

Solid state studies on the effect of fillers on the mechanical behaviour of photocured composites

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Various fillers (cellulose triacetate, glass fibres, Al(OH)₃ powder, and Kevlar pulp) were added in different loadings to a dimethacrylic monomer (DEGDMA) and the systems were photopolymerized. The composites thus photoformed were then mechanically tested (Young's modulus of elasticity and stress-at-break) and the results compared with theory. Scanning electron microscopy (SEM) and lateral force atomic force microscopy (AFM) were used to obtain information about the intimate structure and the surfaces of these composites. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Since the very early stages of the development of the polymer industry it was realized that useful products could only be obtained if certain additives were incorporated into the polymer matrix. This process, normally known as 'compounding',² was first used in the rubber industry after being introduced by Charles Goodyear in 1839, when he discovered that the addition of sulfur to a raw rubber stock gave improved products. Such materials are physically dispersed in the polymer matrix without affecting, significantly, the molecular structure of the polymer (cross-linking agents, catalysts, etc. are excluded)³. Additives in plastics are usually classified according to their specific function rather than their chemical structure⁴. Among the most important are those that modify the bulk mechanical properties: reinforcers, plasticizers, and toughening agents. Our main focus was a study of the influence of the first type of additive (reinforcers) on the mechanical properties of the bulk photopolymers. A material is defined as a composite if it consists of two or more distinct components, one of which constitutes the significant majority of the matrix, with a recognizable interface between them⁵. Composites typically have a discontinuous fibre or particle phase that is stiffer and stronger than the continuous matrix phase⁶. To provide reinforcement, the discontinuous phase must be present in substantial volume fraction (at least 5% volume)³. With plastics composites it is possible to distinguish two cases:

- The plastic material is used to encapsulate the reinforcing elements so that suitable shapes and structures can be fabricated⁷. The plastic material, in this case, is the minor constituent (20–50% volume) and the composites are called *high-performance reinforcement composites*².
- The properties of plastics are enhanced by incorporation of small amounts of short fibrous or particulate

reinforcing fillers (5–20% volume) so that the ease of processing is retained⁷. This type of reinforcement is denoted as *low-performance reinforcement*².

Short fibre-reinforced networks produce composites with mechanical and thermal integrity. Their potential versatility and design flexibility, along with their lower density, high specific strength and modulus, are the major reasons these composites have certain advantages over metals^{8,9}. Due to their properties, the use of polymer composites is oriented towards military, space and high-performance commercial applications. Our group is one of the few exploring the use of high performance reinforced polymeric networks formed photochemically, specifically for use in three dimensional imaging. The basis of this is stereolithography—a technique designed to form three-dimensional objects by the assembly of a series of photopolymer layers¹⁰.

There are several inherent problems in photoforming composite materials the most important of which is reflection or refraction of the incident radiation by the filler if it is insoluble in the matrix. Nevertheless we have made significant progress in overcoming this through a better understanding of the use of longer wavelength initiator systems¹¹, and are approaching the stage of developing an understanding of the chemical interaction of the resin with the filler. In our applications the matrix resin comprises between 20 and 80% of the composite by weight and performs a variety of critical functions in addition to simply maintaining the shape of the composite structure and aligning the reinforcements. The resin protects the reinforcers, which are typically rigid fibres, from premature wear¹². Also, the matrix distributes an applied load and acts as a stress-transfer medium, so that when an individual fibre fails, the composite structure does not lose its load-carrying capability.

Since the mechanical properties have to be the same at any point across a reinforced material, uniform distribution of fillers in the polymer matrix prior to photoformation is

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important. Under ideal circumstances, one would have both additives and monomeric mixture in the same phase, e.g. dissolve the filler and the monomer in the same solvent. We found this to be the case only when cellulose triacetate was used as the filler where we were able to add up to 82%, by weight, cellulose triacetate to diethylene glycol dimethacrylate (DEGDMA). All the other composites of this study were prepared by adding different amounts of solid filler to liquid monomer containing the photoinitiator. The next step was to irradiate with broad spectrum mercury lamp radiation for a period of time, and then mechanically test the samples after photopolymerization of the reactive mixtures. The experimental results were compared with the theoretical equations developed by Kerner¹³, Cohen-Ishai¹⁴, and Guth-Smallwood¹⁵. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used to study the intimate structure of the photoformed polymeric composites.

