Biomimetic High Filler Content Composites using Bisphenol-A Ethoxy Diacrylate

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ABSTRACT

Biomimetic composites of Bisphenol-A ethoxy diacrylate with 77-86 % fillers content were prepared by *in situ* polymerization using two compacting techniques. Centrifugating produced more compacted composites compared with a compression moulding method. Either method was much different from natural formation from layer-by-layer construction, however the composites formed were of high filler content, without achieving the 95 %·w/w level in nature. The filler space was efficiently filled by using a combination of nano and microsize fillers. The composites were effectively compacted so that wetting and adhesion at the resin–filler interface would provide optimum cohesion.

Keywords: composite, biomimetic, thermomechanical property, biomaterial, viscoelasticity, thermal stability

1 INTRODUCTION

Biomimetic materials are those where the components materials, technique of preparation or the microstructure are based upon naturally occurring materials [1,2]. High filler content composites have been prepared in polypropylene, though due to viscosity and processing requirements filler content was limited compared with natural systems [3,4,5].

In this paper we describe materials prepared to be biomimetic of nacre with its layered structure of high filler content. Nacre is based upon about 95 %·w/w calcium carbonate as a composite with a layered block structure. Nacre has a very high modulus, high strength, with low flexibility and toughness. Toughness in filled polymers requires dispersion of an energy absorbing elastomer phase [6]. Biomaterials of this type are formed via a layer-by-layer deposition. This formation method is tedious to replicate manually, though an automated system could accumulate layers with many coating and evaporation or reaction cycles. A problem for synthetic systems is the high viscosity of highly filled resins or resin solutions. If filler is dispersed in a monomer the shrinkage on polymerization will cause stress within the rigid composite.
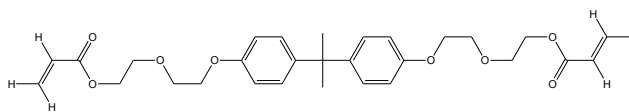
Preliminary experiments were performed with epoxy resin because of their low shrinkage upon cure. A problem was the high filler content was dilution with a significant proportion of hardener. Bisphenol-A ethoxy diacrylate (Ebecryl 150) offer a similar large monomer structure with cure using about 1 %·w/w of a peroxide forming substance, dibenzoyl peroxide was used. The filler used was a combination of nano and micro dimension particles to ensure efficient filler space filling.

2 EXPERIMENTAL

2.1 Materials

Bisphenol-A ethoxy diacrylate monomer (Ebecryl 150 from UCB Chemicals) was used as received. The amorphous fumed silica Aerosil 300 (Degussa, Germany) used in this work has a silica content of >99.8 %·w/w, an average primary particle size of 7 nm and a specific surface area of 300 ± 30 m^2·g^{-1}. Calcium carbonate Omyacarb (CaCO$_3$) with an average particle size of ~1.7 µm was obtained from OMYA (Australia). All fillers were dried in an oven prior to use. The thermal initiator, benzoyl peroxide and solvent, toluene were used as received from Merck, Germany.

Figures 1: Chemical structure of the bisphenol-A ethoxy diacrylate monomer (Ebecryl 150)

2.2 Sample Preparation

The formulations were prepared by using different composition of monomer and fillers, and 1 %·w/w initiator in toluene. The formulation is given in Table 1. The nanosilica was mixed in the monomer resin using propeller blade mechanical stirrer at 300 rpm for 15 min. The filler was further dispersed by ultrasonication for 15 min. CaCO$_3$ was then added and the mixture was stirred for 15 min at 300 rpm, followed by ultrasonication for better dispersion (15 min). The dispersion by ultrasonication was done in bursts to avoid overheating the resin. The resin was degassed in vacuum until entrapped bubbles were removed completely. The initiator was added and mixed at 100 rpm

for 2 min. Immediately after mixing, the resin was centrifuged at 10,000 rpm for 15 min. The filled prepolymer was extremely viscose, however centrifuging the dispersion, maximized the filler concentration. After centrifuging, the dispersion was slowly heated to 90 °C for 5 h in a vacuum oven to cure the resin. The cured composite was removed from the centrifuge tube and cut using a diamond saw to form test specimens from the lower part of the cured resin. The upper fraction contained less filler since the filler had been compacted at the bottom of the tube during centrifuging. An alternative method was to place the initiated dispersion between separators in a heated hydraulic press (90 °C, 6 t, 10 min), followed by post-cured at 90 °C for 5 h in vacuum oven. Some of the resin, together with some filler, flowed from the composite concentrating the filler in the central portion of the molding.

