Improvements in High Specific Strength Epoxy-Based Composites using High Magnetic Fields

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ABSTRACT

Changes occur in the bulk physical properties of polymers, when cured in the presence of high magnetic fields, has been known for some considerable time. It has also long been realized that polymer-based composites containing low-percentage nanoparticle dispersions have attractive mechanical characteristics such as high compressive/tensile strength and stiffness. This paper describes, for the first time, significant improvements in those mechanical properties when epoxy-based composites are cured in high uniform magnetic fields. An interesting additional finding, also described here, concerns concomitant improvements in the thermal stability of these systems.

Keywords: High magnetic fields, magnetic flocculation, nanoparticles, epoxy.

1 INTRODUCTION

Numerous studies have been carried out, over a period of several years, on the detection of changes in physical characteristics of polymers subjected to high magnetic fields during the curing stages. Characteristics changes investigated include viscoelasticity[1], stress-strain behavior[2], fracture toughness[3], and electrical polarization[4]. It has been widely demonstrated that liquid crystal thermosets (LCTs) reveal fundamental changes in structure when cured in high magnetic fields. These include the inducement of anisotropic thermal expansion properties[5]. More recent studies of LCTs by Douglas and various co-workers[6,7] have shown extremely large increases in the tensile elastic modulus, with values of up to 8.1 GPa for samples cured in fields of 12 T, compared to 3.1GPa for samples cured in zero field.

Additionally, a wide body of literature[8-13] provides convincing evidence that an infusion of nanoparticles (NPs) can bring about enhancement of various mechanical properties of polymer composites. Some of the present authors have recently successfully demonstrated enhancements in a wide range of mechanical and thermal characteristics (also discussed in detail below in this paper) of carbon NP- infused bulk composites[11], sandwich composites[12] and polyurethane foams[13].

The present paper describes an attempt to combine these two separate bodies of work and to use high magnetic fields as a means of obtaining superior distributions of NPs in epoxy-based composites. In the following are described the results of preliminary experiments designed to improve upon the bulk mechanical properties of such composites by subjecting the fluid mix, during the curing process, to high uniform magnetic fields. The aim here is to initiate the process of magnetic flocculation[14] of these NPs during the curing process and, in particular, during the pre-gel stage at which time the viscosity of the matrix is still relatively modest.

Magnetic flocculation is a term commonly used to describe the agglomeration of colloidal microscopic particles under the influence of a uniform applied magnetic field[5]. One of the present authors[14,15] has previously demonstrated that, provided sufficiently large magnetic fields are applied, both paramagnetic and diamagnetic particles of microscopic dimensions can be flocculated. The process is characterized by the formation of pairs of these microscopic particles joined end to end within the colloid and parallel to the field axis. Such a phenomenon is termed 'binary' flocculation. Under more favorable conditions, namely high magnetic volume susceptibility particles, coupled with high magnetic fields, low matrix viscosity and higher particle number densities, higher order forms of flocculation (i.e. short chains) become feasible. Monte Carlo simulations have also indicated a tendency of the chains to organize themselves in regularly spaced fashion in cross-section[16,17]. This latter point is consistent with optical transmission studies[17,18] on colloids in high magnetic fields. The task of promoting binary or higher order forms of magnetic flocculation in fluid nanocomposites is a daunting one. The small particle size, coupled with the low magnetic volume susceptibility of the majority of commercially available types, reduces the likelihood of uniaxial inter-particle dipolar interactions having the capability to dominate isotropic clustering induced by Van der Waals interactions. The latter effect compounds the problem further by effectively imposing an upper limit on composite number density (of order 1% by particle volume) due to the tendency of NPs in fluid composites to form the aforementioned clusters in the preliminary sonification and mechanical mixing stages.

In the experiments described here, the fluid matrix chosen was an epoxy resin system, SC-15, of the sort used in high specific mechanical strength systems[11-13]. This epoxy was used in conjunction with a standard (cycloaliphaticamine+ Polyoxyalkyleneamine) hardening agent, comprising

approximately 30% of the total composite volume. With this mix, the composite changes, at room temperature, from a relatively low viscosity system, (SC-15, for example, has about 2.5 times the viscosity of water), to a gel in about one half hour and , eventually, to a solid matrix in 2 – 4 hours, although the complete curing may last up to 24 hours.

