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An experimental study on clay/epoxy nanocomposites produced in a centrifuge

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Abstract
This paper presents a study on the effect of processing variables on the mechanical properties of clay/epoxy nanocomposites produced in a centrifuge. Several experiments were conducted including different types of clay with varying processing conditions such as centrifuge rotor speed and curing temperature. The effects of these variables on the mechanical properties of nanocomposites were then studied. In order to fully understand the experimental results, a TEM was used to investigate the effect of abovementioned variables on microstructure and intercalation/exfoliation of clay/epoxy nanocomposites. The results from this work could be used to determine the best processing window to obtain appropriate levels of strength, stiffness and energy to failure in clay/epoxy nanocomposites.

Keywords: Cure; Mechanical properties; Microstructures; Nano-structures

1. Introduction

With Toyota’s breakthrough in 1980s in the production of nylon–clay nanocomposites [1,2], research in this area has increased dramatically over the last decades. The use of nano-sized fillers in polymer matrices have offered a possibility of new materials with significantly enhanced performance and have drawn interest from governments, universities and many industries. Ongoing research has shown that nanocomposites exhibit greater mechanical properties such as strength and stiffness [3,4] as well as barrier and thermal properties [5,6] with minimal amount of filler loading [7,8]. The main difficulty in the production of nanocomposites is the ability to achieve effective dispersion of the nanoclay in the polymer matrix, which is defined by four levels of dispersion: conventional composites, intercalated, partially intercalated and exfoliated and fully exfoliated nanocomposites [9,10]. Current methods such as in situ polymerization [11–13], solid intercalation, melt processing [14,15], covulcanization and sol–gel method [16,17] have shown that partial intercalation and exfoliation are possible but the ideal case of full exfoliation is difficult to achieve.

Current research, however, has mainly been concentrating on using shearing forces to separate the clay layers and achieve maximum exfoliation. One of the newer shearing methods being considered is centrifugal mixing and involves the use of a high angular velocity to introduce inertial forces on the mixture. Once established the inertial forces will cause the heavier sediments to sink to the bottom while keeping the lighter particles at the top. The aim is to use this force to break up the clumps of clay in a polymer solution and separate some of the clay layers as well [18–20]. There are many factors involved in the use of a centrifuge to mix the clay and polymer such as rotor speed, duration and type of centrifuge to use. The rotor speed will play an important role in the mixing process since the inertial forces will increase with an increase in angular velocity of the centrifuge. It is expected that with
a higher velocity the clay will break up more allowing for better exfoliation.

The amount of clay added to a polymer solution is critical in establishing the final properties of nanocomposites. It has long been proposed that only a small amount of filler is required to achieve optimum property improvements. Unfortunately, not all material properties can be maximized with a certain amount of clay and it remains to be seen what quantities are required to achieve the greatest improvements in different properties. According to Ref. [7] high loading of clay will greatly improve elastic modulus with greater ductility available, however, this will cause a decrease in tensile strength and energy to failure of the nanocomposite. The curing temperature used in the production of polymer–clay samples is also critical in determining the final properties of the nanocomposite. Establishing a suitable curing temperature is essential in the development of nanocomposite materials with optimum properties, which can be mass-produced on a large scale. The individual properties of the polymer and the clay used will also contribute to the selection of curing temperature. In this study, several experiments were carried out to analyse the important effects of the three factors, as mentioned above, on nanocomposite mechanical properties.

2. Experimental method

2.1. Material system

The organoclay used in this project was a Cloisite based natural montmorillonite clay, purchased from Southern Clay Products Inc. There were four types of clay with different exchange capacity and surface modifications. Clay types A, B and C, with exchange capacity of 125, 95 and 90 meq/100 g, respectively, had been modified with a quaternary ammonium salt compatibilizer for improving their dispersion in the polymer. In addition, clay type D with 90 meq/100 g exchange capacity received ternary ammonium salt to help the dispersion. The polymer base used in this work was an Epoxy Araldite K3600 kit (Huntsman Co.) consisting of a low viscosity Epoxy resin and hardener. The polymer and clay were mixed in a centrifuge in the Medical Department at the University of Melbourne. The test samples were produced using standard dog bone moulds for each clay type. PARTALL Hi-Temp mould release wax (Rex Co.) was used on the moulds to assist in the removal of the samples after curing. The curing process took place in a vacuum oven where negative pressure was applied to minimise air bubble formation.