EXPERIMENTAL

General

The monomer used was diethylene glycol dimethacrylate (DEGDMA) purchased from Monomer-Polymer Laboratories. The glass fibres and the Kevlar pulp were purchased from Fibre Glax. The cellulose triacetate in acetone (19% by weight) and same mixture containing additional 10% TiO₂ was a gift of Hoechst Celanese. Al(OH)₃ SpaceRite S-11 was purchased from Alcoa Industrial Chemicals. Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1) was a gift from Ciba-Geigy.

Stress-strain tests were carried out at the ambient temperature (20°C) with no strict humidity control, using the photopolymerized dogbone-shaped sample prepared as described later. The tests were performed using a L-500 instrument (Lloyd Instruments, England), fitted with a NLC-500N load cell. The instrument was controlled by a MCM-4135 GoldStar PC booted with Lloyd's DAPMAT software. This analysis program allows direct observation of the load against elongation behaviour of the sample. After the test ended, the software automatically displayed various

parameters of interest, including stress-at-break (N mm⁻²), Young's modulus of elasticity (N mm⁻²), elongation at break (mm), etc.

Lateral force AFM was performed on a Metris 2000 (Burleigh Instruments) in lateral contact mode. The SEM images were obtained on a Hitachi S2700 equipped with LaB6 electron gun. Final double bond conversions were measured by FTi.r. using the 810 cm⁻¹ bending vibration of the acrylic CH. The CH stretch vibrations at 2800–3100 cm⁻¹ were used as a reference signal to compensate for differences in sample thickness.

Sample preparation

After the solid fillers were added in different ratios (all percentages are by weight) to liquid monomer containing Irgacure 907 (3% by weight), the mixtures were stirred at room temperature for 2 h. In the case of cellulose triacetate composites, the required amounts of monomer and photoinitiator were dissolved in cellulose triacetate (19% by weight) solution in acetone. After the acetone was completely evaporated (5 h in the oven at 50°C), the cellulose triacetate-monomer mixtures were stirred at room temperature for 1 h. All mixtures were poured in dogbone-shaped Teflon moulds and irradiated in a Colight M218 light bath (using two 400 W medium-pressure Hg lamps) for a maximum of 30 min¹⁶. We assumed that after 30 min of irradiation maximum double bond conversions were achieved.

Two drops from each sample were squeezed between NaCl plates divided by 0.1 mm Teflon spacer and irradiated for the same amount of time as the dogbone-shaped samples in the Colight UV bath. The IR spectra before and after irradiation were obtained. By comparing the area of the peak at 810 cm⁻¹ before and after irradiation, the final double bond conversion was measured in all cases.

After irradiation was complete, the dogbone-shaped samples were positioned in the loading cell of the Lloyd instrument for mechanical testing. Cross-sections of the broken samples were used to obtain SEM images. The previously described cellulose triacetate-monomer mixture in acetone was used as the solvent from which films were cast to be used as samples for AFM.

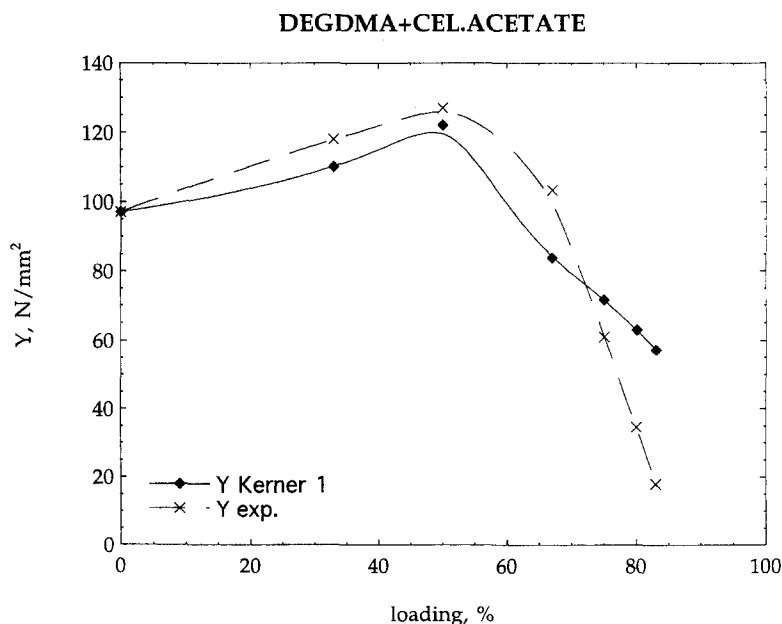


Figure 1 Young's modulus of elasticity (experimental and theoretical data) at different loadings of filler in DEGDMA–cellulose acetate composites

