Accounting for the lack of nano-effect in a thermoset/clay nanocomposite: A positron annihilation study

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Abstract: The effect of nanoclay dispersion on the thermo-mechanical properties of an unsaturated polyester thermoset resin was studied by flexural and dynamic mechanical property measurements. Transmission electron microscopy studies revealed intercalated clay dispersion morphology in the nanocomposites. The thermomechanical measurements showed a steady decrease in the flexural strength and α relaxation temperature, with only moderate increase in the storage modulus at 1% clay loading, followed by a drop at higher clay loadings. In order to understand the absence of nano-effect in this case, free volume measurements were carried out by using positron annihilation lifetime spectroscopy. A bimodal distribution of o-Ps life times was observed. Nanoclay loading resulted in the increase of the o-Ps intensity corresponding to the longest life time as well as free volume fraction suggesting diminished chain packing efficiency in the nanocomposites. We posit that nanoclay induced decreased chain packing efficiency and the presence of higher free volume size elements might cause deterioration in mechanical properties of the nanocomposites.

1. Introduction
Recently, there has been a considerable focus on polymer nanocomposites, as incorporation of very small weight fractions of nanoparticles significantly alters the bulk thermal and mechanical properties [1, 2]. Among various nanofillers, clay minerals are one of the most widely used because of their unique layered structure, high aspect ratio and surface area as compared to other nanoparticles [1]. However, the understanding of structure/property relations in such composites is still an important area of research as it can enable designing materials with desired properties. There have been instances of deteriorating mechanical and thermal properties of polymers upon incorporation of nanoclay i.e. the absence of “nano-effect” [3]. In this study, we report such counterintuitive deterioration in mechanical properties of a thermoset/clay nanocomposite and attempt to account for the reasons for the same by using positron annihilation studies.

2. Experimental
2.1 Materials and methods
A P-444 isophthalic unsaturated polyester resin (Pliogrip Resins and Chemicals Ltd, India) with 39 ± 3% dissolved styrene was used. The curing agents were 1.5% of 6% cobalt naphthenate as a catalyst, 0.1% of N, N-dimethyl aniline as an accelerator and 1.5% methyl ethyl ketone peroxide with 9% of
active oxygen as an initiator. Cloisite-15A from Southern Clay Products was used as the nanoclay. Cloisite-15A was well mixed in the unsaturated polyester resin at different amounts (1, 3, 5 wt. %) and the curatives were added to the mixture and poured into aluminium moulds. The mixture was allowed to cure at room temperature for 24 hours, and subsequently post cured in an oven for 5 hours at 80°C. The 1,3,5 wt% clay loaded samples are referred to as USP-1, UPS-3 and USP-5, respectively in further discussion.

For TEM, thin sections (45 nm) of the nanocomposites were obtained using a RMC MT-X ultramicrotome. These cryotomed sections were then transferred to copper grids. Unstained TEM lamellae were observed with a Philips CM 200 containing a LaB$_6$ filament and imaged using a Gatan digital camera.

The flexural tests were carried out on rectangular shaped samples according to ASTM D790, using a Hounsfield 50KN (UK) universal testing machine. The $\alpha$ relaxation temperature ($T_g$), storage modulus ($E'$), and the dissipation factor (tan $\delta$) of the nanocomposites were determined in tensile mode using a Gabo, Eplexor 100 N, dynamic mechanical analyzer over a temperature range of 40-150°C at a frequency of 1 Hz, a ramp rate of 2°C min$^{-1}$ and an initial strain of 0.2%.

2.2. Positron annihilation lifetime spectroscopy (PALS)

PALS measurements of the nanocomposite samples were carried out under ambient conditions using a lifetime spectrometer based fast-fast coincidence and time resolution of 260 ps for gamma-rays of $^{60}$Co was. A 15 $\mu$Ci $^{22}$Na positron source was sandwiched between two pieces of the same samples. The total area under each lifetime spectra was about $10^6$ counts. The lifetime distributions were extracted from the lifetime spectra using CONTIN [4]. The probability density of the annihilation rates were converted to free volume radius distributions as described in ref [5].

3. Results and Discussion

3.1 Clay dispersion

Figure-1 shows the TEM micrograph of the USP/clay nanocomposites containing 3 and 5 wt % of nanoclay. It is seen that intercalated clay domains of silicate layers consisting of a few nearly parallel layers with basal spacing of 3-5 nm are uniformly distributed in the polymer matrix. Only a very few exfoliated single clay layers with a thickness of $\approx$ 1 nm thick are present, implying a dominant intercalated clay dispersion morphology.

