

SYNTHESIS OF UNSATURATED-POLYESTER/ORGANO-CLAY NANOCOMPOSITES: A FUNDAMENTAL APPROACH

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Abstract

Unsaturated-polyester (UP) nanocomposites, based on UP-alkyd usually dissolved in styrene monomer, may be synthesized using numerous possible approaches. The conventional approach is the synthesis of styrene-containing UP-resin/organo-clay nanocomposites via a single-step procedure. Applying this approach the effects of various mixing processes, using several organically modified clay types, were investigated. Incorporation of these organo-clays resulted in an intercalated structure, the extent of which depended on the clays' organic treatment. The second approach is the employment of a two-step procedure, in which the first step is the synthesis of styrene-free UP-alkyd/organo-clay nanocomposites. The effects of various mixing processes and several processing parameters were studied. Inducing high shear levels for prolonged time durations promoted the intercalation and exfoliation of the silicate layers, resulting in a better dispersion of clay particles. The high shear level effects were achieved by vigorous mechanical mixing and were intensified by using large amounts of clay and appropriate matrix viscosity. The UP-alkyd/organo-clay nanocomposites may be cured without styrene, using a new procedure recently developed in our laboratory, thus attaining thermoset UP-alkyd/organo-clay nanocomposites. The structure, thermal and dynamic mechanical properties of the thermoset nanocomposites were found to be highly affected by the peroxide content used. This methodological approach provides a basis for understanding the structuring processes involving the formation of the UP/clay nanocomposites and establishing materials-processing-structure interrelations.

1. Introduction

Thermoset polymers such as epoxies and unsaturated polyester (UP) resins, offer a wide range of industrial applications and are often used as matrices for composite systems. Nanocomposites may exhibit enhanced properties compared with the conventional composites, however, whereas epoxy based nanocomposites have been extensively investigated, there are only few studies on UP based ones. Unsaturated polyester resins are bi-component systems comprising an UP pre-polymer (alkyd) which is usually dissolved in styrene monomer. In the presence of a peroxide initiator, the system cures to an insoluble, infusible, cross-linked matrix. The multi-component system allows numerous approaches in synthesizing UP nanocomposites. Two different ways of mixing an organically modified clay with UP may be applied [1, 2]. The first method, simultaneous mixing, is similar to the method used for preparing conventional UP/filler composites. The second method is the sequential mixing, which is a new approach for synthesizing UP nanocomposites.

In the first step, a mixture of the alkyd and the organo-clay are prepared. The second step is the addition of styrene to the alkyd/clay pre-intercalates. Recently, a new method for crosslinking the UP chains was developed in our laboratory [3]. In this method styrene-free UP-alkyd chains are crosslinked in the presence of a peroxide curing-agent. It was found that curing with changing amounts of peroxide affects the curing kinetics and the final properties of the cured material. Thus, the UP-alkyd/clay nanocomposites may be cured through the addition of peroxide, undergoing decomposition in the UP/clay nanocomposites, ultimately forming thermoset styrene-free UP/clay nanocomposites.

These approaches were employed to synthesize UP/clay nanocomposites. The effects of preparation by various mixing processes, shearing levels applied, organo-clay contents and mixing temperatures were studied. This paper includes the highlights of a more elaborated study [2]. The effect of curing the UP-alkyd/clay systems with various amounts of peroxide was investigated. This methodological approach provides a basis for understanding the structuring processes involved in the formation of the UP/organo-clay nanocomposites and establishing materials-processing-structure interrelations.

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2. Experimental

Two basic mixing approaches for the synthesis of UP nanocomposites were employed, the simultaneous mixing method and the sequential mixing method. In the simultaneous mixing method, a commercial UP-resin (containing ~35wt% styrene) was mixed with various clay powders. Organically treated montmorillonite (MMT) clays and untreated MMT clay (used as a reference) were obtained from Nanocor, Inc., Illinois, USA. The Nanocor clays used were: Nanomer-I.35L (containing 60-70wt% MMT and 30-40wt% poly(oxyethylene decyloxypropylamine); basal spacing: 29.0E), Nanomer-I.30E (containing 70-75wt% MMT and 25-30wt% octadecylamine; basal spacing: 24.5E), Nanomer-I.28MC (containing 70-85wt% MMT and 15-30wt% octadecylamine; basal spacing: 22.1E), Nanomer-I.24TL (containing MMT and aminododecanoic acid; basal spacing: 17.5E), Nanomer-I.30TC (containing MMT and an unspecified treatment; basal spacing: 24.9E), and Nanomer-PGW (untreated clay, used as reference; basal spacing: 12.3E). Two mixing processes were used, mechanical mixing, or ultrasonication. Both methods were applied for 1h, at room temperature. To initiate polymerization (curing), 0.6wt% accelerator, cobalt octoate (6% in white spirit), and 2-2.5wt% of a free-radical initiator, methyl ethyl ketone peroxide (MEKP) were added. The nanocomposites were cured at room temperature and post-cured at 80°C for 4h. The clay content was 5 parts per hundred (phr) of the cured resin. The reference system was an UP-resin/untreated-clay (PGW) composite mixed at the same conditions.

