

The Effect of Nanoclay and MWNT on Fire-Retardency and Mechanical Properties of Unsaturated Polyester Resins

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ABSTRACT: The influence of nanomaterials such as Multi-Walled Carbon NanoTubes (MWNT) and organoclay (Cloisite 30B) on the physical and mechanical properties of thermoset matrix such as Unsaturated Polyester (UP) resins is investigated. Although styrene containing UP resins have a wide spread application in industry, lack of information exists regarding the behavior of MWNT/organoclay/polyester ternary nanocomposite systems. The main aim of this research was first to evaluate the effect of nanofiller on the flammability of UP resins and, second, to characterize their mechanical properties such as toughness and their tensile strength. The rheological studies showed shear thinning for samples of UP resins containing MWNT and Cloisite 30B.

The cone calorimetry measurement was used to evaluate the flame-retardency, the gas emission of the nanocomposite and whether or not this system can be designated as a nanocomposite. This was understood in the test by the peak heat release rate being lowered and shifted to shorter times. Furthermore, the tensile and impact properties of samples were evaluated. The obtained results indicated that nanofiller particles caused both increase and decrease in the impact and tensile strength. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1154–1159, 2012

Key words: unsaturated polyester; nanoclay; MWNT; flame-retardency; mechanical properties

INTRODUCTION

The unsaturated polyester (UP) resins are widely used in composite industry because of their low price, ease of processing, and good chemical resistance. The UP based materials have been used in many applications including automotive, construction, transportation, storage tanks and piping. Their poor impact properties and high flammability are the most important disadvantages of cured resins which limit their applications. Ordinary flame-retardents such as aluminum or tin compounds must be used in large amounts (>30 wt %) to render the resins flame-retardent. The amount of additive may increase the viscosity of the resin in such a way that limits the processability of the filled resin in applications such as the Resin Transfer Molding (RTM).^{1–3} These compounds will also affect the mechanical properties and make the resin more brittle after curing. To overcome these problems, scientists have recently focused on nanofillers such as MWNT and nanoclay. Nanoclays exhibit some superior properties when compared with their microsized or macrosized counterparts. MWNT exhibits higher aspect ratio as well as mechanical, thermal, and electrical properties when compared with nanoclays, which make them prime

candidates as reinforcing constituents in various polymers for the production of nanocomposites. A work conducted by Nazare et al.⁴ and Beyer⁵ showed that incorporating nanoclays results in a fair flame-retardency in the UP resins. Another group has reported that the ethylene-vinyl acetate (EVA)-based nanocomposites using organoclay and carbon nanotubes have shown an improvement in flame-retardency and a lower toxic smokes emission.⁶ Peeterbroeck et al.⁷ have incorporated various types of MWNT into EVA copolymers by melt blending and showed that they have strong influence on the fire-retardency of nanocomposites. In another study, Liqun Ju et al. and Seyhan found that nanoclay increases impact strength and decreases tensile strength but MWNT led to an improvement in tensile strength.^{8,9} Elsewhere, Beyer¹⁰ reported that the simultaneous use of nanoclay and MWNT improves the flame-retardency of poly vinyl acetate (PVA) up to 150 percent more than that of the pristine polymer. To our knowledge, there is no or little study on the simultaneous use of organoclays and multi-walled carbon nanotubes in the UP based nanocomposites. In this work, the effect of MWNT and organoclay mixture on the rheological behavior, mechanical properties, and, specially, the flame-retardency of UP resins will be investigated.