2 EXPERIMENTAL PROCEDURE

The preparation of the nanocomposites was undertaken in two separate stages. First, spherical NPs were added at a 1% loading, by weight, to (part A) SC-15 epoxy resin (60-70% diglycidylether of bisphenol A, 10-20% aliphatic diglyciylether, 10-20% epoxy toughener) and dispersed by acoustic cavitation. Two principal types of NPs were used: SiC and TiO_2, with respective diameters 29nm and 30 nm. This dispersion was carried out in a Sonic Vibra Cell Ultrasound liquid processor for about 30 minutes at room temperature. The vessel containing the composite was externally cooled during this process to prevent undesired temperature rises. Following infusion of the nanoparticles, this modified epoxy part A was mixed with part B hardener, comprising 70-90% cycloaliphatic amine and 10-30% polyoxylalkylamine. The hardener was added to part A at a volume ratio of 3/10. Mixing was promoted with a high-speed mechanical stirrer for about 5 minutes. The mixture was then vacuum-degassed for 10-15 minutes. After completion of this sample preparation step, the admixture was added to cylindrical PVC vessels of a length designed to match the most uniform portion of a high-field Bitter magnet. The curing process of the various samples took place within the magnet at various high fields and for a variety of times of exposure.

3 RESULTS AND DISCUSSION

Static compression tests were performed on test coupons of dimension 12.7 mm x 12.7 mm x 25 mm, cut from the cylindrical samples. Four replicate test coupons of each sample were examined on a hydraulically-controlled MTS machine to ASTM standards. In addition, dynamical mechanical analysis (DMA) tests were undertaken to determine the thermal transition temperature and the elastic response of polymers as a function of temperature. Thermo-gravimetric analyses were also carried out on all samples as a means of detecting any magnetic-field induced changes in the thermal stability of the composites.

The stress-strain characteristics of magnetically cured composites under quasi-static compression loading were investigated and the resulting mechanical strength and stiffness data (for 1% SiC NP loading) are shown, respectively, as a function of exposure time in a magnetic field of 16T in Figs. 1 and 2.

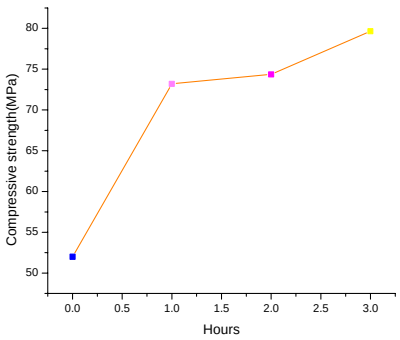


Fig.1. Shows increase in Strength with time at a Magnetic strength of 16 Tesla.

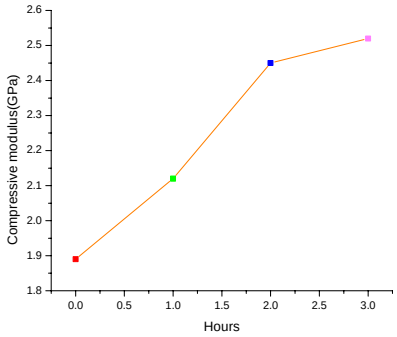


Fig.2. Shows increase in Stiffness with time at a Magnetic strength of 16 Tesla.

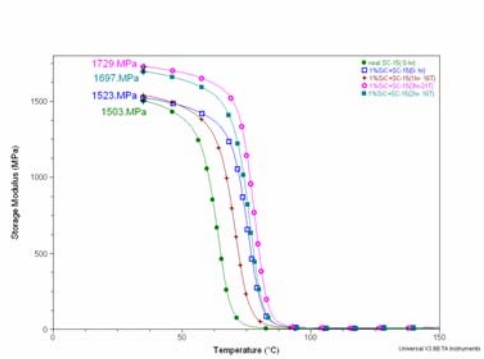
Here, it was seen that strength and stiffness of 1% SiC-epoxy composite prepared at 16T for 3 hours showed increase, respectively, by 35% and 72% compared to neat control sample values and 49% and 33% compared to control sample values of same % NP loading. Clearly, in both instances, experimental data give no hint of saturation of the magnetic field effect. Similar experiments, performed in a field of 21T for 3 hours, show even bigger improvements in these parameters with 1% TiO_2 NP loading (98% and 114%, respectively) over neat control sample values as shown in table 1.

Table 1: Compressive response of polymers cured in zero field and in magnetic field at magnetic strength, 21 Tesla.

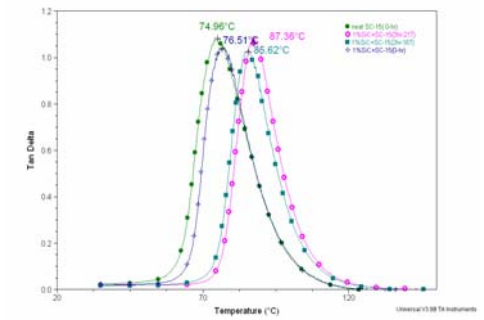
Material	Magnetic curing (hrs)	Compressive Strength (MPa)	Gain/loss in %	Compressive Modulus (GPa)	Gain/loss in %
Neat SC-15	0	58.47	-	1.46	-
Neat SC-15	3	70.46	+20	2.17	+48.6
1%SiC	0	53.46	- 9	1.92	+34.2
1%SiC	3	104.85	+79	2.71	+85.6
1%TiO_2	0	65.96	+13	2.35	+60.9
1%TiO_2	3	116.1	+98	3.12	+114.7