In the first step of the sequential mixing method, styrene-free UP-alkyd (experimental grade, supplied by Makhteshim, Israel) and various organo-clay powders were mixed using three mixing processes: a static process, mechanical mixing or ultrasonication. The ultrasonication and static process were applied at 80°C for 2 and 24h, and the organo-clay content was 7.3wt% of the UP-alkyd/clay composite. The mechanical mixing was applied under two shear rate levels (~400 and ~1800rpm), at either 80 or 130°C, for several durations up to 24h. The organo-clay content was 7.3wt% and 24wt% of the UP-alkyd/clay composite. The organo-clay types used for the sequential mixing method were chosen in light of the foregoing studies of the simultaneous mixing method. The reference systems were neat alkyd and alkyd/24wt% untreated-clay (PGW) composite, mechanically mixed at 1800rpm and 80°C for several durations up to 24h.

The UP-alkyd/24wt% I.28MC organo-clay nanocomposites mixed for 20h were diluted into UP-alkyd/5wt% organo-clay and UP-alkyd/2.5wt% organo-clay systems through thorough mixing with fresh UP-alkyd using an Hsiangtai HG-300 homogenizer. To induce polymerization (curing), 2 or 6wt% of a selected free-radical peroxide, tert-butyl peroxy-3, 5, 5-trimethylhexanoate (Trigonox 42PR) by Akzo Nobel, the Netherlands, was added. Degassed samples were cured in an oven at 110°C for 24h, followed by post curing at 150°C for 4h.

The structure of the composites was examined with a Philips X'PERT X-ray diffraction (XRD) system with a Cu K α radiation source operated at 40kV and 40mA, at a scanning rate of 0.5°/min. The morphology of ultrathin cross-sections was investigated using a Philips CM120 cryo-transmission electron microscope (cryo-TEM) operated at -175°C and at 120kV. A TA AR1000-N parallel plates rheometer was used to study the steady rheological properties of the UP-alkyd/clay composites prior to curing. Tests were carried out at 80°C for the UP-alkyd/clay systems, except for the UP-alkyd/24wt% I.28MC organo-clay nanocomposite, mechanically mixed at 1800rpm and 80°C, which was tested at 100°C due to its extremely high viscosity. Dynamic mechanical thermal analysis (DMTA, Perkin Elmer series 7) was conducted in the three point bending mode at 1Hz. Heating was carried under an inert nitrogen atmosphere at a rate of 3°C/min under force control.

3. Results and Discussion

3.1 Simultaneous Mixing

UP-resin was admixed with several types of organically modified MMT clays and an untreated clay (PGW). The structure of the cured UP-resin/clay blends was characterized by XRD. Fig. 1 illustrates the clays' basal spacing of the as received clay and of the formed composites. The increase in the untreated clay basal spacing is regarded as insignificant. Intercalation of the treated clays by the UP chains, styrene monomer, accelerator, peroxide, or all of the species takes place, and nanocomposites are formed. The maximum intercalation is achieved in the Nanomers I.28MC, I.30E and I.30TC, the first two treated with octadecylamine (the treatment of the Nanomer I.30TC is unspecified). The difference in the level of intercalation between the I.28MC and I.30E organo-clays seems to be a result of the amount of organophilic treatment, which is probably larger for the I.30E clay as implied by its higher initial basal spacing, and the data given by Nanocor (detailed in the experimental section). As indicated by Fig. 1 there

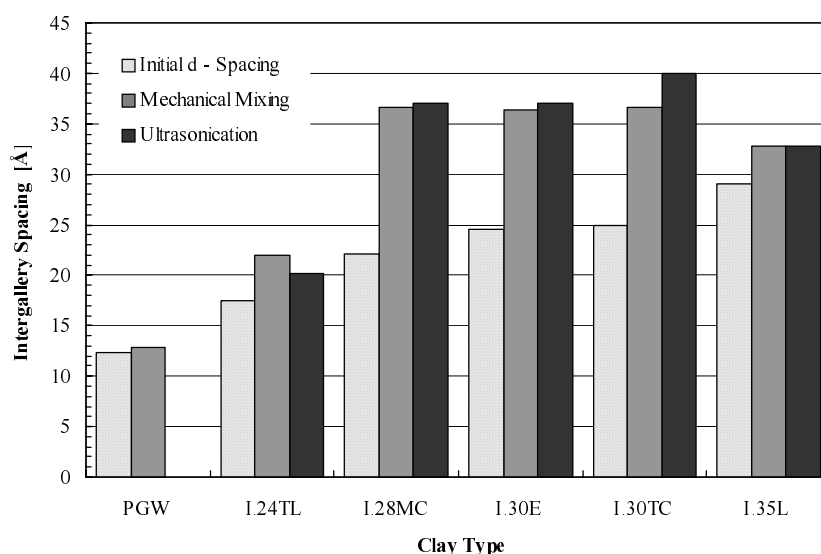


Fig. 1: Clay gallery height of several UP-resin/5phr organo-clay nanocomposites, prepared by mechanical mixing and ultrasonication.

is no conclusive evidence as to the superiority of one mixing method over the other (mechanical mixing or ultrasonication).