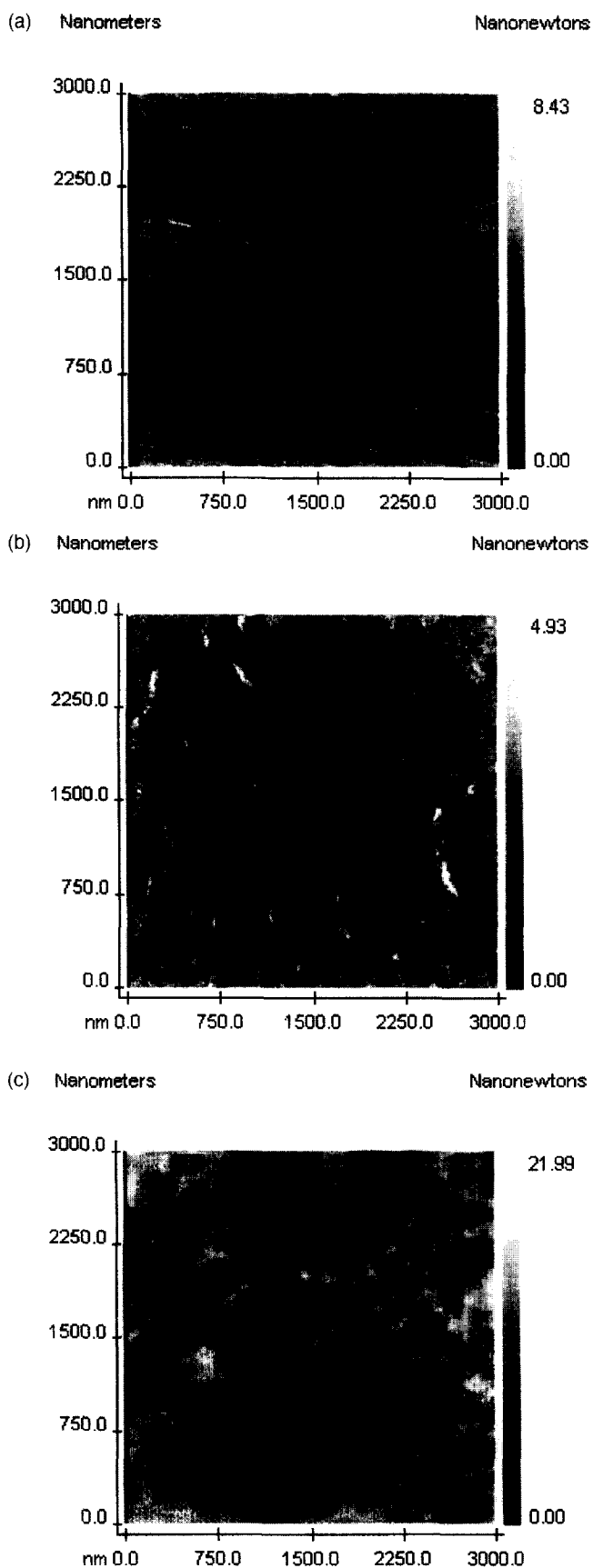


Figure 2 AFM images of DEGDMA–cellulose acetate composites: (a) 50% cellulose acetate; (b) 67% cellulose acetate; (c) 75% cellulose acetate

RESULTS AND DISCUSSION

Inorganic fillers are currently added to polymers for many purposes, such as to increase stiffness (modulus), strength,

impact resistance, dimensional stability, to modify electrical properties, and reduce cost.