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EXPERIMENTAL

TABLE I
Composition of Samples

Sample	Unsaturated polyester	Organoclay (phr)	MWCNT (phr)	MEKP (phr)	Co (phr)
CLP1	100	5	–	3	0.2
CCP2	100	5	0.2	3	0.2
CCP4	100	5	0.4	3	0.2

to mix nanoclay (Cloisite30B from the Southern Clay™) and polyester (RTM1000 supplied by Resitan Co.) for ca. 5 h using a stirrer rotating at a speed of 1200 rpm at room temperature. The ultrasonic agitation was used to further boost the organoclay/resin dispersion. The ultrasonic agitation was carried out at 40°C for 3 h. Finally, the MWNT was added to the organoclay/polyester mixture. The prepared liquid samples were cured at room temperature using some peroxide such as methyl ethyl ketone peroxide (MEKP) (50% solution supplied by Iran Peroxide) and Cobalt Naphtanate (1% solution supplied by Merck) as accelerator. The cured samples were kept at room temperature for 2 days and post-cured at 90°C for 6 h. The tensile and impact measurements were performed using ASTM D638 and ASTM D256 standards, respectively. To investigate the rheological properties of samples at room temperature a modular compact rheometer (MCR300) from Physica Anton Paar (Stuttgart, Germany) was used. The cone calorimetry measurement (according to ISO5660-1:2002 using dual core FTT Cone Calorimeter apparatus, England) was carried out to evaluate the flame-retardency of the sample and to see if the sample can be regarded as nanocomposite. The compositions of samples are listed in Table I.

RESULTS AND DISCUSSION

Figure 1 shows the viscosity as a function of shear rate for the raw UP resin and the UP filled with 5 parts per hundred resins (phr) of nanoclay and 0.2–0.4 phr MWNT in the solution state (without any curing agent). The viscosity of samples containing both MWNT and nanoclay was significantly

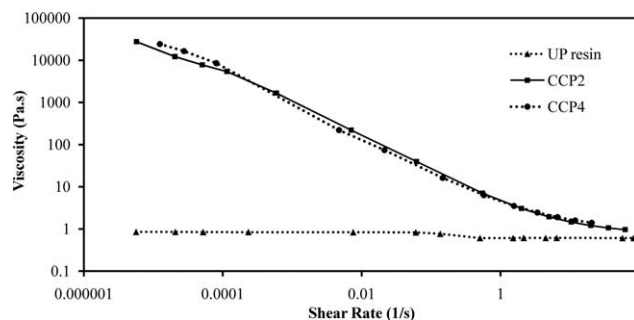


Figure 1 Viscosity of UP and UP with MWNT and clay as a function of shear rate.

higher than the pure UP resin. Also, shear thinning behavior was observed for the nanofilled samples, that is, the viscosity is reduced with increasing shear rate. This non-Newtonian behavior should be due to the compatibility and interaction of nanofillers, for example, MWNT and nanoclay with polyester. On one hand, the high aspect ratio of carbon nanotubes and the orientation interaction between MWNT and polymer at higher shear rates reduces the viscosity of filled UP system and creates shear thinning behavior. On the other hand, slippage of polymer chains between silicate layers of nanoclay at high shear rates is another reason for shear thinning. The viscosity of samples at shear rate of ca. 10 s^{-1} was almost the same as that of the raw UP resin. It is very important in a process such as RTM, where a low viscosity resin is required for the uniform filling of the mold cavity.^{10,11} The filler incorporation may cause an increase in viscosity, making it harder for the resin to penetrate into the porous mat. Should a shear thinning resin is designed to show appropriate shear thinning when required and sustain a high viscosity upon the cessation of flow, it would be our goal in this regard.

The X-Ray Diffraction (XRD) pattern of UP/clay hybrid (this sample introduced in Table I as CLP1) is given in Figure 2. The characteristic XRD peak of pure Cloisite30B is observed at 5.1° . For the UP/Cloisite30B, this peak was shifted to 2.21° , and based on Bragg's law, d-spacing increases to ca. 43 \AA suggesting an ordered intercalation of the polymer chains into the organoclay layers. On the other hand, the presence of a small secondary peak in ca. 4.85° means that the nanoclay is dispersed in UP matrix via fully intercalated structure but it did not lose its ordered platelet structure via dispersion or exfoliation. To reach appropriate mechanical properties in nanocomposites, a fully intercalated structure is desired since the complete dispersion or exfoliation of clay in thermoset resin matrix significantly decreases the cross-link density (CLD) of resin and leads to poor mechanical properties of final nanocomposite.