3.2 Sequential Mixing

Three types of organo-clays were chosen to be further investigated, Nanomers I.28MC, I.30E and I.35L. Mixing of the UP-alkyd and organo-clay was carried out by several processes (static process, mechanical mixing at ~400rpm, or ultrasonication) at various processing durations (2 or 24h). The nanocomposites of UP-alkyd/organo-clay show similar interlayer spacing as those prepared by the simultaneous mixing method, for each organo-clay type. The various mixing methods and durations did

not show any significant differences in basal spacing.

The rheological properties of particulate suspensions are sensitive to their composition, structure, particle size and shape and surface characteristics of the dispersed phase. Thus, rheology potentially offers a means to assess the state of dispersion in nanocomposites while still in the uncured state, and may offer a tool complimentary to the X-ray scattering technique, electron microscopy, etc. [4]. An increased viscosity may be attributed to three simultaneous processes. First, a higher intercalation level which results in a higher effective clay content and less polymer segments and chains participating in the bulk flow process [5, 6]. Second, exfoliation, which results in a higher exposed clay surface and

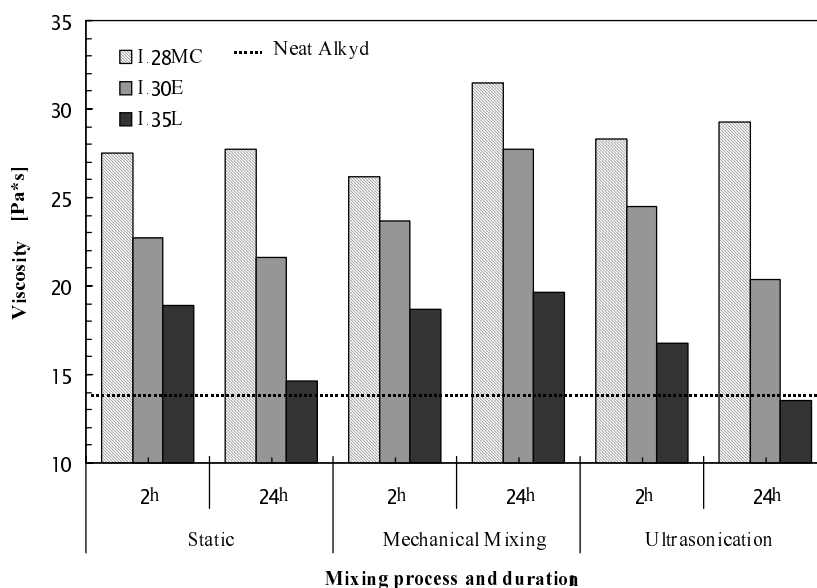


Fig. 2: Viscosity of various alkyd/7.3wt% organo-clay nanocomposites, prepared by a static process, mechanical mixing at 400rpm or ultrasonication, at 80°C for 2 or 24h. All the samples were tested at 80°C.

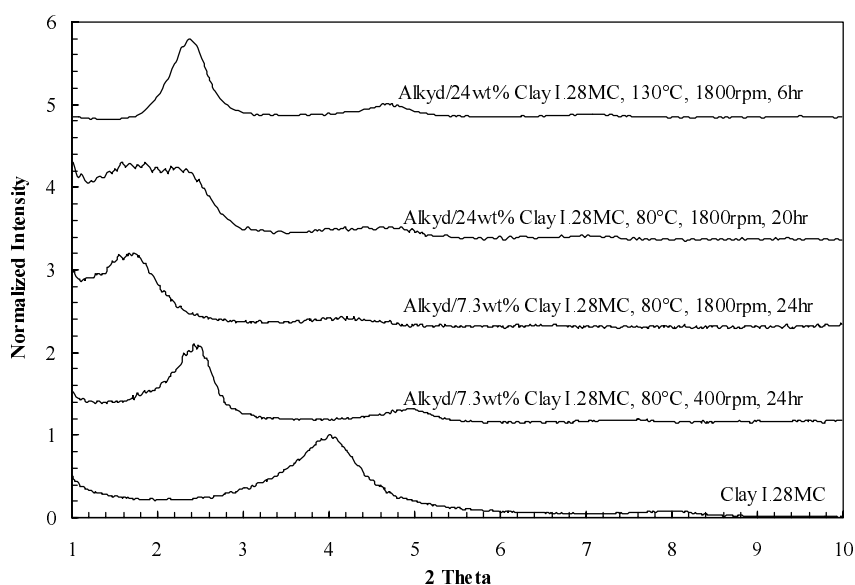


Fig. 3: X-ray diffraction patterns of neat I.28MC organo-clay, UP-alkyd/7.3wt% I.28MC organo-clay nanocomposite, mechanically mixed for 24h at 80°C and 400rpm/1800 rpm and UP-alkyd/24wt% I.28MC organo-clay nanocomposite, mechanically mixed at 1800 rpm and 80°C for 20h or 130°C for 6h. Intensity values were normalized and diffraction patterns shifted for clarity.