Modulus, which is a bulk property, depends mainly on the size, shape, and weight percent of the filler particles. The modulus of composites is generally discussed on the basis of theories originally developed for the viscosity of suspensions, because the filler particles restrict the chain mobility and thus increase the rigidity of the matrix¹⁷. Theoretical data for Young's modulus of elasticity were calculated for all samples and plotted for each composite in comparison with the experimental data. The equations used for these calculations were:

- (1) Guth–Smallwood equation¹⁵ (equation (1)) which is a relationship between the composite modulus (Y_c), the polymer modulus (Y_p), and the volume fraction of the filler (Φ).

$$Y_c = Y_p(1 + 2.5\Phi + 14.1\Phi^2) \quad (1)$$

- (2) Kerner¹³ (we will call this equation Kerner-2) has derived equation (2) as an alternative to equation (1) in the case of low loading of materials (below 40% by weight).

$$Y_c = Y_p \{ 1 + [15(1 - \nu_p)/(8 - 10\nu_p)]\Phi/(1 - \Phi) \} \quad (2)$$

where $\nu_p = 0.3$ is the Poisson ratio for methyl methacrylate (we assumed that the Poisson ratio is the same for diethylene glycol dimethacrylate).

- (3) In the case of high loading of material (above 50% by weight) we used a modified Kerner equation¹⁸ (we will call it Kerner-1):

$$Y_c = Y_p(1 + \Phi - 1.8\Phi^2) \quad (3)$$

- (4) In the case of rigid and spherical filler particles, Cohen–Ishai have proposed equation (4).

$$Y_c = Y_p[1 + \Phi/(1 - \Phi)^{1/3}] \quad (4)$$

Cellulose triacetate composites

Since cellulose triacetate is soluble in acetone it is possible to incorporate large quantities of this additive into DEGDMA monomer. As can be seen from *Figure 1*, the highest quantity of cellulose triacetate added was 83.3%. Six different mixtures were tested. Only the first two mixtures (33.3% and 50% filler) had a positive influence (increase) on the value of the modulus, 115 and 126 N mm⁻² respectively. Further increase in the amount of cellulose triacetate produced rapid deterioration of the mechanical properties of the composites.

The best fit for the experimental results proved to be the Kerner-1 equation (equation (3)) since the amount of filler loading well exceeded 50% by weight.

The decrease in the modulus values is explained by the phase separation which occurs between the polymeric matrix and the cellulose triacetate fibres at high loading. Phase separation occurs due to the differences in the hydrophobicity of both major components of the composites. The dimethacrylate matrix is hydrophobic whereas cellulose triacetate fibres are hydrophilic. Changes in the surface morphology of the composites as the amount of filler increased can be monitored in the lateral mode of scanning by AFM. Images obtained for three different loading of cellulose triacetate are presented in *Figure 2*.

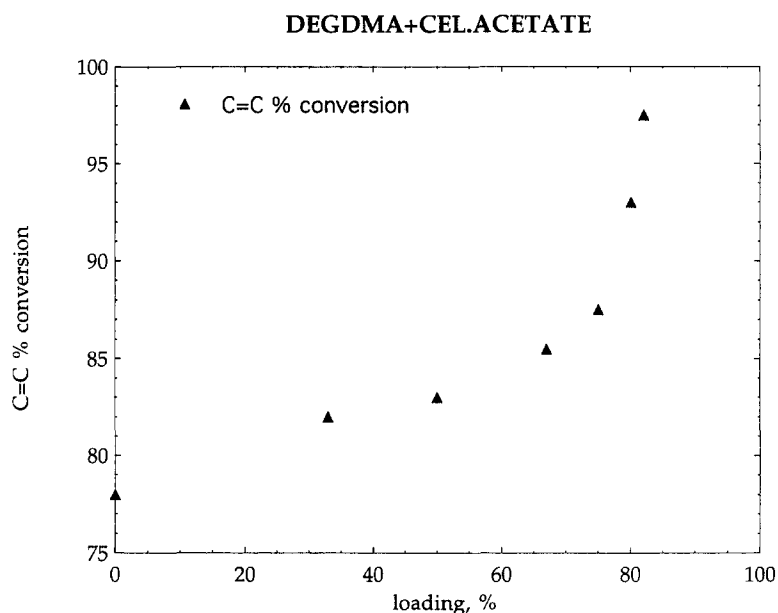


Figure 3 Double bond conversion variation with percentage of cellulose acetate in DEGDMA–cellulose acetate composites

