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Characterization and Mechanical Properties of Epoxy Resin Reinforced with TiO_2 Nanoparticles

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Abstract: Epoxy resins with widely different mechanical properties were used as matrices in which functionalized TiO_2 particles were randomly dispersed to produce nanocomposites. These nanoparticles are 21 nm in diameter. They are dispersed in epoxy resin , using ultrasonication or magnetic stirring process for 5, 30 and 60 min. The composites with nanometer scale, TiO_2 particles at 0.5, 1, 5 and 20% weight were characterized by hardness tests and tensile tests. The results are then compared with the neat epoxy resin.

Key words: Epoxy matrix, TiO_2, nanocomposite materials, mechanical property characterization, magnetic, matrices

INTRODUCTION

Now-a-days, Epoxy (EP) resins are intensively used in various technical applications such as coatings, composite matrices, potting compounds or structural adhesives. Resin Transfer Moulding (RTM) is rapidly gaining acceptance as one of the most promising manufacturing routes for composite structures in applications such as aerospace and automotive industries (Merad *et al*., 2009).

Nanocomposites are a novel class of composite materials where one of the constituents has dimensions in the range between 1 and 100 nm. Nanocomposite materials garner most of their material improvements from interactions at the molecular scale, influencing physical and material parameters at scales inaccessible by traditional filler materials (Xu *et al*., 2004).

However, the effective reinforcement by TiO_2, nanoparticles of thermosetting polymers such as the epoxy resins favored in aerospace and other industries, still presents great challenges (Liu and Wagner, 2005). The mechanical properties of the final nanocomposite materials can be easily measured, using various kinds of standard tests for engineering materials. To achieve maximum performance from the nanoparticles, uniform dispersion and good wetting of nanoparticles within the matrix must be ensured (Xu *et al*., 2004). The aim of this study is to understand the influence of particles size of TiO_2 on the mechanical properties of epoxy reinforced with nanometer sized particles.

Choice of matrix material and reinforcement agent: The matrix used in this research was a commercially available grade of the diglycidyl ether of bisphenol A ((4-(2, 3 epoxypropoxy) phenyl) propane) abbreviated as DGEBA (Merad *et al*., 2009). It was used under its commercial designation (Dow Chemical Company; DER 332). Properties of resin cured with the ARADUR 3298 (HUNTSMAN) curing agent are shown in Table 1 and 2.

Table 1: Matrix material properties

Viscosity at 25°C	30-60 mPa.sec
Density	0.9-1 g cm^{-3}

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Table 2: Characteristics of the TiO_2 particles

Properties	Nanometer sized particles
Nominal average diameter	21 nm
Specific area	50 m^2 g^{-1}

Table 3: Different times of dispersion

Magnetic Stirring (MS)	5 min	30 min	60 min
Ultrasons (US)	5 min	30 min	60 min

Fabrication of nanocomposites

Casting of TiO_2 epoxy

Sample 1: About 1% weight nanometer TiO_2 particles were added to the epoxy resin, mixed with a glass rod and then dispersed by placing the mixture in a beaker in an ultrasonic bath for about 5 min.

Sample 2: About 1% weight nanometer TiO_2 particles were added to the epoxy resin, mixed with a glass rod and then dispersed by placing the mixture in a beaker in an ultrasonic bath for about 5 min. At the end of the sonication hardener was added.

The dispersion was better in sample 2 because the curing agent was added during the reaction for sample 1 which caused the fluidity of the mixture to decrease resulting in poor dispersion of nanometer TiO_2 particles. The curing agent was simply added at the end of the sonication for sample 2.

Curing cycle: The curing cycle of epoxy resin modified the final properties. The curing cycle selected from those proposed was to cure the samples for 24 h at room temperature and then heated at 100°C for 4 h.

Dispersion of nanometer TiO_2 particles: New developments in the synthesis of nanometer TiO_2 particles have enabled the processing of exciting new nanoparticle/epoxy composites (Ng *et al*., 1999). Magnetic stirring and ultrasonic methods were used to disperse the nanoparticles in epoxy. Samples were successively removed after different periods of dispersion (typically 5, 30 and 60 min) (Table 3).

Fabrication of specimens: The specimens had nominal length L of 24 mm height, width of 4 mm and a thickness B of 2 mm as per NF T 51-034 standard; all samples were polished at room temperature for 30 min in order to have a plane area.