thus higher interaction levels between the polymer and clay, may partially hinder segmental movements [7]. Third, higher viscosity values are also obtained due to better dispersion of clay particles [8]. As shown in Fig. 2, the viscosity of all UP-alkyd/organo-clay nanocomposites increases due to the addition of clay, i.e. nanocomposites of organo-clays I.35L, I.30E and I.28MC show an average viscosity increase of 23%, 70% and 106%, respectively, in respect to the neat alkyd. This may imply the highest level of intercalation/exfoliation for the I.28MC nanocomposites, and the lowest for the I.35L nanocomposites. As far as intercalation is concerned, this trend is supported by the interlamellar spacing increase of the treated clays, as depicted by XRD studies (not shown). Interestingly, for all nanocomposites the highest viscosity increase is observed for the 24h mechanical mixing process. Relative to static annealing [9] and ultrasonication, the application of shear appears to be advantageous in achieving disruption of the silicate structure and dispersion of the resulting particles. It was previously suggested [10] that increasing the mixing time allows the formation of both intercalated and exfoliated nanocomposites.

When nanocomposites formation is thermodynamically favoured, intercalation kinetics should be considered. Hence, parameters such as alkyd viscosity, level of shear stresses, mixing temperature and time may influence the dispersion of clay in polymer matrices. Due to the foregoing results, the alkyd/I.28MC organo-clay system was selected for further study.

Fig. 3 shows the XRD patterns of various UP-alkyd/I.28MC organo-clay systems, processed by mechanical mixing at different clay loadings, applied shear levels and temperatures for the longest time employed for each system. As shown elsewhere [2], when high shear levels are applied during the mixing process, the intercalation extent increases due to longer processing durations. To investigate the effect of shear level on the UP-alkyd/I.28MC organo-clay structure, the rotation speed of the mechanical mixer was increased from 400 to 1800rpm. The XRD patterns for UP-alkyd/7.3wt% I.28MC organo-clay composites prepared by mechanical mixing at 1800rpm and 80°C, for various processing durations (not shown) shows that the basal reflections, characteristic of the neat treated clay shift to lower angles as a result of the melt-mixing process. The extent of intercalation increases with mixing time, and the system goes through a disordered phase until it reaches, interestingly, after 24h, an ordered structure again with an interlayer spacing of 51.7E, as shown in Fig. 3. Thus, the intercalation extent in the UP-alkyd/7.3wt% I.28MC organo-clay nanocomposites has been significantly increased due to the increase in mixing speed (mixing at high versus low shear levels), from 36.4E to 51.7E, after 24h of mixing (Fig. 3).

A higher organo-clay content containing system, UP-alkyd/24wt% I.28MC organo-clay, was prepared by mechanical mixing at 1800rpm and 80°C for various processing durations. Mixing for 20h results in an increase of the basal spacing to 55.7E, larger

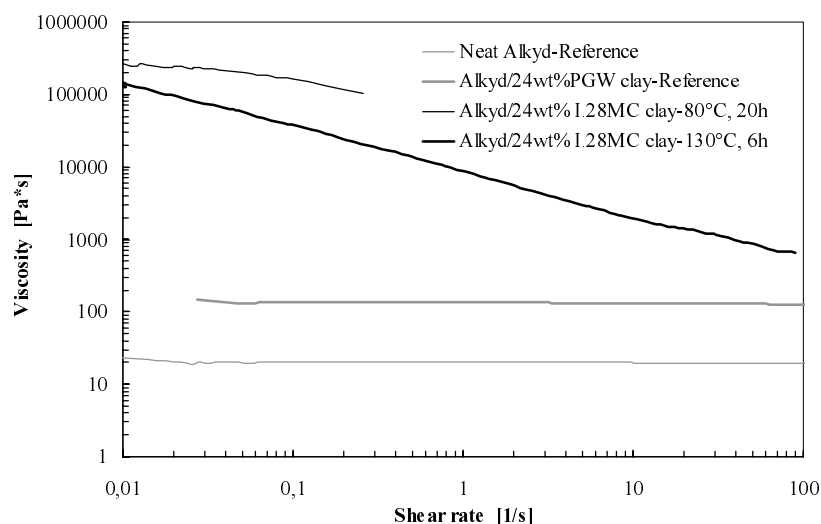


Fig. 4: Viscosity of UP-alkyd/24wt% I.28MC organo-clay nanocomposite, mechanically mixed at 1800rpm and 80°C for 20h or 130°C for 6h, and of two reference systems: neat UP-alkyd and UP-alkyd/24wt% PGW-clay systems, prepared by mechanical mixing at 1800rpm and 80°C for 24h. Samples were tested at 80°C, except for the UP-alkyd/I.28MC organo-clay nanocomposite, mechanically mixed at 1800 rpm and 80°C for 20h tested at 100°C.

