig. 3) of PF associated with an increase of XNBRL content. It can be observed that with the increase of nano XNBRL content, the flowing length rapidly shortens, and the cone plate viscosity dramatically rises. It indicates that the incorporation of nano XNBRL deteriorate



**Figure 4** TG-DTG pattern of carboxylated nitrile rubber latex (XNBRL).



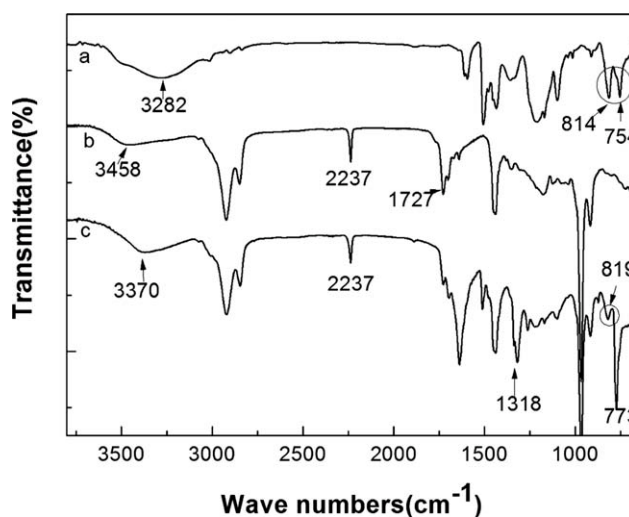
**Figure 5** (a) TG pattern of phenolic resins with different rubber content; (b) DTG pattern of phenolic resins with different rubber content.

the flowability of phenolic resin, which will cause difficulties in processing.

To understand the influence of nano XNBRL on the thermal properties of the toughened PF, TGA tests of pure XNBRL (Fig. 4) and XNBRL-PF (Fig. 5) were carried out in this work. Figure 4 shows the TG-DTG curves of pure nano XNBRL. It can be observed that the thermal decomposition temperature of XNBRL is about 420°C, and when the temperature reaches 500°C, the carbon residue of XNBRL is less than 10%.

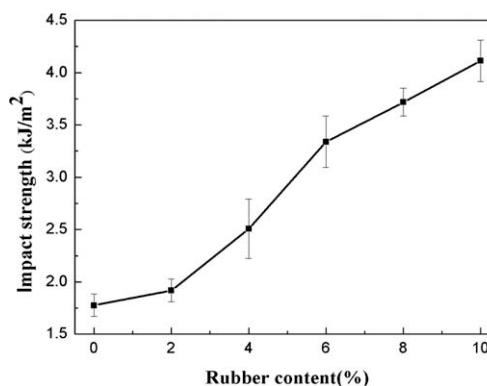
**TABLE I**  
Residual Weight at Different Temperature with Different Rubber Content

Wt % XNBRL	Residual weight at different temperature (%)							
	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C
0	100	96	92	82	69	59	55	54
2	100	97	94	86	70	59	55	54
4	100	97	94	85	68	58	54	53
6	100	97	94	85	68	56	52	51
8	100	97	94	85	65	54	51	50
10	100	97	94	84	64	53	49	48



