

# EXPERIMENTAL AND THEORETICAL STUDY ON THE MECHANICAL PROPERTIES OF NOVOLAC PHENOLIC RESIN NANOCOMPOSITES: EFFECTS OF NANOCLAY AND MULTIWALLED CARBON NANOTUBE

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## Abstract

*The present work focused on the characterization of mechanical properties of novolac phenolic resin (PF) filled with two types of clays, including modified and unmodified ones, and multiwalled carbon nanotube (MWCNT). It was found that the solution mixing method is able to disperse the nanoparticles within the PF resin appropriately. It was also shown that the unmodified clay (Cloisite Na<sup>+</sup>) has the highest influence on the mechanical properties possibly due to the good level of dispersion as well as the good interfacial interaction. Theoretical analysis based on the rubber elasticity theory showed that the nanoparticles influence the evolution of crosslinking density and network structure.*

## 1 Introduction

Phenolic (PF) resin is a kind of thermosetting polymers which are widely used in many areas such as molding compounds, coating, fiber reinforced composites, foundry shells and cores, printed circuit boards, brake friction materials and insulating materials due to its excellent thermal stability, high ablative properties, good solvent/chemical resistance, high electrical resistance, high char yield and good mechanical properties. This material is commercially available in two different forms including liquid resole and powdery novolac. These two types of PF resin differ sensibly in their molecular structure and cure reactions. Therefore, each type is much suited for some applications due to their initial physical state and curing process. For instance, resoles are preferably employed for coating applications while novolacs are widely used in molding compounds. Similar to many polymer nanocomposite systems, the incorporation of nanofiller in the PF resin has also attracted the attention of researchers. Among the nanoparticles, nanoclays and carbon nanotubes have been much considered recently in literature for improving various aspects of PF for different applications.

Literature shows a limited investigation on the novolac/clay and novolac/carbon nanotube (CNT) nanocomposites. Choi and Chung [1] investigated the role of functionality of organoclay on the mechanical properties of novolac/clay nanocomposites prepared by melt mixing method. Kang et

al. [2] used the same mixing method, i.e. melt mixing, to examine the role of organic modifier of clay on the nanodispersion of novolac/clay nanocomposites. Melt mixing method is considered as commercially attractive approaches for preparing polymer nanocomposites, owing to its simplicity and economic viability. However, it suffers from poor dispersion of nanoparticles, particularly for composites composed of a large volume of nanoparticles, and damage of fibrous nanoparticles caused by high shear stresses. Moreover, the melt mixing of highly reactive resin like novolac, which is commercially contained with curing agent, is risky and may lead to evolution of curing process during the mixing. Alternatively, solution mixing method is so efficient to obtain uniform dispersion of nanoparticles within the polymeric matrix and does not have the risk of resin curing during the mixing process. Additionally, the solution mixing method retains the aspect ratio of original nanoparticles which is much important for carbon nanotubes. Tai and Yeh [3] used the solution mixing method to investigate the effect of CNTs on mechanical properties of novolac/CNT nanocomposites. Recently, Zhang et al. [4] reported the morphological characteristics and thermal stability of novolac/clay nanocomposites with variable clay content up to 4 wt% prepared by solution mixing. The present work focused on the investigation and comparison of the mechanical properties of novolac/clay and novolac/CNT nanocomposites prepared by solution mixing method. In this study, the content of nanoparticles varied up to 20 wt%. The attempts were also made to explore the structure-property relationship in these nanocomposites as well.

## **2 Experimental**

Novolac phenolic resin (IP 502) was obtained from Resitan co., Iran. This resin contained 8-10 wt% amount of HMTA as curing agent. Two types of clay based on sodium montmorillonite including unmodified Cloisite Na<sup>+</sup> (abbreviated by CN) and organically modified clay, Cloisite 30B (abbreviated by CB), both from Southern Clay Co, were employed. Meanwhile, multi-walled carbon nanotube (MWCNT) functionalized with carboxylic group (TNMC2 from Timesnano) was used as fibrous reinforcement.