than the one exhibited by the 7.3wt% organo-clay containing system, mixed for longer duration, as shown in Fig. 3. Thus, the extent of intercalation increases with mixing time (not shown) and clay content. However, another peak appears, corresponding to an interlayer spacing of 39.3E, ($2\theta=2.2^\circ$), accompanied by its higher order peak ($2\theta=4.5^\circ$). Thus, two co-existing intercalated-clay populations are realized, probably since the content of polymer in this system (containing 24wt% clay) is insufficient to intercalate all the clay to the larger extent. It should be noted that after 20h of mixing, the 24wt% I.28MC organo-clay containing nanocomposite's viscosity was extremely high, and further mixing could not be performed.

The rheological behaviour of neat alkyd, alkyd/24wt% PGW-clay composite and UP-alkyd/24wt% I.28MC organo-clay nanocomposite, prepared by mechanical mixing at 1800rpm and 80°C, and of UP-alkyd/24wt% I.28MC organo-clay nanocomposite, prepared by mechanical mixing at 1800rpm and 130°C all mixed for the longest time employed for each system (24h, 24h, 20h and 6h, respectively) is exhibited in Fig. 4. The first two systems serve as reference. Most systems were tested at 80°C. Due to its high viscosity, the rheological test of the UP-alkyd/24wt% I.28MC organo-clay nanocomposite, mechanically mixed at 80°C could not be performed at 80°C, and therefore was tested at 100°C. Its corresponding neat alkyd reference system (tested at 100°C) exhibits a viscosity of 2Pa*s [2]. The increase of organo-clay content results in high melt viscosity and thus a higher shear stress level during mixing at a constant rotor speed. The low-shear viscosity (at 0.01s^{-1}) of the

nanocomposites increases by more than three orders of magnitude due to the addition of the I.28MC organo-clay (0.5, 2 and 6 hours of mechanical mixing - not shown). The largest viscosity increase is observed for the 20h mixed nanocomposite, presenting an increase of about five orders of magnitude compared to the neat alkyd, showing a low shear viscosity of about 300,000Pa*s (Fig. 4). The viscosity of the UP-alkyd/24wt% PGW untreated clay, the reference system, increases by only one order of magnitude after mixing for 24h. Thus, the vast viscosity increase exhibited by the treated-clay containing system may be attributed to the large degree of intercalation, previously observed for these nanocomposites, and to a better dispersion of clay particles in the polymer matrix. Moreover, exfoliation of the clay particles should be considered, increasing the interaction levels between the polymer and clay. The morphology of the UP-alkyd/24wt% I.28MC-clay nanocomposites was investigated using the cryo-TEM method. Fig. 5 shows a combination of intercalated and exfoliated structures. The intercalated regions maintain the original ordering of the silicate layers, however, the interlayer distance is expanded to 3-5 nm, which is in agreement with the XRD results. In addition, there are regions where single silicate layers are observed; some peeled off from the ordered tactoids. The tactoids and individual silicate layers show no preferential orientation. The length of the silicate particles varies widely between 8-80 nm, where the individual layers are generally shorter than the ordered tactoids. Thus, the prolonged mixing at high levels of shear stress, aid in the break-up of clay particles and ultimately improve clay platelet

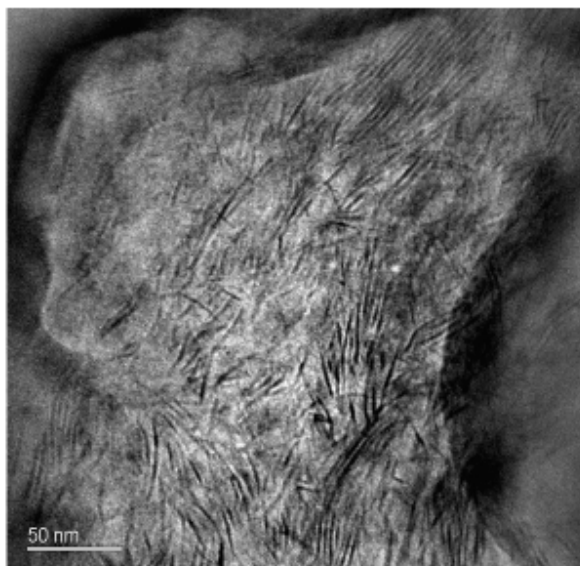


Fig. 5: TEM image of UP-alkyd/24wt% I.28MC organo-clay nanocomposite, prepared by mechanical mixing at 1800rpm and 80°C, for 20h.

exfoliation and dispersion. As observed, this takes time and requires the matrix polymer to have sufficient affinity for the clay surface to cause spontaneous wetting.