MATERIALS AND METHODS

Testing and characterization

Hardness test: It was performed with BUHLER MACROVICKERS 5114, equipped with a microscope that allows you to position the imprint on the desired phase. The force applied is selected from the 10 values between 100 mN to 20 N. We measured the average of the two diagonals, 0.002 mm meadows through the microscope micrometer connected to the machine.

Tensile test: Tensile testing of the TiO_2 epoxy composites was performed using an INSTRON 8801 with a 5 KN load cell at a crosshead speed of 0.01 mm sec^{-1}. The tensile test was carried out at room temperature. Typical sample dimensions were 4 mm (width) 2 mm (thickness) 24 mm (length). To ensure data accuracy and repeatability, five samples of each type were tested. In this case at least five samples were measured for each specimen type.

RESULTS AND DISCUSSION

Figure 1 shows the effect of different modes of dispersion of nanometer TiO_2 particles ultrasonication or magnetic stirring process vs. the hardness.

The usefulness of nanometer sized particles, however is marred by processing difficulties such as the formation of particle agglomerates and non-uniform dispersion. This has motivated research for finding better ways of processing, the particles to achieve de-agglomeration and ensure better dispersion. Techniques such as ultrasonication and magnetic stirring have been used by Zunjarrao and Singh (2006).

Figure 1 shows the results obtained for the addition of TiO_2 nanoparticles which increases the viscosity of the resin. However, prolonged agitation significantly reduces the hardness of the nanocomposite. Aggregates start to form and eventually, we get the opposite of what is expected (Guan *et al*., 2006). Similarly, magnetic stirring is not a good solution as the viscosity of the TiO_2/epoxy is very important.

The curing agent was simply added during the dispersion of TiO_2 nanoparticles by ultrasonication for 30 min. The particles, thus treated were then dispersed in epoxy and composite was fabricated in the same way as before (Fig. 1).

Hardness test

Effect of load and times: The hardness tests are done on both sides of the samples. The hardness values are the same. Dispersion of nanofillers is therefore consistent throughout the resin and there is no effect of gravity that would have formed some agglomerates in the lower part of the epoxy resin during the reaction. The value of the load will then be used; we tested the influence of the load on the hardness of a specimen of neat resin. Initially, the hardness of the unit continues to increase. But from about 3000 mN, hardness stabilizes. We therefore, chose to work with a force of 2942 mN because the machine works by predetermined increments. Figure 2 shows the influence of the duration of

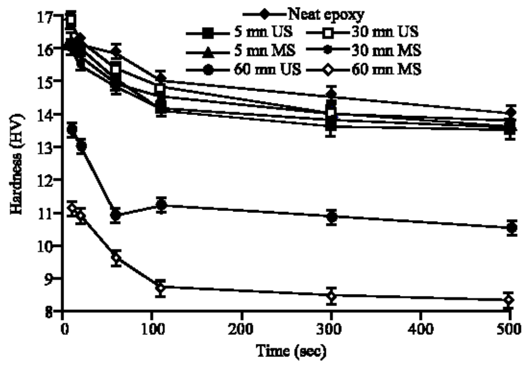

Fig. 1: Effect of different mode dispersion TiO_2 particles vs. hardness in 1% weight nanometer TiO_2 particles in epoxy resin

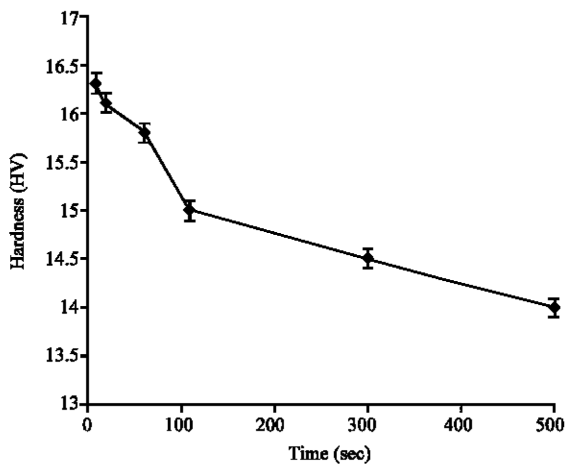

Fig. 2: Influence of the duration

application of this force on the same sample. We note that while the hardness decreases with time the reduction diminishes and tends to stabilize (Ratna *et al.*, 2003). This variation is interesting and reveals the viscous behavior of material found for example in the creep. This part has led to the preparation of samples that will be the following:

- Resin+Y% TiO_2
- The TiO_2 epoxy was ultrasonicated for 30 min using a 20 kHz frequency and a 9.0 sec on-off cycle
- After cooling this mixture, the curing agent was added and hand-mixed thoroughly
- This material was cast and subjected to the same curing cycle (24 h at room temperature)
- Heated at 100°C for 4 h as the particle reinforced composites

Study on TiO_2-epoxy nanocomposite: The weight percent nanometer TiO_2 particles in the following samples:

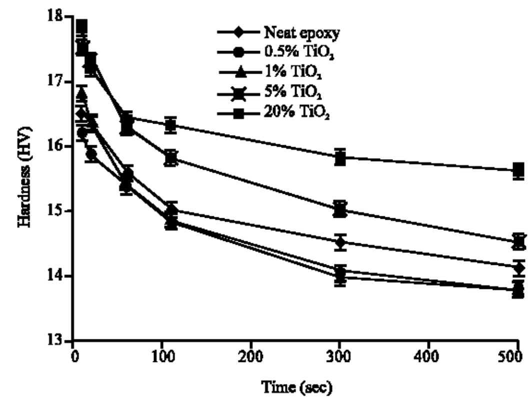

Fig. 3: Influence of the weight percent nanometer TiO_2 particles vs. hardness

- Sample 1 without TiO_2 nanoparticles (neat epoxy)
- Sample 2 with 0.5 % TiO_2 nanoparticles
- Sample 3 with 1% TiO_2 nanoparticles
- Sample 4 with 5% TiO_2 nanoparticles
- Sample 5 with 20% TiO_2 nanoparticles

Hardness test: Figure 3 shows the influence of weight percent nanometer TiO_2 particles vs. hardness. The hardness is weak varying between 14 and 18 HV, compared with the hardness of the steel grades between 150 and 700 HV (Narayanan and Schadler, 1999). It can be seen from the graph that 5% weight of nanosized TiO_2 is within the hardness. Adding small weight percent nanometer TiO_2 particles (from 0.5-1) reduced the hardness of nanocomposite while a high weight percent of TiO_2 nanoparticles (5 and 20%) increases the hardness. In addition, the hardness decreases with increasing time of load application. Samples with low nanofiller are more sensitive to this phenomenon which is related to viscosity. But unless the material is loaded, it is more viscous more hardness evolves with time under load (Lu *et al.*, 2004). This is the phenomenon of creep.

Figure 4 shows the hardness of steel XC 100 and nanocomposite. The steel hardness is about 215 HV. For comparison of the two materials, the hardness has been normalized at 1 (Hardness/hardness$_{max}$). After 500 sec, the hardness of nanocomposite decreased by >15% while that of the steel XC 100 dropped by only 5%. Hardness of steel has leveled but that of the nanocomposite stabilization has not yet stabilized.

Tensile test: Tensile tests measurements were carried out for neat epoxy and epoxy reinforced with TiO_2 nanoparticles. For each case, five samples were tested. The results were obtained for the Young's modulus

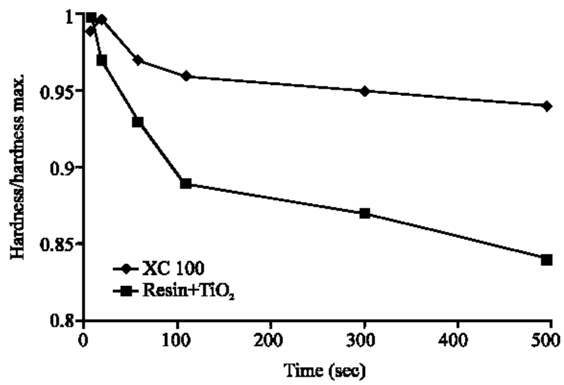

Fig. 4: Hardness of steel XC 100 and Nanocomposite

Table 4: Young's modulus for the neat epoxy

Specimens	1	2	3	4	5	Average	SD
Young's modulus	2.51	2.44	2.45	2.46	2.45	2.462	0.028