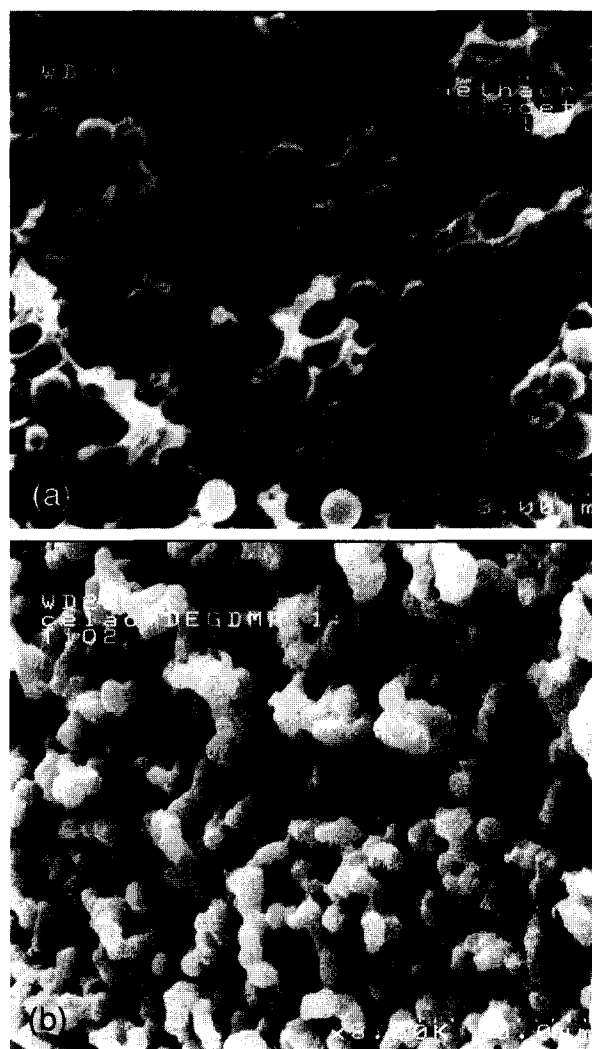


Figure 4 SEM images of DEGDMA–cellulose acetate composites (50%): (a) cellulose acetate; (b) cellulose acetate with 10% hydrophilic TiO₂

In sample (a) 50% cellulose triacetate 15 × 15 μm portions having a relatively smooth and uniform surface can be identified. As the amount of cellulose triacetate is increased (67%), samples of the same size appeared wrinkled (b) as phase separation commenced. At higher loadings (75%) this phase separation was clearly visible as the surface of the sample indicated the presence of two phases (c): one honeycomb-like (polymer matrix) and the other spherical (cellulose triacetate).

When double bond conversion was monitored for all six composites photoformed with cellulose triacetate as the filler, an increase in final double bond conversion was observed (Figure 3), although a decrease in mechanical properties occurred.

Two explanations can account for this effect. First cellulose triacetate fibres can act as a support for long-chain macroradicals, thus decreasing the mobility of the macroradicals, and hence decreasing chain termination rate constants. Second, the cellulose triacetate fibres act as displacement for the liquid monomer ‘pools’ present in the network, making them more available for photopolymerization.

As the SEM pictures show (Figure 4), the first explanation is less probable. Had macroradicals been ‘stuck’ on the surface of cellulose triacetate fibres, an intimate contact between the filler and the polymeric matrix would have been observed. As can be seen from Figure 4a, the cellulose triacetate fibres reorganize in spheres which have almost no intimate surface contact with the polymeric phase. Such structures of the composite are recognized as ‘ball-and-socket’¹⁹ indicating no chemical interaction between the filler and polymer matrix.

When cellulose triacetate containing 10% hydrophilic TiO₂ was used as a filler, phase separation was even more accentuated with the spherical phase having smaller dimensions, Figure 4b.

Therefore, we conclude that the increase in the final double bond conversion is due to the small spheres of cellulose triacetate ‘pushing out’ the monomer present in the network holes, making the latter available for photopolymerization.