Generally, increasing the mixing temperature results in reducing the polymer viscosity, affecting both the shear level exerted during the mixing process and the mobility of the polymer chains and segments. Low matrix viscosity imparts low shear stresses on the clay agglomerates, which may skew the stack of

platelets rather than separate them [11], and might also facilitate the aggregation of clay, hindering the penetration process of polymer chains and segments into the clay layers. At the same time, increased polymer mobility is expected to facilitate intercalation of clay at shorter times. The effect of mixing temperature was studied by preparing UP-alkyd/24wt% I.28MC organo-clay composites at 130°C and 1800rpm, for various processing times. As exhibited in Fig. 3, after 6h of mixing, the basal reflections characteristic of the neat treated clay shift to lower angles ($2\theta=2.3^\circ, 4.7^\circ$; $d_{(001)}=37.6\text{E}$). Thus, intercalation has occurred, resulting in an ordered structure. However, mixing at 130°C does not result in a large intercalation extent and does not present any advantage compared to the mixing at 80°C. Hence, reduction of shear stress level has a stronger effect on structuring than the increased polymer chain mobility. Since the T_g of the alkyd occurs at 5.2°C, the mobility of the polymer at 80°C is sufficiently high. Therefore, the polymer mobility is not highly affected by the temperature increase to 130°C.

As shown in Fig. 4, the low-shear viscosity is increased by about four orders of magnitude due to the addition of the I.28MC organo-clay and mixing for 6h. In this system, the degree of intercalation is not very high and the viscosity increase cannot be attributed only to intercalation. Thus, other reasons should be considered. The morphology of this nanocomposite was investigated using the cryo-TEM

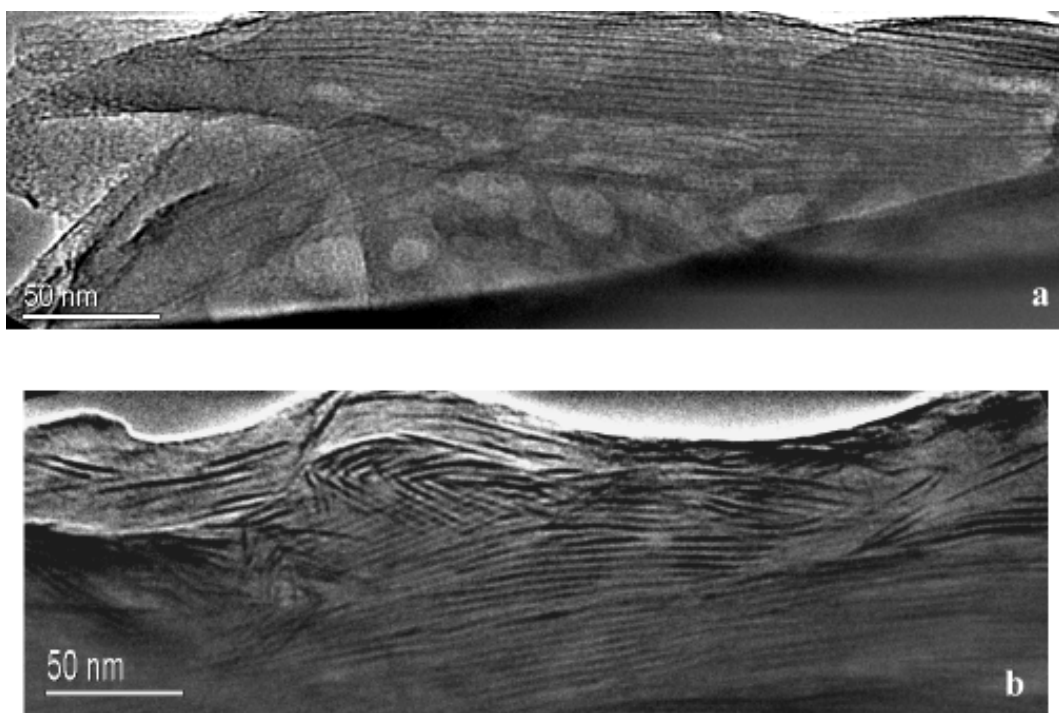


Fig. 6: TEM images of UP-alkyd/24wt% I.28MC organo-clay nanocomposite, prepared by mechanical mixing at 1800rpm and 130°C, for 6h: areas representing (a) longer and (b) shorter clay tactoids.