The morphology of the clay nanocomposites and neat clay were examined by X-Ray diffraction analysis (XRD) using Philips diffractometer (40 kV, 30 mA,  $\lambda=17.9$  nm, Netherlands). The dispersion of PF/clay samples were also examined by a transmission electron microscope (TEM, model CM120; Philips, Netherlands) at an accelerating voltage of 120 kV. The fractured surface of the PF/MWNT was examined using scanning electron microscopy (FESEM, HITACHI, Japan S-4160). The dynamic mechanical tests were performed using a Perkin-Elmer DMA 8000 analyzer. The specimens were deformed under bending mode using a single cantilever clamp arrangement. The measurements were performed at fixed frequency of 1 Hz and the temperature from ambient to 350 °C at a heating rate of 5°C/min. The glass transition temperature ( $T_g$ ) was determined as the temperature at the maximum of  $\tan\delta$  vs. temperature curve. Mechanical properties were determined using a HIWA 2126 universal testing machine from Hiwa Eng, Co. The tensile tests were performed on rectangular strip according to ASTM D3039 and the flexural properties were measured according to ASTM D790 with rate of 2 mm/min.

PF resin was dissolved in methanol at ambient temperature using high speed mixer (shimifan mixer). The nanoparticles (both clays and MWCNT) were added to the PF/methanol solution and then the mixtures were stirred using a high speed mixer at 2000 rpm for 10 min to get homogenous suspensions. Then the suspensions were followed by sonication using Bandelin Sonorex (35 kHz) sonicator for 30 min at ambient temperature in order to get good degree of nanodispersion. Eventually, the compounds were dried at room temperature for 24 h followed by

vacuum drying at 70° C for 2h to remove the methanol and humidity. The dried samples were grounded in the form of fine powder to prepare the final test specimens using the compression molding. Prior the compression molding, all the compounds were polymerized at 130°C for 6 min under vacuum to obtain B-staged samples. Then the prepolymerized samples were poured into steel mold frame (200×130×2 mm<sup>3</sup>), hot pressed under 200 bars at 140°C for 8 min to fabricate PF/clay composites. Finally, postcuring of the specimen compounds was accomplished by heating them in an oven for 12 hr at 150-200°C to improve the crosslinking of matrix in composites.

### **3 Results and discussion**

#### *3.1 Morphology*

The dispersion of clays in PF resin could be analyzed by XRD. Table 1 presents the d-spacing of cured samples at different loadings of clays. In all samples only a single peak was observed in the XRD spectrum which has been shifted with respect to the corresponding neat clay.

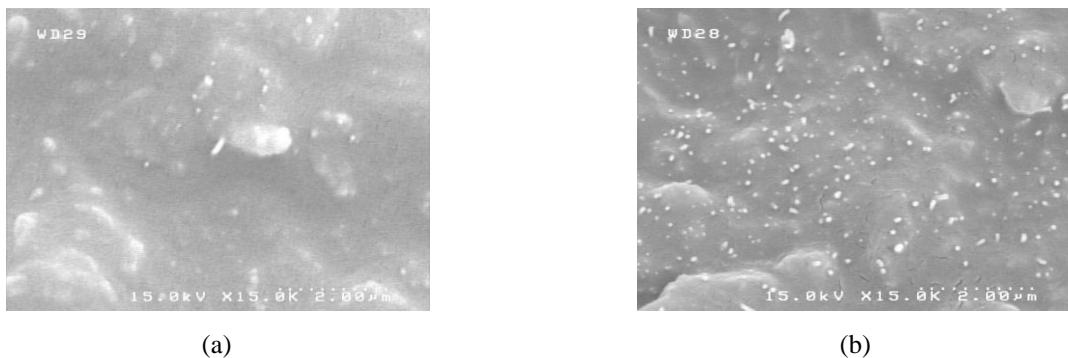
It is revealed that the d-spacing of neat Cloisite Na<sup>+</sup> has increased in the nanocomposites, suggesting the formation of intercalated morphology in PF/CN system. It is noteworthy that such intercalation has not been observed when the PF/CN is mixed with melt mixing method [4], while, as observed here, the solution mixing method is capable to accommodate PF molecules between the clay gallery even at high clay loadings possibly with the aid of solvent. The dispersion state for Cloisite 30B follows a reverse behavior in which the d-spacing of neat Cloisite 30B powder is higher than that of CB in the PF matrix. The decrease of d-spacing for organoclay in presence of PF has already been reported by some researchers as well [4]. Figure 1 shows TEM images of PF/clay nanocomposites at 2.5 wt%. In this figure presence of intercalated morphology is clearly evidenced. Figure 2 shows FESEM images of fracture surfaces of PF/MWCNT at 2.5 and 20 wt%. Good dispersion of MWCNTs in resin can be detected even at high nanotube loadings showing the effectiveness of solution mixing method in preparation of PF/MWCNT nanocomposites.