Table 5: Young's modulus for 1% TiO_2

Specimens	1	2	3	4	5	Average	SD
Young's modulus	2.58	2.49	2.64	2.38	2.66	2.550	0.116

Table 6: Young's modulus for 5% TiO_2

Specimens	1	2	3	4	5	Average	SD
Young's modulus	2.83	2.85	2.58	2.96	2.86	2.813	0.163

Table 7: Young's modulus for 20% TiO_2

Specimens	1	2	3	4	5	Average	SD
Young's modulus	2.73	2.65	2.44	2.75	3.11	2.736	0.243

experiments. The statistical spread of experimental data is denoted by the standard deviation (Table 4-7). The presence of individual TiO_2 particles embedded in an epoxy matrix. There were some agglomerates but overall, the dispersion was good. During the fabrication of test specimens, they were degassed of any trapped air bubbles. These air bubbles result in fragile specimens and are initiation sites of breaking. The specimen will fracture at a stress lower than it would without bubbles. We thus obtain a fairly large dispersion for the breach of the same series of specimens. Between different Nanocomposites, comparison cannot be done directly for the stress and strain to failure because there is significant uncertainty of the results. However, we can compare the Young's modulus. It was tensile tests with specimens from samples of neat epoxy 1, 5 and 20% TiO_2 (Table 4-7).

The Young's modulus increases with the weight percent TiO_2 particles. Conversely if 5% weight of TiO_2 nanoparticles is exceeded, the Young's modulus will decrease (Huang *et al*., 2006). The material at 20% weight of TiO_2 particle is very fragile. The break occurs for a weak constraint either because the high weight percent of TiO_2 prevent the complete polymerization reaction and due to the higher occurrence of

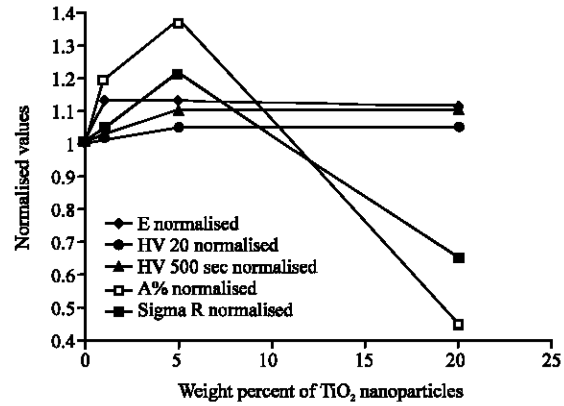

Fig. 5: Normalised values vs. weight percent of TiO_2 nanoparticles

agglomeration under the gravitational interaction between TiO_2 nanoparticles which hinder the extrusion of epoxy resin's molecular chains or because the presence of very large aggregates acting as sites of boot failure like a bubble. Collects the results obtained during different tests (Fig. 5). The evaluation of various mechanical properties compared against the weight percent of TiO_2. These differences shows that low levels of particles almost do not affect the characteristics of the material.

Too much of these particles will also not be useful. It is assumed that the particles results in difficulty of obtaining a complete epoxy resin cure which makes the material less durable. If a significant change in characteristics of the epoxy resin is desired, adding 5% TiO_2 appears to be very interesting because all the features of nanocomposites (E = Young's modulus, stress at break = sigma R, strain at break A% and Hardness (HV) are 35% better compared with neat epoxy. The biggest improvement is in the properties at break. The Young's modulus defining rigidity has a maximum increase at 10% weight of TiO_2 while the stress and strain at break increase at 20 and 35% weight of TiO_2 nanoparticles.

CONCLUSION

Systematic mechanical property characterizations including hardness and tensile properties for a new functionalized TiO_2/epoxy composite were conducted. Investigations were carried out on the influence of some process parameters on the dispersion of nanofillers and the mechanical properties of the nanocomposite were obtained but we have to go further in testing. In fact, we tried to get the best possible protocol to disperse the nanofillers but be aware that this dispersion was not perfect and there is still room for improving the protocol to improve the dispersion of nanofillers in epoxy resin. Mechanical tests on nanocomposites with different weight percent of TiO_2 nanoparticles showed that they have certain influence on the mechanical properties of nanocomposite. The nanometer size TiO_2 was most interesting at 5% wt. of TiO_2.

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