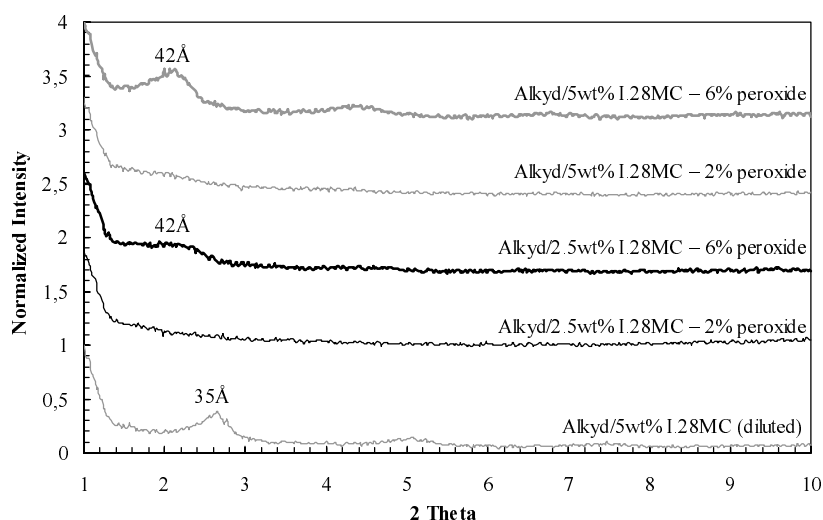


Fig. 7: X-ray diffraction patterns of uncured UP-alkyd/5wt% I.28MC organo-clay nanocomposite and of 2 and 6wt% peroxide cured UP-alkyd/2.5wt% and UP-alkyd/5wt% I.28MC organo-clay nanocomposites. Samples were diluted from the UP-alkyd/24wt% I.28MC-clay nanocomposite processed at 1800rpm and 80°C, for 20h. Intensity values were normalized and diffraction patterns shifted for clarity.

(Fig. 6). Compared to the UP-alkyd/24wt% I.28MC organo-clay nanocomposite prepared at 80°C, its counterpart prepared at 130°C shows a different morphology, consisting of only intercalated structures. These structures exhibit the original ordering of the silicate layers, however, with an interlayer distance of 2-3.5 nm, which is in agreement with the XRD results. The length of the silicate tactoids varies between 25-160 nm (Fig. 6a: longer tactoids, Fig. 6b: shorter tactoids), whereas the majority of tactoids has a length of 70-90 nm, much longer than the length presented by the nanocomposite prepared at 80°C. These long tactoids result from the low alkyd viscosity, decreasing the extent of clay fracturing during mixing at elevated temperatures. Evidently, the low alkyd viscosity also reduces the intercalation extent and minimizes exfoliation and dispersion of clay particles. Since no individual silicate layers were observed, the high viscosity (Fig. 4) presented by the nanocomposites prepared at 130°C cannot be attributed to exfoliation; alternatively, it may be assigned to the tactoids' length [2].

As was previously shown for epoxy/clay nanocomposites [12], it is crucial that the intragallery and extragallery polymerization rates are of the same order; if the latter is faster, exfoliation may be hindered. Thus, for UP-alkyd/clay systems, it is essential that the peroxide will intercalate into the clay galleries. XRD patterns show that upon incorporation of excess peroxide the clay gallery height increases from 22E to 36E, implying that the peroxide intercalates into the I.28MC organo-clay galleries. The nanocomposite showing the highest intercalation level accompanied by some exfoliation (UP-alkyd/24wt% I.28MC-clay

nanocomposite processed under high shear rates and 80°C for 20h) was diluted into UP-alkyd/5wt% clay and UP-alkyd/2.5wt% clay systems, which were further cured using various amounts of peroxide. The diluted uncured systems containing 2.5wt% and 5wt% clay show similar XRD patterns, exhibiting only one peak, corresponding to an interlayer spacing of 35E. The XRD pattern of the diluted UP-alkyd/5wt% I.28MC organo-clay system is exhibited in Fig. 7. It is feasible to assume that the clay population resulting in the peak of the undiluted system (Fig. 3) originally located at the low angles (corresponding to an interlayer spacing of 55.7E) has further intercalated beyond the measuring ability of XRD due to addition of fresh alkyd, resulting in a highly intercalated structure, while the peak located at the high angles (corresponding to an interlayer spacing of 39.3E) is nearly unchanged.