<b>Compound</b>	<b>d-spacing (nm)</b>	<b>2θ (°)</b>
	<b>[cured sample]</b>	
Cloisite Na <sup>+</sup>	1.19	8.63
Cloisite 30B	1.85	5.56
PF/CN-2.5	1.56	6.58
PF/CN-20	1.47	6.99
PF/CB-2.5	1.59	6.46
PF/CB-20	1.65	6.21

**Table 1.** Effect of nanoparticle on d-spacing of PF/CN and PF/CB composites



**Figure 1.** TEM images of PF/clay nanocomposites at 2.5 wt%. a) PF/CN b) PF/CB.



**Figure 2.** FESEM images of PF/CNT nanocomposites a) PF/MWCNT-2.5 b) PF/MWCNT-20.

### 3.2 Dynamic mechanical analysis

DMA is a very useful technique for investigating the dynamic mechanical behavior and viscoelastic response of a polymeric material. Figures 3-5 show the temperature dependency of loss tangent and storage modulus of the neat PF and its nanocomposites. As shown in Figures 3-5, the presence of the nanoparticles decreases the value of  $\tan\delta$  peak. The loss tangent peak is associated with the molecular movement of polymeric chains within the network structure. It is well established that the higher the peak  $\tan\delta$  value, the greater the mobility of the polymeric chains. On comparing the peaks in Figures 3-5, it can be seen that the neat novolac has the highest value of  $\tan\delta$  peak. It is revealed that the incorporation of nanoparticles, regardless of the type, decreases the  $\tan\delta$  peak, however, the extent of reduction and trend of variation with nanoparticle contents differ for each nanoparticle.

From Figures 3-5, it is deduced that the maximum reduction belongs to PF/CN system, among other nanocomposites, and the  $\tan\delta$  peak decreases continuously by increasing the content of Closite Na<sup>+</sup>. This offers that the chain mobility of PF molecules is restricted greatly in presence of Closite Na<sup>+</sup> suggesting the good interfacial interaction in this case. For PF/CB system,  $\tan\delta$  peak decreases by increasing the content of Closite 30B up to 5 wt% loading, however, beyond that concentration it enhances by increasing the content of Closite 30B. This behavior is possibly related to the role of Closite 30B on the reduction of crosslinking density at higher loadings. For PF/MWCNT system, the  $\tan\delta$  peak decreases continuously by increasing the content of nanotubes, however the extent of reduction is lower than those of two clays. This is possibly

attributable to the role of MWCNT on the evolution of crosslinking density of PF. The broader  $\tan\delta$  curve of PF/MWCNT compared to other clays filled samples confirms this behavior.

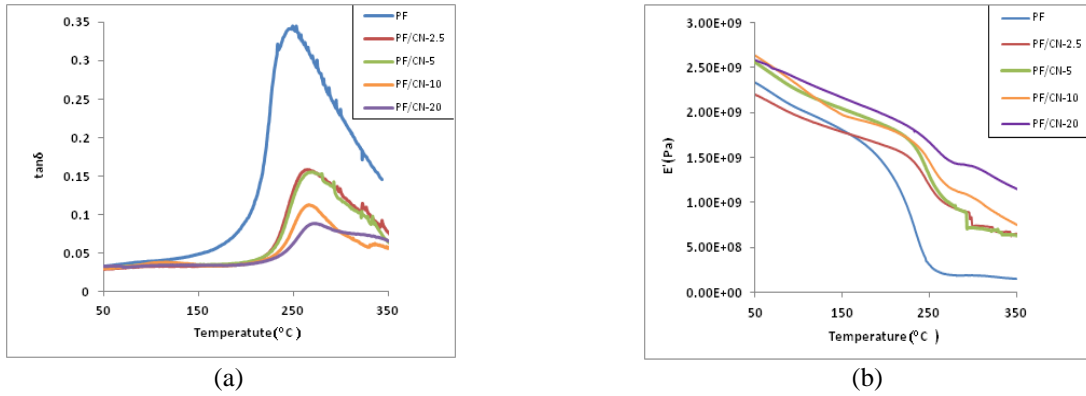


Figure 3. DMA curves of the cured PF/CN composites. a)  $\tan\delta$ -temperature b) storage modulus-temperature