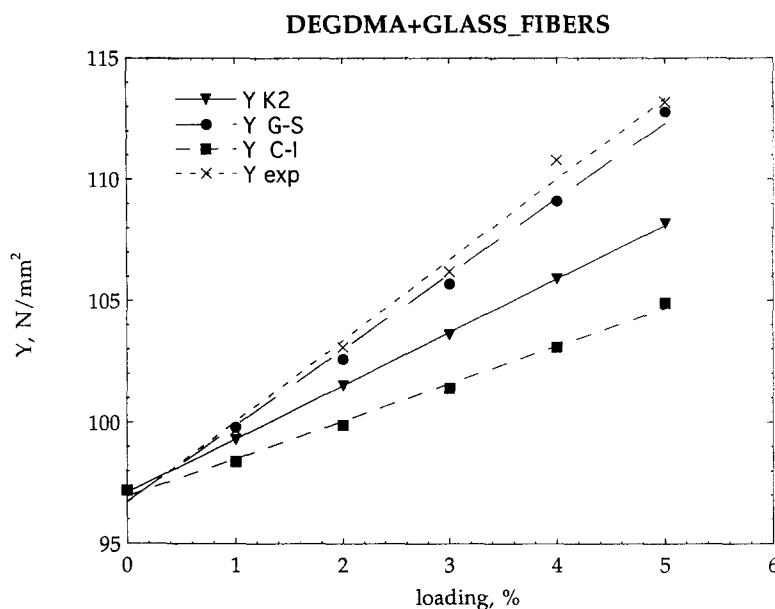


Figure 5 Young's modulus of elasticity (experimental and theoretical data) at different loadings of filler in DEGDMA–glass fibre composites

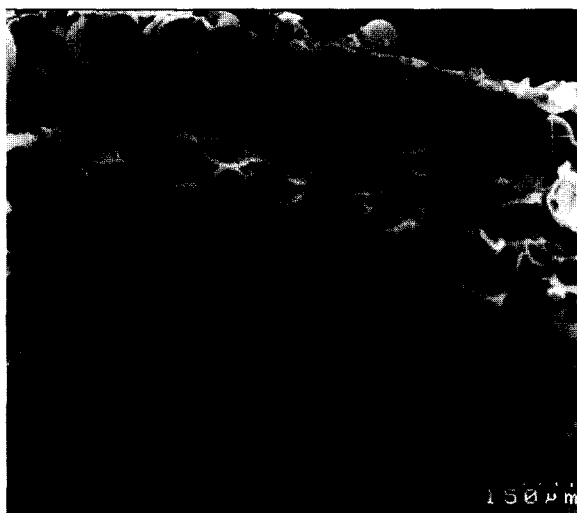


Figure 6 SEM image of DEGDMA–glass fibre composites (5%)

Glass fibres

Since the glass fibres used were without any surface treatment (generally employed in order to improve the dispersity of the fibres in the monomeric phase), small quantities of such fillers (between 1% and 5%) were used to form five different composites.

The experimental and theoretical data for Young's modulus of elasticity in the case of glass fibre composites is shown in *Figure 5*.

The best fit for the experimental data is the Guth–Smallwood equation (equation (1))—a general equation applicable for most inorganic composites. In contrast to the situation with cellulose triacetate, a small quantity of glass fibres (5%) produced a significant increase in modulus (by 25%).

Although the manufacturer claimed the glass fibres were small spheres, we found them disc-like with a diameter of 70–80 μm from SEM pictures, *Figure 6*.

Since the glass fibres were untreated (as were all of our reinforcers used in this study), most of them agglomerate close to the surface of the polymer matrix (*Figure 6*), and very few of them participated in reinforcing the network.

$\text{Al}(\text{OH})_3$

The $\text{Al}(\text{OH})_3$ particles supplied were small spheres (around 1 μm). The best theoretical equation to fit the experimental data is the Cohen–Ishai equation (equation (4)), *Figure 7*. A good fit also was provided by the Kerner-2 equation (equation (2)) since low amounts of filler were used in making all seven composites.

In comparison to the case with glass fibres, significant modulus improvement (300%) resulted because the small spheres allowed the addition of up to 50% (by weight) $\text{Al}(\text{OH})_3$ particles into the dimethacrylic monomer. Good distribution of the filler (even at higher loading, 40%) in the polymeric matrix (*Figure 8*) resulted because these fillers have the possibility of hydrogen bonding, a phenomenon often observed in ethylene glycol monomers. This hydrogen bonding might also influence the modulus and this will be the focus of our future studies.