The transmission electron microscopy (TEM) micrographs of sample containing 5 phr organoclay and 0.4 phr MWNT are shown in Figure 3. As is

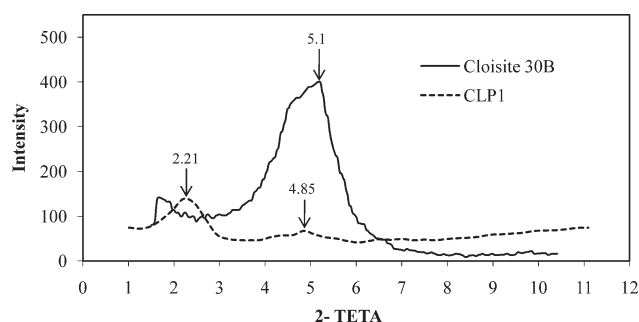


Figure 2 XRD patterns of UP and nanofilled samples.

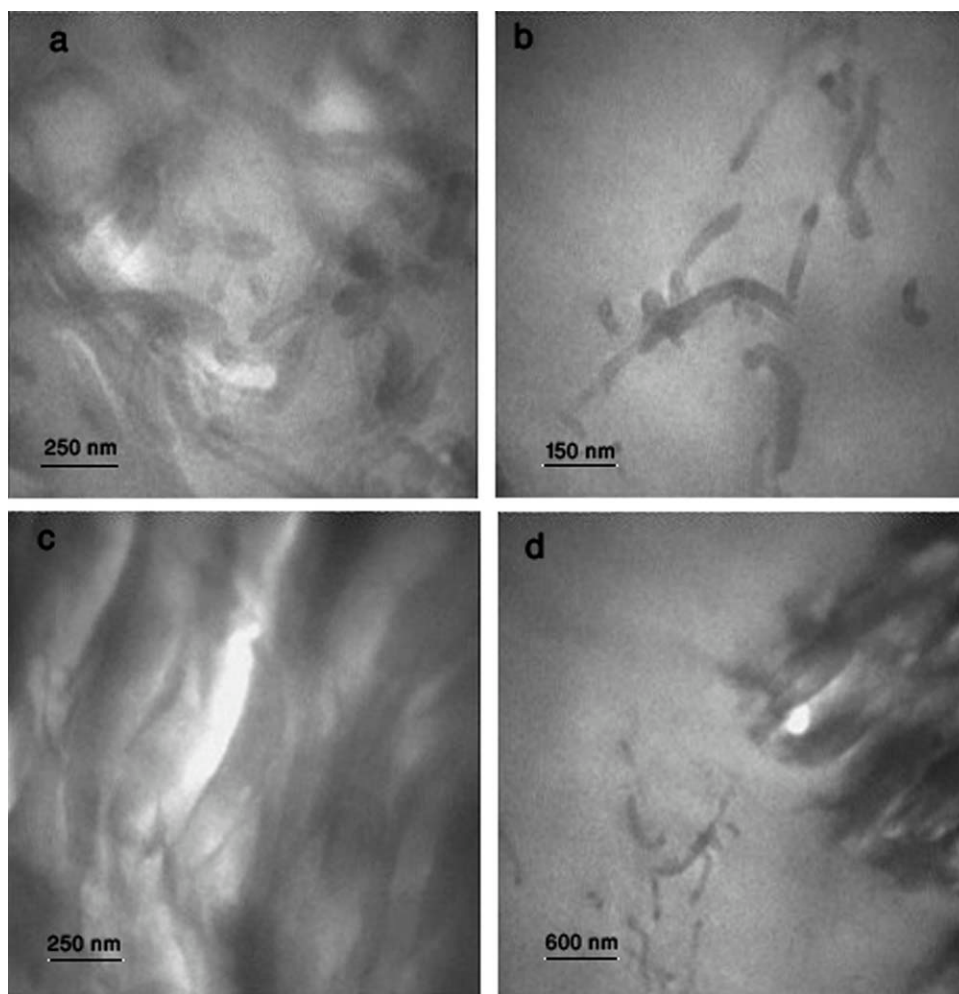


Figure 3 TEM micrographs of sample containing 5 phr organoclay and 0.4 phr MWNT: (a) dispersion of MWNT, (b) dispersion of MWNT, (c) silicate layers of organoclay, and (d) dispersion of nanofillers.