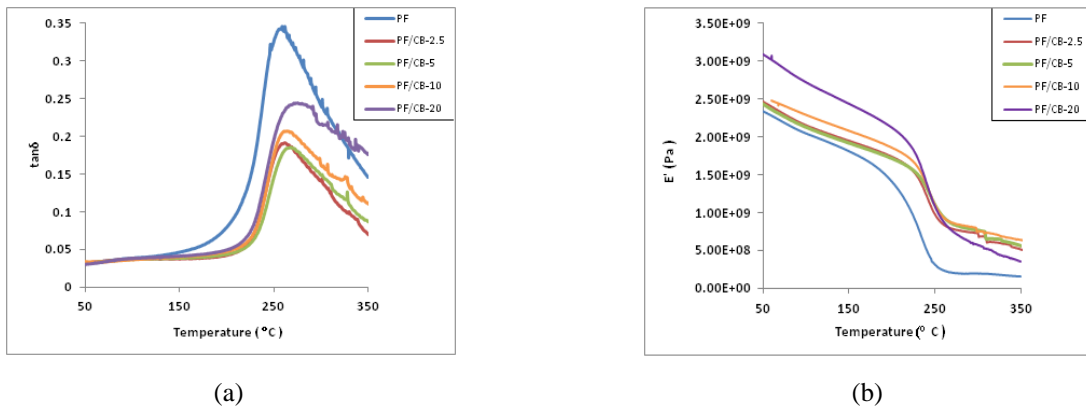


Figure 4. DMA curves of the cured PF/CB composites. a)  $\tan\delta$ -temperature b) storage modulus-temperature

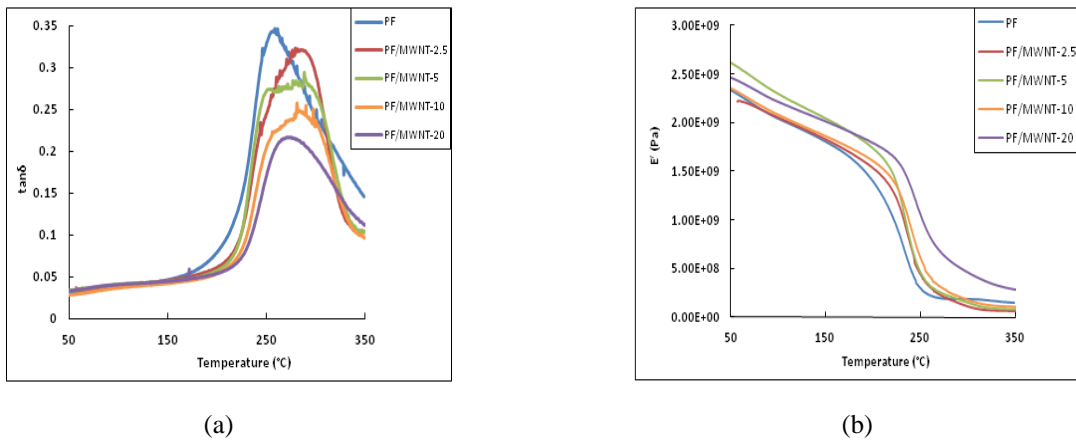


Figure 5. DMA curves of the cured PF/MWCNT composites. a)  $\tan\delta$ -temperature b) storage modulus-temperature

Table 2 exhibits the  $T_g$  for all of the samples. The  $T_g$  increase with addition of nanoparticles to the novolac resin and this indicated that the chain mobility of the crosslinked novolac is restricted by the presence of nano particles. According to the theory of rubber elasticity, it is possible to estimate the effect of nanoparticles on crosslinking density of novolac network using Eq. (1) [5]:

$$v_e = \frac{E'_r}{3RT_r} \quad (1)$$

where  $v_e$  is the crosslinking density,  $E'_r$  is the dynamic modulus at the rubbery state,  $T_r$  is taken to be 340°C, higher than that of  $T_g$  of the samples, and R is the universal gas constant. Table 2 presents the crosslinking density calculated by Eq. (1). It is inferred that all three nanoparticles influence the crosslinking density. It is noteworthy that the crosslinking density obtained here is in good agreement with the trend of variation of  $\tan\delta$  peak with nanoparticle loading. The results show that novolac nanocomposite containing Closite Na<sup>+</sup> has much higher  $v_e$  value than the nanocomposites containing Closite 30B which can be due to an appropriate interaction at the polymer/particle interface. Interestingly, crosslinking density of phenolic resin decreased with addition of MWCNT, except for 20wt%. These results show that nanotube have reducing effect on crosslinking density. In summary, we can conclude that MWCNT decreases the crosslinking density and the reduction of  $\tan \delta$  peak by incorporation of MWCNT is related to its good interaction with phenolic resin. Both clays increase crosslinking density but unmodified one had better effect due to the better interaction with resin.