It was observed that the neat epoxy polymer cured in an uniform magnetic field have significant increase over neat controlled polymers. With the increase in magnetic strength and cure time, properties enhanced significantly in almost linear fashion. In making a comparison between the flocculated and non-flocculated systems, at least half of the enhancement in properties is contributed by magnetic flocculation. It gives a clear indication that properties of polymers can be further enhanced by choosing better susceptible particles, higher magnetic strength and/or longer magnetic field curing.

A *Dynamic mechanical analysis* was also used to determine the elastic response of these nanocomposites by subjecting the test coupons in flexural mode. Fig. 2(a) and (b) shows, respectively, storage moduli for 1% SiC and 1% TiO_2 composites prepared under various field conditions. In Fig. 2(a) an increase in the storage modulus of around 226MPa was observed for SiC composite cured for 3 hrs in a 21T field. Storage modulus of polymers decreases as they approach their glass transition temperature. Significant increase in glass transition temperature was achieved that can be inferred From Fig. 2(b), Tan delta vs. temperature curves, 1% SiC composite cured for 3 hrs in a 21T field, showed increase of about 14^0C. Similar results were seen with TiO_2 composites similarly treated with a significant enhancement of mechanical stiffness (approximately 315Mpa).



(a)

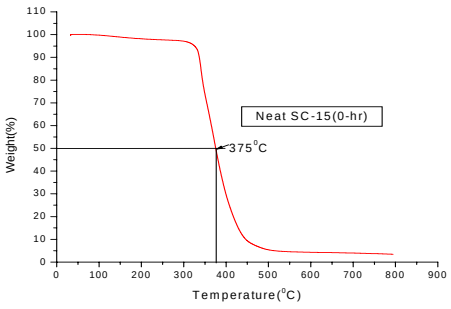


(b)

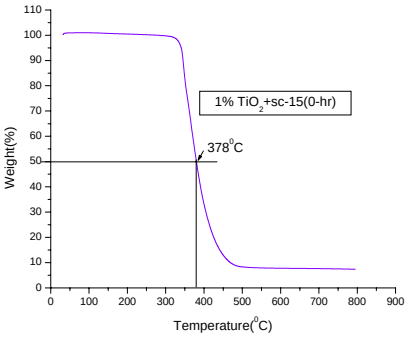
Fig.2 (a,b)Elastic response and glass transition temperatures of SiC polymer composites cured in an uniform magnetic field for different length of time.

It was observed that with increase in magnetic field curing, significant increase in storage moduli and glass transition temperature were achieved. This results clearly suggests that with the combination of field magnitude, time of exposure, effective flocculation and susceptibility of particles, the properties can be further enhanced.

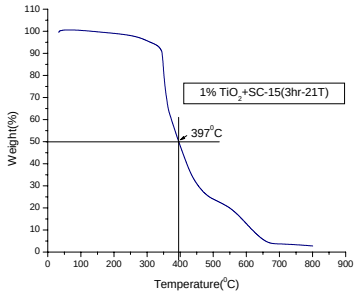
Thermo-gravimetric analysis (TGA) was carried out for these systems to understand the effect of magnetic field on the thermal stability of the nanocomposites. Figure 3 (a,b)show, TGA outputs for neat epoxy and TiO_2–epoxy nanocomposites prepared under zero field. It was found that 50% by weight of the neat sample was decomposed at ~ 375^oC temperature where as the 1% TiO_2 decomposed at ~ 378^oC under similar conditions. This small difference in decomposition temperatures were due to the effect of nanoparticles presence in epoxy[10]. The Figure 3(c) represents the TGA output of 1% TiO_2 nanocomposite cured at 21T in a magnetic filed. In this graph 50% by weight of the sample was decomposed at ~ 397^oC showing significant increase in decomposition temperature. This increase of about ~ 20^oC clearly shows the effect of magnetic field curing and this increase in temperature may be due the alignment of particle as a result of magnetic flocculation.



(a)



(b)



(c)

Fig.3 (a,b,c). TGA of zero field cured epoxy polymer and magnetically cured epoxy polymers at 21T.