seen in Figure 3(a,b), MWNT exhibits good dispersion in the UP without any critical agglomeration. As can be seen in Figure 3(c), the organoclay layers did not lose their ordered platelet structure supporting the XRD results. Overall, it can be inferred from both the XRD and TEM micrographs that some nanostructures were formed in the prepared samples.

As shown in Figure 4, the tensile strength of samples is smaller than the neat UP resin. This response

is characteristic of the systems reinforced with the stiff materials and is particularly noticeable for the intercalated nanocomposites of a thermoset matrix. This is due to the chemistry and reduction of cross-link density of the matrix by formation of intercalated structure.⁶ On the other hand, the higher surface area of the carbon nanotubes and good dispersion of MWNT in matrix pronounce a covalent bonding and may result in a better load transfer

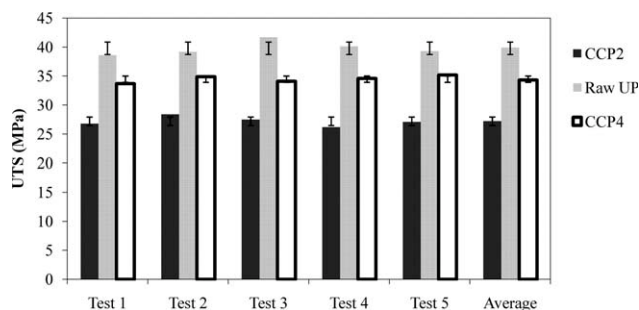


Figure 4 Ultimate tensile strength of raw UP and UP/MWNT/clay samples.

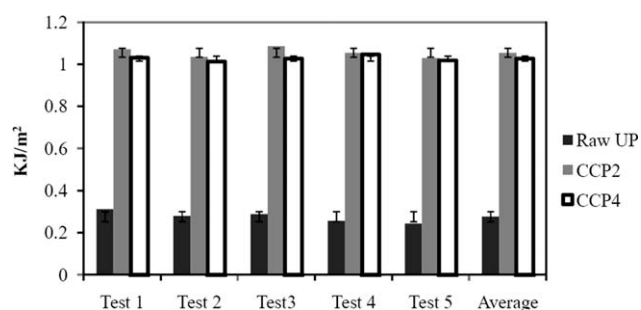


Figure 5 Impact test results for raw UP and UP/MWNT/clay samples.

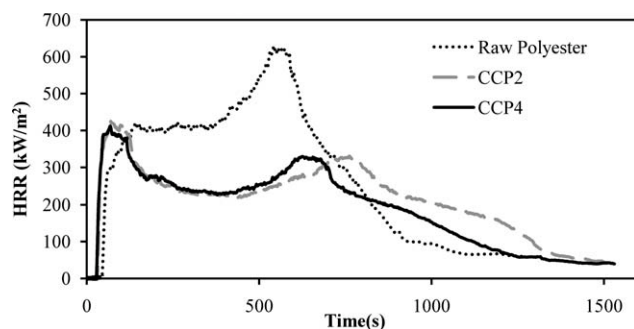


Figure 6 Heat release rate of UP and UP/MWNT/clay samples.

efficiency at the interface region leading to an improvement in tensile strength. Because of the lower level of MWNT when compared with that of organoclay in the system, it is impossible to observe the tensile strength of nanocomposite in a range comparable to the values of raw UP resins.⁷

An stretched MWNT has a crucial role in the tensile strength value of the system. Although there is a lower level of MWNT when compared with that of organoclay, there would be a lack of improvement in total tensile strength of the nanocomposite when compared with the values of raw UP resins. However, because of the higher level of MWNT in CCP4, the ultimate tensile strength of this sample was significantly larger than CCP2.