2.2. Experimental procedure

The following outlines a simple procedure for producing polymer–clay samples for this study. The batch of epoxy was initially measured based on the mould volume taking into account the addition of clay as well. The clay quantities considered in this work were 1, 3, 6 and 10% and all were measured based on the weight of epoxy. The individual clay batches were immersed in a separate epoxy batch and the mixtures were stirred slightly to allow the epoxy to completely impregnate the clay. The mixing of the clay–polymer mixture was performed in a J2-21M/E Beckman Centrifuge set at 3000 rpm for 25 min.

Investigating the effect of the rotor speed was performed using only the 6% samples for each clay type. The batches were mixed in the centrifuge at four different rotor speeds 1500, 2000, 3000 and 4500 rpm. Again to maintain consistency, 6% clay samples were used to study the effect of curing temperature with four different types of clay while a rotor speed of 3000 rpm was in use. Once the mixtures were removed from the centrifuge, they were placed in the oven for degassing, at room temperature at a pressure of −10 kPa. After 30 min the hardener was added based on the weight of the total clay–epoxy mixture. Each mixture with the hardener was then poured into a separate mould. The moulds were then placed into the vacuum oven, which was set to 80 °C and 10 kPa vacuum pressure. The specimens were left in the oven for 2 h for initial curing and then they were post cured for a further 3 h at 110 °C. This procedure was used for all batches except when the effect of the curing temperature was considered where the batches were cured at four different temperatures 70 °C, 80 °C, 95 °C and 120 °C.

2.3. Mechanical testing

Each batch of 16 specimens (four specimens for each clay type at selected quantity) was left to cool for 20 h before conducting any experiment. The samples for mechanical properties determination were tested according to ASTM D638M at 5 mm/min in a MTS universal testing machine. The tests were carried out to evaluate the mechanical properties of the epoxy–clay samples, which were initially observed via load–displacement graphs specifically concentrating on the ultimate tensile strength, strain to failure and energy to failure (area under the load–displacement curve) of the samples. For further analysis a comparison was made between the clay quantity and the effect it has on each of the three abovementioned properties.

3. Results and discussion

3.1. Effect of clay quantity

The elastic modulus of nanocomposite samples tends to increase with an increase in clay quantity up to a maximum of 6%, as shown in Fig. 1a. After the maximum is reached, elastic modulus decreases slightly as more clay is added. The addition of a small amount of clay to pure epoxy may take away its ductility thereby increasing the elastic modulus of nanocomposite. After a certain point (6%) in this study the extra clay no longer negates the ductility of the polymer but its own ductility may come into play.
causing the modulus of clay–epoxy nanocomposite to begin to decrease. Type D clay modified with ternary ammonium produced a much higher elastic modulus than that of types A, B and C. This may be contributed to the different surface modifications.

Effect of clay quantity on the ultimate tensile strength and energy to failure (area under the load–displacement curves) of the epoxy–clay nanocomposite specimens is presented in Fig. 1b and c. The general behaviour of both plots is very similar since the energy to failure is proportional to the strength. The plots show an increase in the tensile strength and energy to failure with higher clay quantities. Specimens with type A, B and D clays all become stronger and tougher with an increase in the amount of clay while specimens with type C increase toward a maximum of 6% then decrease with a further addition of clay. These changes in the mechanical properties of clay–epoxy nanocomposites might be related to the clay structure,
nature of epoxy, polarity of resin or any other chemical parameters, which are not the target of this study.