4 CONCLUSION

The ability of high magnetic fields to affect, in a positive manner, the mechanical strength of an epoxy resin nanocomposite has been clearly demonstrated. The NP systems chosen here - diamagnetic SiC and paramagnetic TiO_2- have extremely weak magnetic susceptibilities (-6.3 x 10^{-6} and 3.54 x 10^{-6} cgs units, respectively). The fact that the results for TiO_2 are better than for SiC, even though the numerical susceptibility is smaller can be explained by the fact that the magnetic dipolar interaction depends on the *effective* volume susceptibility, χ_{eff} (i.e. on the difference between the susceptibility of the particle and that of the background fluid). The SC-15 epoxy is, clearly, diamagnetic, meaning that its volume susceptibility effectively adds to that of the TiO_2 and subtracts from that of the SiC. What has not yet been shown in this study is an optimized nanocomposite, given that higher fields applied during curing continue to show additional improvement. Clearly, the use of higher magnetic susceptibility nanoparticles would offer an easier opportunity for system optimization. Further studies of this kind are being planned. Furthermore, in the case of strongly paramagnetic substances, the likelihood of securing viable higher nanoparticle loading values in the mix is much increased. The dipolar interaction due to the magnetic field increases as $(\chi_{eff})^2$, meaning that initial spherical particle clusters, held together by Van der Waals forces, ought to be effectively distributed by the magnetic field into more favorable dispositions.

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6 REFRENCES

1. S. Jaromi, W.A.G. Kuipers,B. Norder, W. J. Wijs, *Macromolecules*, 1995, 28, 2201.
2. A. Shiota, C. K. Ober, *J. Polymer Sci. Part B: Polym. Phys.*1998, 36, 31.
3. C. Carfagna, E. Amendola, M. Giamberini, *Liquid Crystalline Polymers*:*Proceedings of the international Workshop on Liquid Crystalline Polymers*, C. Carfagna Ed.; Pergamon Press: Oxford, U.K.1994, 69-85.
4. W-F. A. Su, *J. Polymer Sci., Part A: Polym. Chem.,* 1993, 31, 3251.
5. G. G. Barclay, C.K. Ober, K.I. Papathomas, D. W. Wang, *Macromolecules*,1992, 25, 2947.
6. B. C., Benicewicz, M. E., Smith, J. D. Earls, R. D. Priester, S. M Setz., R. S. Duran, E. P. Douglas. *Macromolecules* 1998, 31, 4730-473.
7. M.D.Lincoln, E.P.Douglas *Polymer Eng. and Sci.* 1999, 39, 1903-1912.
8. E. Reynaud, C. Gautier and J. Perez, "Nanophases in Polymers", Review Metallurgie, 96, pp169-176, 999.
9. L.W. Chun, Q. Z. Ming, Z. R. Min and F. Klaus, "Tensile Performance Improvement of Low Nanoparticle-Filled Polypropylene Composites", Composites Science and Technology, 62, pp1327-1340, 2002.
10. H. Mahfuz,, N. Chisholm, and S. Jeelani, "Mechanical Characterization of Nanophased Carbon Composites," 2002 ASME winter Annual Meeting, New Orleans, Louisiana.
11. H. Mahfuz, V. Rangari, A. Adnan, and S. Jeelani, "Carbon Nanoparticles/Whiskers Reinforced Composites and their Tensile Response," Composites Part A: Applied Science and Manufacturing**,** Vol. 35 (2004), pp519-527.
12. H. Mahfuz, M**.** Islam, V. Rangari, M. Saha, and S. Jeelani, "Response of Sandwich Composites with nanophased Cores under Flexural Loading,"Composites Part B: Engineering**,** in press, 2004.
13. H. Mahfuz, V. Rangari, M. Islam, and S. Jeelani, "Fabrication, Synthesis and Mechanical Characterization of Nanoparticles Infused Polyurethane Foams,"Composites Part A: Applied Science and Manufacturing**,** Vol. 35 (2004), pp453-460.
14. M. R. Parker, R. P. A. R. van Kleef, H.W. Myron, P. Wyder, "Particle Aggregation in Colloids in High Magnetic Fields", J. Mag. and Mag. Materials, Vol. 27, pp250-256, 1982.
15. R. P. A. R. van Kleef, H. W. Myron, P. Wyder, M. R. Parker, "Flocculation of Diamagnetic Particles in High Magnetic Fields", J. App. Phys., Vol. 54, pp 4223-4225, 1983.
16. J. J. Miles, R. W. Chantrell, M. R. Parker, "Model of Magnetic-Field Ordering in Dispersions of Fine paramagnetic Particles", J. App. Phys., Vol. 57(1), pp 4271-4273, 1985
17. A. Tasker, R. W. Chantrell, J. J. Miles, M. R. Parker, A. Bradbury, "Monte- Carlo Simulations of Light Transmission in Dispersions of Paramagnetic Particles", I.E.E.E. Trans. on Magn., Vol. 24, pp1671-1673, 1988.
18. J. J. M. Janssen, Ph.D. Dissertation, University of Nijmegen, 1989.