The impact results showed in Figure 5 demonstrate a favorable toughness improvement of the brittle UP resin by adding a small amount of nanofiller. The toughening mechanism in this system is the creation of a new surface as the primary mechanism. Another factor that affects the fracture toughness is the polymer–silicate and polymer–MWNT interfaces where the failure mechanisms were located mainly at this point. Thus, a route to improve the toughness of these materials is through strengthening the bonding between the polymer–silicate and polymer–MWNT surface.⁶

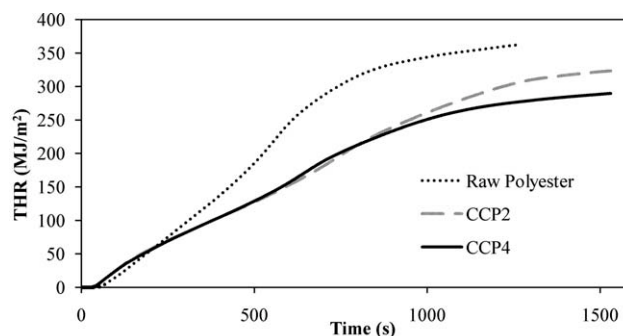


Figure 7 THR rate of UP and UP/MWNT/clay samples.

Cone calorimetry

To understand the flammability and thermal stability of nanocomposites, the cone calorimetry technique was implemented. This test was run at a heat flux of 50 kW/m². Under this condition, the UP resin ignited after 46 s reaching a peak heat release rate (PHRR) of 622.521 kW/m² and burnt for 1078 s. As shown in Figure 6, the PHRR of UP containing nanofiller was shifted to a lower value and the burning process took longer time to complete. It is a sign of good dispersion of MWNT and organoclay in the UP matrix and the formation of nanostructure in the system which results in a flame-retardant nanocomposite.

The flame-retardency is understood to be due to the formation of a barrier layer (char) by MWNT and clay at the samples of surface. When the sample containing MWNT and clay are exposed to fire or heat flux, at an early stage, MWNT would move to the surface of samples and make the primary insulating layer. It is due to the shape and size of MWNT allowing those to migrate to the surface of material and form initial insulating layer faster than systems containing only organoclay. At a later stage, silicate layers of organoclay also move to the surface and form the main heat insulating layer in conjunction with MWNT. An important factor that is



Figure 8 Images of samples before cone calorimetry test.

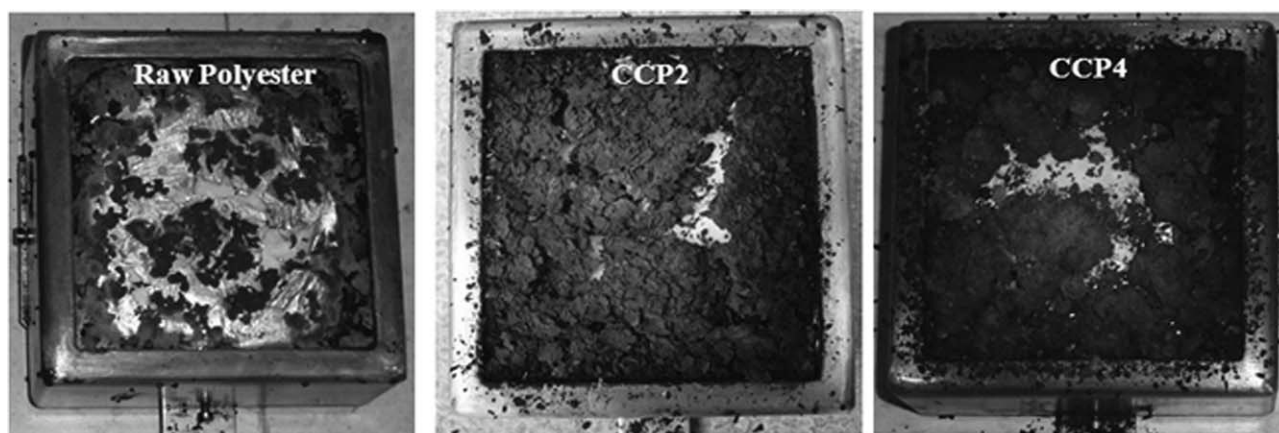


Figure 9 Images of samples after cone calorimetry test.