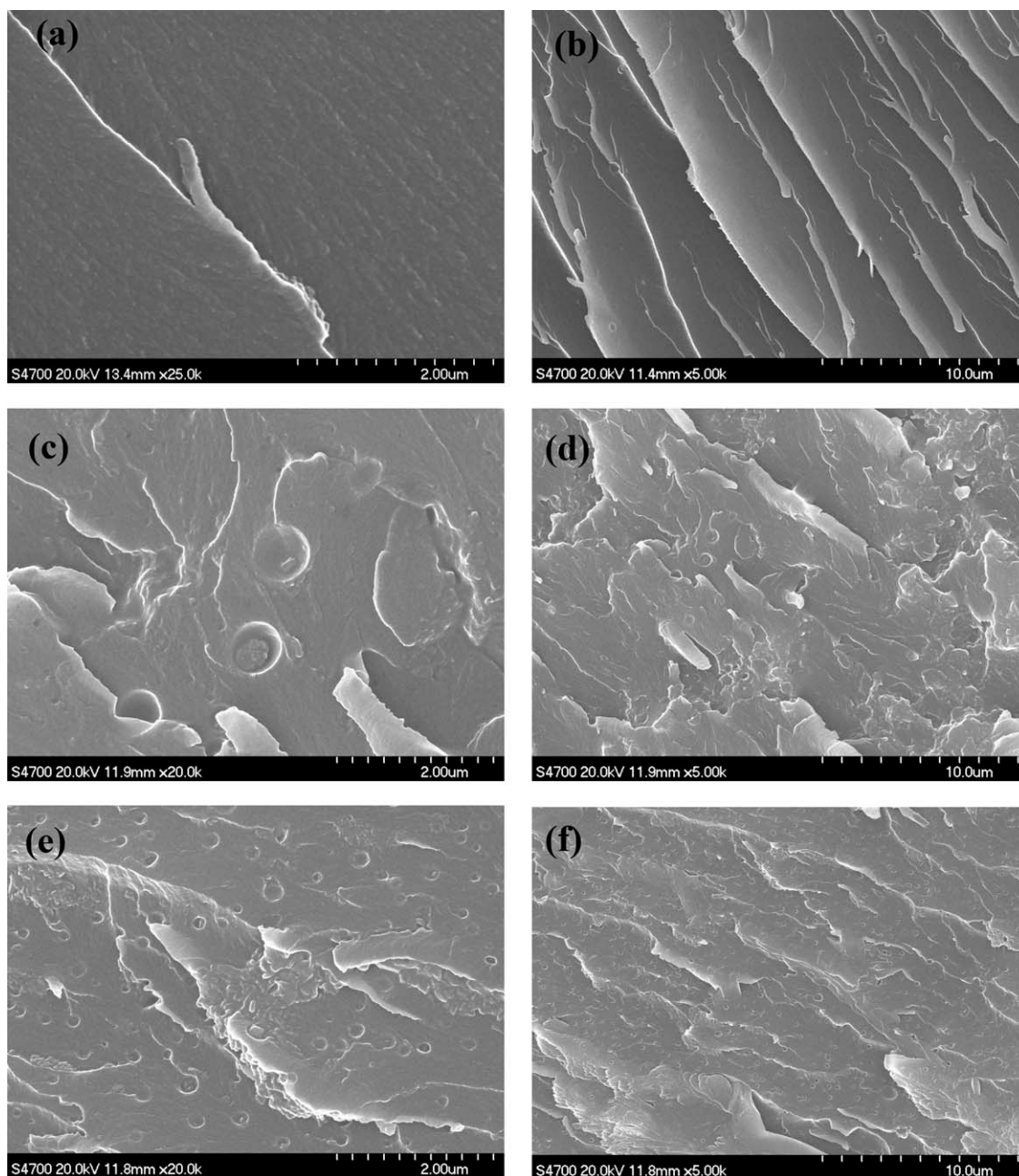
**Figure 6** FT-IR spectra for (a) pure PF, (b) pure XNBRL, and (c) the purified XNBRL-PF.

Figure 5 gives the TG-DTG curves of the phenolic resins with different rubber content. It shows that at low temperature region (below 400°C), the carbon residue amount of XNBRL-PF is higher than that of pure phenolic resin, while at intermediate and high temperature regions (above 400°C), the weight loss rate of XNBRL modified phenolic resin increases; and the more the rubber are added, the faster the weight lost [Fig. 5(a)]. It can be clearly seen in Table I that the carbon residue of the modified phenolic resin containing 10% XNBRL is 8% lower than pure phenolic resin. Figure 5(b) shows that the first decomposition peak for pure phenolic resin occurs at 330°C, while for the XNBRL toughen PF, this peak shifts to a higher temperature (close to 420°C). Obviously, the peak intensity of the XNBRL toughen PF is higher than that of pure PF, and with the increasing amount of XNBRL, the peak intensity increases correspondingly. Both the two figures illustrate that the rubbers improve the thermostability of PF at low temperatures, but when the temperature is



**Figure 7** The impact strength of phenolic resin as a function of rubber content.





**Figure 8** SEM photographs of impact fracture surface of phenolic resins. (a) and (b) un-toughened; (c) and (d) 4% XNBRL toughened; (e) and (f) 8% XNBRL toughened.

high, the thermostability of the composite deteriorate. This can be attributed to the reaction between XNBRL and phenolic resin, which may favor the thermostability of PF at low temperature. At the temperature above  $420^{\circ}\text{C}$ , XNBRL is almost completely decomposed (as shown in Fig. 4), so the thermostability of the composite is poor.