From the SEM picture (*Figure 8*), we measured the sizes of $\text{Al}(\text{OH})_3$ particles as being below 1 μm .

Kevlar pulp

Kevlar pulp is among the lightest fillers and highly abrasion resistant. Composites used in areas requiring high impact strength (automotive industry, space craft, defence, etc.) can be easily reinforced with this strong and durable material. We photoformed seven composites containing different quantities of Kevlar pulp (5–50%), though the samples were difficult to prepare due to the agglomerating properties of the pulp. Each sample had to be manually prepared so a uniform distribution of the Kevlar pulp (along the dogbone-shaped mould) could be achieved.

The experimental data fit the Guth–Smallwood equation (equation (1)), which best simulated the real values of the modulus, *Figure 9*.

At 40% filler, the modulus improved fivefold compared with the pure polymeric network. The sample containing 50% Kevlar pulp did not break at the highest possible mechanical loading (500 N mm^{-2}) our machine can achieve, *Figure 9*.

When we crushed the sample containing 50% Kevlar pulp, we observed that the Kevlar fibres appeared to be agglomerated (*Figure 10*) on the surface of the polymeric

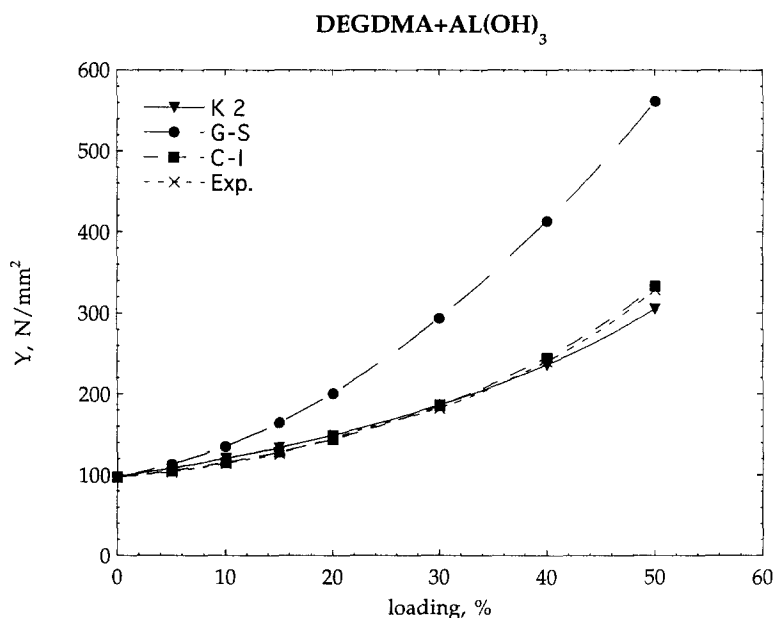


Figure 7 Young's modulus of elasticity (experimental and theoretical data) at different loadings of filler in DEGDMA-Al(OH)₃ composites

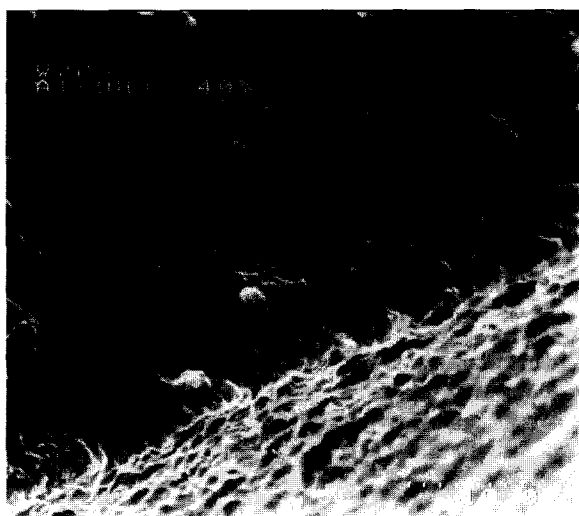


Figure 8 SEM image of DEGDMA-Al(OH)₃ composite (40%)

matrix. Although we observed no fibre incorporation into the polymeric network, this configuration substantially improved the mechanical properties of the composites.