effective in the migration of organoclay silicate layers is the intercalated structure. In the intercalated structure, the silicate layers of organoclay were less captive between the UP chains when compared with that in the exfoliated structure. In which case, they could migrate more easily to the surface. Therefore, the nanofillers provide a barrier to both mass and energy transport and make the samples flame-retardant.

The Total Heat Release (THR) of the raw UP and the UP with MWNT and clay is shown in Figure 7. It is clear that the THR of nanofilled samples is lower than that of raw UP resin. As mentioned above, the insulating barrier layer is the main reason for reduction in the THR. The lower THR values of sample indicate that it has a little tendency to spread the fire and burning the surrounding objects.⁴

The images of the raw UP and the samples containing nanofillers before and after the cone calorimetry measurement are shown in Figures 8 and 9. As one can see, the nanocomposite samples have more burning residue than the residue observed for the raw UP. More char formation of samples is due to the barrier effect of nanofillers. It is in agreement with the previous results.

Another important factor in the burning process is CO and CO₂ content. The cone calorimetry results indicate that CO and CO₂ smoke values of nanofilled UP resins are much lower when compared with the raw UP resin as shown in Figures 10 and 11. The reduction in these values is considered to be due to the formation of a protective layer by nanofillers. It reduces the required fuel for burning and, as a result, the emissions of burning samples were significantly reduced when compared with the raw UP.^{11,12}

CONCLUSIONS

The nanocomposites containing MWNT, organoclay, and UP resin showed shear thinning behavior. The nanofillers interact with the polymer resin leading to the formation of a stable microstructure. The XRD and TEM results indicate the formation of an intercalated structure for organoclay and fine dispersion of MWNT in the UP resin. Furthermore, the mechanical properties measurements reveal that the simultaneous use of organoclay and MWNT causes a decrease in the tensile strength but, on the other hand, improves the toughness of the UP resin. Based on the cone calorimetry technique, the flammability of the

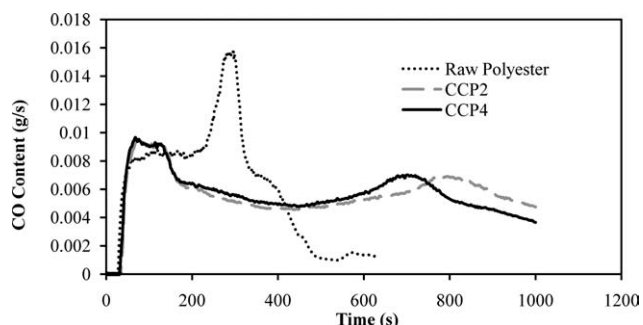


Figure 10 CO content of UP and UP/MWNT/clay samples.

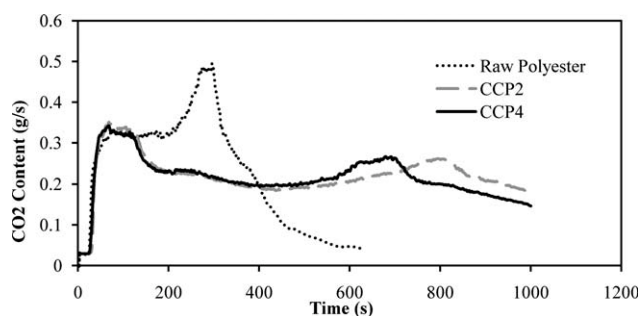


Figure 11 CO₂ content of UP and UP/MWNT/clay samples.

UP resin filled with nanofillers is decreased. It supports the formation of nanostructure in the system.

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