3.2. Thermomechanical properties

The flexural strength of the nanocomposites as compared to the samples made of pure synthesized resin is shown in Figure 2. A monotonic decrease in the flexural strength with increased clay loading is observed despite the intercalation of the clay platelets in the resin. The DMA scans in the form of variation of the dissipation factor, tan $\delta$ vs. temperature for the neat USP resin and its nanocomposites are shown in Figure 3. The tan $\delta$ peak position for the polyester resin is located at 95°C and is observed to shift towards lower temperatures with clay loading, implying decreasing glass transition temperatures for the nanocomposites.

Figure 3B shows the variation of storage modulus with temperature. Contrasting effect of nanoclay on the dynamic storage modulus of USP resin is observed in the glassy and rubbery region. At 30°C (glassy region) the E' trend is USP = USP-1 >USP-3 >USP-5, post $T_g$ at 120°C (rubbery region) the trend is found to be USP-1 > USP =USP-3 >USP-5. This trend reversal is in accordance with the fact that the reinforcing effect of the clay is as expected larger at temperatures above $T_g$ as compared to below $T_g$ due to the decrease of the modulus of the polymer matrix when transitioning from the glassy to the rubbery state [6]. From the above thermomechanical results it is evident that there is a clear lack of nano-effect in the present case despite the evidences of intercalation of clay layers in the thermoset matrix. Reduced flexural strength, $T_g$ and storage modulus with clay addition may be attributed to a number of factors, such as clay induced alteration in the curing kinetics of the USP resin leading to decreased cross-link density.
This is one of the plausible reasons as nanoclay incorporation may alter the conductivity of the system [7]. The second probable mechanism is the possible network disruption as the USP network in the vicinity of the clay particles may be disrupted compared to the bulk matrix, which in turn decreases the effective cross-link density and $T_g$. In order to substantiate the above mentioned mechanistic origins of the altered thermomechanical properties free volume measurements were carried out using PALS.

3.3. Free volume characterization
The positron annihilation lifetime spectra were fitted to lifetime distributions using CONTIN. The spectra could be best fitted to bimodal distribution of o-Ps lifetimes. The free volume hole radii distributions obtained from the o-Ps lifetimes ($\tau_3$, $\tau_4$) are shown in figure 4. While the PALS spectra of most polymers are described by a single o-Ps lifetime, $\tau_3$, some high-free-volume polymers possess a second, longer o-Ps lifetime [6, 8, and 9]. It has been suggested that $\tau_4$ corresponds to large, possibly interconnected free volume elements in such materials [6]. As seen from figure 4, the average of the shorter o-Ps lifetimes ($\tau_3$) has marginally decreased with clay loading except in USP-3 while the intensity corresponding to large hole sizes increased monotonically with clay loading. To get a clearer picture, the free volume fractions in the samples are calculated (Figure 5) based on average hole radius estimated using Tao-Eldrup model and o-Ps intensities. It is clearly seen from figure 5 that the free volume fraction increased with increase in clay loading and the increase is primarily due to the increase in the number of larger free volume holes. This evolution of higher free volume defects with increased clay loading imply diminished chain packing efficiency of the nanocomposites with clay loading. We posit that the inclusion of nanoclay disrupts the molecular packing efficiency of the USP...
matrix, leading to the observed deterioration in mechanical properties of the nanocomposites compared to the neat polymer matrix. Thus the ability of nanoparticles to significantly alter the physical and thermal properties of the polymer is significantly decreased in highly cross linked thermoset matrices. This is consistent with the observations of Putz et al. that increases cross-link density leads to increased network disruption by incorporation of nanoparticles in an otherwise densely connected system [7].

**Figure 4.** Free volume size distribution of USP and its nanocomposites

**Figure 5.** Free volume fraction in clay loaded samples and the contributions from different hole sizes

### 4. Conclusions

A clear absence of the nano-effect in unsaturated polyester resin/clay nanocomposites through thermomechanical property measurements is observed even though the clay particles seemed to be well intercalated in the thermosets matrix. PALS measurements showed that clay loading caused an increase of the free volume fraction, suggesting a lower chain packing efficiency in these intercalated USP/clay nanocomposites. Furthermore, the o-Ps formation probability corresponding to the longer lifetime component increased with clay loading, implying nanoclay induced voids or defects in the USP matrix, which in turn may result in the observed lack of nano effect in the present case.

### References

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