As exhibited in Fig. 7, upon curing using 2wt% peroxide, XRD patterns of both systems (containing 2.5wt% and 5wt% clay) show no peak, meaning that the interlayer spacing has increased beyond the measuring ability of XRD (ca. higher than 88E). However, curing with 6wt% peroxide results in a peak corresponding to an interlayer spacing of 42E, a slightly higher intercalation extent than that exhibited by the diluted system. There may be various reasons for the exhibited different structures: as was previously discussed, the peroxide may intercalate into the galleries, causing crosslinking of the alkyd chains located there and further penetration of alkyd chains into the interlayer region, as was previously suggested by Pinnavaia et al. [13] in an epoxy/clay system. Another reason could be that during the curing process

alkyd chains further intercalate into the galleries, again resulting in a higher intercalation extent. A combination of both may also occur. As shown by Mironi-Harpaz et al. [3], crosslinking of UP-alkyd with increasing amounts of peroxide results in a decreasing gel time. Chemorheological experiments have shown that the gel time at 110°C for UP-alkyd cured with 2% and 6wt% peroxide is about 1.5h and 0.5h, respectively. Thus, the high peroxide content results in a shorter gel-time, hence a fast viscosity increase is realized which kinetically hinders the above mentioned occurring processes.

The effect of the different clay contents and peroxide concentrations on the dynamic mechanical properties was studied. Table 1 summarizes the T_g values obtained from loss modulus curves of the reference system (thermoset neat UP-alkyd) and of the thermoset alkyd/I.28MC nanocomposites as well as the glassy and rubbery storage moduli (at 0°C and 90°C, respectively). As exhibited by the neat UP-alkyd systems, the crosslinking degree has a vast effect on the rubbery modulus, that is the storage modulus magnitude above T_g , reflecting a restriction of segmental mobility [14]. The storage modulus of the nanocomposites below T_g is higher by about 150-250% than that of the neat system, while above T_g it is higher by 150-850%. The lowest rubbery modulus is exhibited for the 2.5wt% clay containing system crosslinked with 2wt% peroxide while the highest is exhibited by the 5wt% clay containing system crosslinked with 6wt% peroxide, showing a 50% increase with respect to each other. Thus, both the filler and peroxide contents affect the modulus above T_g . Fillers are known to have a larger effect in raising the modulus above T_g than below it, since above T_g the reinforcement effect of fillers becomes prominent and the filler size effects become significant [14, 15].

In the studied system, although the absolute modulus value increases with both clay content and peroxide concentration, a comparison with the neat UP-alkyd systems shows that the effect is more pronounced when the nanocomposites are crosslinked with low peroxide concentrations (2wt%). This is probably due to the highly intercalated/exfoliated structure (Fig. 7), restricting the movement of the polymer chains [16].

The T_g values are known to increase upon addition of filler particles, the shift in T_g should be proportional to the surface area of the filler, since the polymer adsorbed upon the filler surface experiences restriction of segmental mobility [14]. Indeed, the T_g values of the clay containing systems are higher than that of the neat UP-alkyd system (Table 1), reflecting the highly intercalated/exfoliated nanostructure previously observed in this system.

In summary, it is demonstrated that the individual processing steps and conditions have a key role in determining the structure and related physical properties of UP-alkyd/organo-clay nanocomposites. Intercalation and exfoliation of the silicate layers are promoted by inducing high shear levels for prolonged times. The high shear level effects are achieved by vigorous mechanical mixing and are intensified by using large amounts of clay and appropriate matrix viscosity. The structure of the diluted and crosslinked UP-alkyd/clay nanocomposite is changed due to application of both processes. The thermoset nanocomposites' structure is particularly affected by the peroxide content used.

4. Conclusions

Unsaturated polyester nanocomposites are formed using a novel approach. Employing different routes, processing steps and conditions results in diverse nanocomposite structures, exhibiting different physical

Table 1: Glass transition temperatures (T_g – derived from loss modulus data) and storage modulus values below and above T_g of thermoset UP-alkyd and UP-Alkyd/I.28MC clay systems.

	Clay content after dilution/ %	Peroxide content/ %	T_g / °C	E'(0°C)/ Pa	E'(90°C)/ Pa
Neat Alkyd	0	2	24	3.50E8	1.27E6
		6	29	5.00E8	4.98E6
Alkyd/24wt%I.28MC clay - mixing at 80°C for 20h	2.5	2	36	1.15E9	8.89E6
		6	34	1.34E9	1.16E7
	5	2	37	1.17E9	1.23E7
		6	38	1.26E9	1.37E7

properties. The measured viscosities and the interlayer spacing of all studied nanocomposites are in good agreement.

Incorporation of all treated clays into an UP-resin using the simultaneous mixing method results in an intercalated structure, the extent of which depends on the type of organic treatment.

In the sequential mixing method, achieving high intercalation levels accompanied by exfoliation of the silicate layers and improved dispersion of clay particles may be realized by inducing high shear levels for prolonged durations. The high shear levels effects are achieved by vigorous mechanical mixing and are intensified by using large amounts of clay and appropriate matrix viscosity.

The nanostructure of the most highly intercalated/exfoliated studied system is altered due to its dilution and crosslinking. The thermoset nanocomposite's nanostructure is also affected by the peroxide content used, resulting in either an exfoliated or in a combined structure including both intercalated and exfoliated clay tactoids. The thermal and dynamic mechanical properties are affected by both clay and peroxide contents.

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