CONCLUSIONS

In this paper we demonstrate the wide variety of materials that can be obtained by photochemically forming composite materials. The conditions are not optimized and much improved results can be anticipated with other initiation packages. Four different fillers have been tested in differing amounts in a matrix formed in a cross-linked methacrylic network.

As expected, when filler is soluble in monomer, high material loading can be obtained (up to 83%). However, when composites having a high loading of cellulose triacetate were photoformed, mechanical properties (Young's modulus of elasticity) degraded significantly suggesting phase separation between the two major

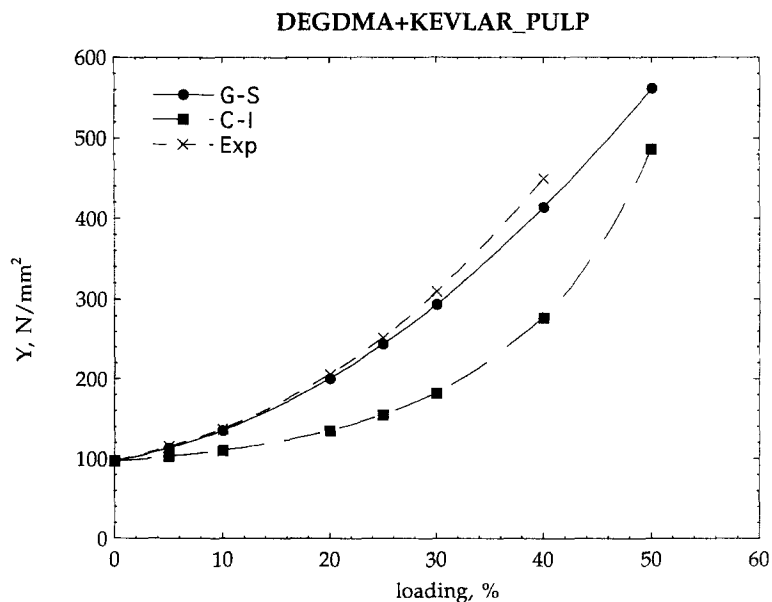


Figure 9 Young's modulus of elasticity (experimental and theoretical data) at different loadings of filler in DEGDMA-Kevlar pulp composites



Figure 10 SEM image of DEGDMMA-Kevlar pulp composite (50%)

components of the composite due to the difference in the hydrophobicity of the matrix and the filler. Phase separation was confirmed by lateral force mode AFM and SEM images. The failure of the reinforced materials was also predicted theoretically by the Kerner-1 equation (equation (3)). Upon addition of hydrophilic TiO_2 to the cellulose triacetate monomer mixture, phase separation was accentuated, and we observed by SEM that the sizes of the cellulose triacetate spheres decreased significantly. In addition, SEM techniques elucidated the reason for the increase in double bond conversion with an increase in the quantity of filler. Excess cellulose triacetate spheres pushed out the non-polymerized monomer from the network 'pools', thus making it available for polymerization reaction.

The experimental data for the glass fibres and $\text{Al}(\text{OH})_3$ -reinforced materials were fit well by the theoretical equations. Since such glass fibres were not surface treated, we were only able to use them in small amounts. Therefore, the best fit for the experimental data proved to be the general equation for the composites, the Guth-Smallwood equation (equation (1)). $\text{Al}(\text{OH})_3$ fillers have the possibility of hydrogen bonding with the polymer matrix and, as can be seen from SEM image, formed the most homogeneous composites, Figure 8. Since they have a spherical structure, it was not surprising that the best theoretical fit for the experimental data was the Cohen-Ishai equation (equation (4)). Also the Kerner-2 (equation (2)) equation provided a close fit for this particular system.

In the case of Kevlar pulp, high performance composites were obtained. The modulus was increased five times, and in the case of 50% filler, the reinforced material had been able to dissipate all mechanical stress on the Kevlar fibres, so that our machine could not break the sample. The experimental data were fitted satisfactorily by Guth-Smallwood equation (equation (1)).

Our work will continue in photoforming reinforced materials with different fillers in different monomeric systems.

ACKNOWLEDGEMENTS

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