compounds	$T_g(^{\circ}\text{C})$	$E'_r$ (Pa)	$v_e$ (mol/m <sup>3</sup> )
PF	257.6	$1.611 \times 10^8$	10534
PF/CN-2.5	265.6	$6.709 \times 10^8$	43869
PF/CN-5	269.9	$6.414 \times 10^8$	41940
PF/CN-10	266.6	$8.024 \times 10^8$	52467
PF/CN-20	271.3	$1.204 \times 10^9$	78727
PF/CB-2.5	261.6	$5.461 \times 10^8$	35708
PF/CB-5	267.6	$6.010 \times 10^8$	39298
PF/CB-10	264.7	$6.540 \times 10^8$	42764
PF/CB-20	274.2	$3.850 \times 10^8$	25174
PF/MWNT-2.5	279.2	$0.60475 \times 10^8$	3955
PF/ MWNT-5	287.8	$0.8515 \times 10^8$	5570
PF/ MWNT-10	280.5	$1.050 \times 10^8$	6867
PF/ MWNT-20	271	$3.0913 \times 10^8$	20216

Table 2.  $T_g$  and Crosslinking density of cured samples

### 3.3 Mechanical properties

Table 3 shows the tensile and flexural moduli of PF resin and its nanocomposites reinforced with both types of clay and MWCNT at various loadings. Tensile and flexural moduli of the nanocomposites reinforced with 2.5, 5, 10 and 20wt% nanoparticles are higher than the neat

phenolic resin. As the silicate layer and MWCNT have very high mechanical properties compared with PF resin, the enhancement in mechanical properties of nanocomposites can be related to nanodispersion level and polymer-filler interaction. It is revealed that tensile modulus increases significantly by incorporation of 2.5 wt% of all nanoparticles which can be attributed to the uniform dispersion of nanopartilces at such a low content. Therefore at higher nano particles loading, the loss in nanodispersion restricts the improvement of tensile modulus. In spite of tensile modulus, the flexural modulus increases continuously with increasing the nano particles content for all of them. This indicates that the flexural modulus is less sensitive to the state of dispersion and it is mainly dominated by the nano particle content.

As can be found from Table 3, the modulus of PF/CB composites at given clay content is lower than that of PF/CN. This can possibly be attributed to the lower portion of silicate layer in CB compared to CN because of its organic modifier. According to manufacturer, the ignition loss of CB is 30 wt% while for the CN this parameter is 7 wt%. The CNT modulus (~1 TPa) is higher than silicate layer (170 GPa) but as can be seen from Table 3, tensile modulus of PF/MWCNT nanocomposites are lower than PF/clay nanocomposites. This difference can be explained by the positive effect of clay on crosslinking density and better dispersion of clay in matrix in comparison with MWCNT.

In order to describe the reinforcing efficiency of nanoparticles in PF resin, Halpin-Tsai model was used to analyze the elastic modulus of PF nanocomposite. The Halpin-Tsai model is described as follows [6]:

$$\frac{E_c}{E_m} = \frac{1 + \eta\xi\phi_f}{1 - \eta\phi_f} \quad (2)$$

where  $\eta$  is given as:

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \xi} \quad (3)$$

In Eqs.2 and 3,  $E_c$  is the tensile modulus of the nanocomposites,  $E_m$  is the tensile modulus of the matrix, taken to be 2.4 GPa,  $E_f$  is the tensile modulus of nanoparticlaes,  $\phi_f$  is the volume fraction of the filler, and  $\xi$  is a shape parameter depending on the shape and aspect ratio of the filler. Table 3 shows the  $\xi$  parameters obtained by curve fitting. This result indicates that  $\xi$  decreases by increasing the nanoparticle content which can be attributed to the suppression of dispersion at higher loadings.

compounds	Tensile Strength (MPa)	Tensile Modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	$\xi$
PF	28	2.4	99	3.4	-
PF/CN-2.5	44	4.3	100.5	4.1	375.552
PF/CN-5	41	3.4	98	4.3	14.38294
PF/CN-10	39	3.6	103	4.4	6.328339
PF/CN-20	38	4.4	95	4.8	3.419126
PF/CB-2.5	45	3.9	100	3.5	73.78685
PF/CB-5	40	3.5	98	3.6	13.06603
PF/CB-10	37	3.1	103	4	1.742346
PF/CB-20	35	4.1	69	4.4	1.819699
PF/MWNT-2.5	30	3.9	85	3.7	52.2674
PF/ MWNT-5	32	3.4	79	3.7	8.338698
PF/ MWNT-10	35	3.2	83	4.0	1.869591
PF/ MWNT-20	25	2.6	61	4.6	1

Table 3. Mechanical properties of samples

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