Figure 6 shows the FTIR spectra of pure PF (a), pure XNBRL (b), and the purified XNBRL-PF (c). The existence forms of hydroxyl group are noticeably changed after the reaction. Before the reaction, the stretching vibration of phenolic hydroxyl group shows a broad peak at  $3282\text{ cm}^{-1}$  [shown in Fig.

6(a)], and the stretching vibration of hydroxyl group of XNBRL shows a peak at  $3458\text{ cm}^{-1}$  [shown in Fig. 6(b)]. After the reaction, the peak appears at  $3370\text{ cm}^{-1}$ , which indicates that some hydroxyl groups have reacted with each other. Moreover, for the purified XNBRL-PF, a new peak occurs at  $1318\text{ cm}^{-1}$ , which is attributed to the stretching vibration of C—O. It implies the appearance of the COOC group, due to the reaction between —COOH of XNBRL and —CH<sub>2</sub>OH of PF. Finally, the peak at  $754\text{ cm}^{-1}$  and  $814\text{ cm}^{-1}$  is attributed to the out-of-plane deformation vibration of C—H at the ortho and para position of phenolic hydroxyl group. In Figure 6(c),

the peak at  $819\text{ cm}^{-1}$  is noticeably weakened, indicating the hydrogen atoms at ortho position of PF were subject to substitution of some active functional group on XNBRL surface during the *in situ* reaction. Anyhow, FTIR analysis does testify the chemical reaction between XNBRL and PF, which finally results in the enhancement of interfacial interaction between XNBRL and PF matrix.

Mechanical properties of XNBRL-PF are shown in Figure 7. It is evident in Figure 7 that the impact strength is enhanced with the increase of the rubber content correspondingly. When rubber content increases to 4 wt %, the increase of impact strength is particularly evident. Impact strength of the phenolic resin with 2, 4, 6, 8, and 10 wt % XNBRL increase by 8, 42, 88, 109, and 130% compared with the pure phenolic resin. The reason will be discussed in the following text. It should be noted that the toughening effect of PF modified by XNBRL or CNBEP (carboxylic nitrile butadiene elastomeric nanoparticle) is similar.<sup>11</sup>

SEM photographs of impact fracture surface of phenolic resin are shown in Figure 8. The fracture surfaces of pure phenolic resin [Fig. 8 (a,b)] are relatively smooth, suggesting that no significant plastic deformation has occurred near the fracture surface, and the fracture toughness is quite poor. The fracture surfaces of the toughened phenolic resin are relatively rough and contain many voids uniformly dispersed throughout the PF matrix [Fig. 8 (c-f)]. The diameters of these voids range from 200 to 400 nm, slightly bigger than the initial size of nano XNBRL (169.2 nm). It is obviously that, the rubber particles formed cavitations when they subjected to a shear deformation. The success of XNBRL rubber as a toughening agent for phenolic resin can be summarized as follows. First, it is closely related to the rubber's ability to form cavitations. The rubber cavitations cause local constraint relief in the material, which in turn promote the formation of crazing and shear bands in the matrix. Given sufficient rubber cavitations, the stress state in a constrained body can be changed into a plane stress state. As a result of this constraint relief, the crazing and shear bands initiation process in the phenolic matrix is circumvented, and the surrounding phenolic matrix can undergo more plastic deformation and absorb more plastic energy.<sup>15-18</sup> Besides, during the propagation of the crazing and shear bands, they may encounter rubber particles, and the rubber particles will prevent them from further expansion. The generation and development of crazing and shear bands will spend a lot of energy in the material, so that the

impact strength increases significantly.<sup>19,20</sup> What's more, the good interface between PF and XNBRL also contributed to the good impact strength. It should be noted that in some holes some residue rubber particles can be clearly seen, which indicate the strong force between rubber particles and PF matrix.

## CONCLUSIONS

A new type of XNBRL/PF nano-composite is introduced and the toughness of PF is remarkably improved. It can be observed that the XNBRL particles are uniformly dispersed in the PF matrix with diameters ranging from 200 to 400 nm. With the increase of rubber content, the impact strength of the composite increased correspondingly, while the flowability decreased inversely. The rubber cavitations, the crazing, shear bands and the shear yielding of the phenolic resins contribute to the toughness of phenolic resins. Furthermore, it was proved that new chemical bond was formed between XNBRL and PF under the condition of high shear and high temperature. The incorporation of XNBRL can improve the thermostability of pure PF at low temperatures, but when the temperature increase further, the thermostability of the composite will decrease.

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