3.2. Effect of rotor speed

The effect of the rotor speed on the mechanical properties of nanocomposites is shown in Fig. 2. Type D clay, as shown in Fig. 2a, is again found to have the highest modulus, which remains fairly constant at lower speeds but begins to decrease as the speed approaches 4500 rpm. The other clays, all show some fluctuations at lower speeds but even out as the speed reaches 4500 rpm. These
fluctuations could be attributed to the presence of air bubbles that were found in some specimens. The differences are also due to the different surface treatments used on the clays and which would affect the amount of intercalation and exfoliation that would occur. The decrease in the modulus at 4500 rpm comes from the fact that at high speeds, the large inertial forces no longer act to separate clay layers but also break some of the layers as well making them no longer effective as filler. Therefore, the dimensions of clay particles may contribute to these changes in the mechanical properties of nanocomposites.

The tensile strength and energy to failure of the specimens at different rotor speed again shows some fluctuations at lower speeds, as presented in Fig. 2b and c. In type A and C samples, these properties tend to increase as speed increases towards 3000 rpm while in type B and D to decrease continually. In the end, all graphs decrease toward 4500 rpm making 3000 rpm a significant speed after which the properties no longer show any improvement. The reason again can be attributed to the breakage of clay layers due to very high inertial forces. The broken clay layers may no longer contribute as effective fillers to improve the polymer properties.

3.3. Effect of curing temperature

Fig. 3 shows the elastic modulus, tensile strength and energy to failure variations with curing temperature. The elastic modulus tends to increase with curing temperature initially until 95 °C is reached and then stops increasing and begins to even out, as shown in Fig. 3a. The tensile strength and energy to failure again exhibit similar behaviour with their maximum values at lower temperatures and then decreasing as the temperature increases toward 120 °C (see Fig. 3b and c). The higher temperatures would cause the specimens to become brittle, as indicated by load–displacement curves shown in Fig. 4.

4. TEM micrography

To determine the relative success of the centrifugal mixing method and the degree of exfoliation and intercalation that has been achieved, a Transmission Electron Microscope (TEM) was used. All microscopic investigations were performed on a JEOL JEM-100CX TEM operating at 100 kV. The TEM images, detailing the microstructure of the epoxy–clay specimens allowed the explanation of the
The optimum temperature range again showed best results at lower temperature with higher relative as nanocomposite fillers. The curing temperature ally break rather than separate, making the layers ineffective but only slightly intercalated.

The TEM imaging was also used to analyse the effect of the rotor speed on the intercalation and exfoliation of the nano-clays layers. Fig. 6a–d represent the nanocomposite microstructure formed using four different rotor speeds, namely 1500, 2000, 3000 and 4500 rpm all which were used for 25 min. At 1500 rpm there is a reasonable amount of exfoliation with only some layers clumped together as shown by the dark wavy lines. With 2000 rpm there is less exfoliation when compared to 1500 rpm and only some intercalation has been achieved as indicated by the parallel wavy lines. At 3000 and 4500 rpm the exfoliation that is present is very poor and even the intercalation is minimal with large clumps still present. At the highest speed of 4500 rpm another problem evident is that the clay layers are no longer parallel or very straight but have fractures along their length indicating breakage which would reduce the effect of clay as filler.

5. Conclusion

As the amount of clay is increased, the elastic modulus of epoxy–clay nanocomposites increased up to a maximum of 6% clay after which the modulus no longer increases as much but begins to slightly decrease. The tensile strength and energy to failure, however continually increase with clay quantity all the way up to 10%. The amount of increase in a particular property depends on the type of clay used and the surface treatment of that clay. For the rotor speed the slower speeds were found to be the best, while the higher speeds caused the properties to deteriorate with the critical speed being around 3000 rpm. After 3000 rpm the higher speeds caused the clay layers to actually break rather than separate, making the layers ineffective as nanocomposite fillers. The curing temperature again showed best results at lower temperature with higher temperatures causing specimen brittleness and deterioration of its properties. The optimum temperature range was about 80 °C to 100 °C.

References