Samples	Ebecryl (%·w/w)	$CaCO_3$ ((%·w/w)	Silica ((%·w/w)
BA	100.0	0	0
BA-CC	50.0	50.0	0
BA-Si-CC	50.0	48.0	2.0

Table 1: Sample formulation and identification of abbreviations for polymer composites.
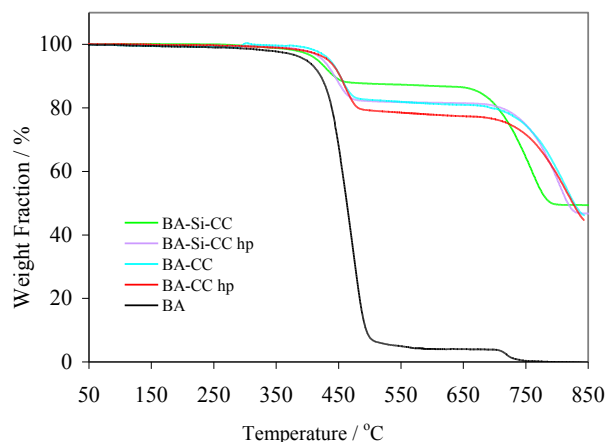
2.3   Characterization

The cured resin and composites were characterized by thermal gravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). TGA was carried out using Perkin-Elmer Pyris 1 thermogravimetric analyzer. Samples of about 3.0 mg were heated from 35 to 850 °C at a heating rate of 10 °C·min^{-1}. The purging gas (flow rate: 20 mL·min^{-1}) was nitrogen from 35-700 °C, then it was changed to air at 700 °C. The WAXD patterns were taken with Bruker D8 Advance X-ray diffractometer with Cu K$_\alpha$1 radiation (λ = 1.541 Å) in the 2θ range from 10° to 60°, in steps of 0.02°. The DMA was performed with a Perkin-Elmer DMA8000, using a single cantilever bending mode, at a frequency of 1 Hz and oscillation amplitude of 0.05 mm. The specimens were heated from 30 °C to 90 °C at 2 °C·min^{-1}. The surface morphologies of the fractured and etched surface composites were examined under SEM (FEI nova nanoSEM).

3   RESULTS AND DISCUSSION

The polymer and the composites were produced by *in situ* polymerisation around the inorganic fillers. Given the preparation route, the final fillers composition in the prepared composites had to be verified by thermal gravimetric analysis (TGA). The thermal analysis of the cured bisphenol-A ethoxy diacrylate (BA) and the composites are presented in Figure 2 and the data are summarized in Table 1. The weight loss curve (TGA curve) of the cured resin and its composites showed that degradation occurs in two stages. In the first stage, at temperature between 35 to 650 °C, the weight loss of BA (95.7 %) is due to the evaporation of moisture, volatile organic solvent and the thermal decomposition of the organic compound in the polymer matrix. The second weight loss (4.3 %) at temperature > 650 °C is ascribed to the further combustion or carbonization of organic compound especially when air was introduced at 700 °C. No residue remained at 850 °C.

Figures 2 : TGA curve of BA and its composites.

Sample	W loss 1 (%·w/w)[a]	W loss 2 (%·w/w)[b]	Residue (%·w/w)	$T_{d, 10\%}$ (°C)[c]
BA	95.7	4.3	0	418
BA-CC	19.0	35.0	46.0	452
BA-CC hp	22.7	33.6	43.7	453
BA-Si-CC	13.6	37.0	49.4	443
BA-Si-CC hp	18.5	34.8	46.7	444

[a] Weight loss at 35 – 650 °C

[b] Weight loss at 650 – 850 °C

[c] The decomposition temperature ($T_{d, 10\%}$) is defined as 10 %·w/w loss
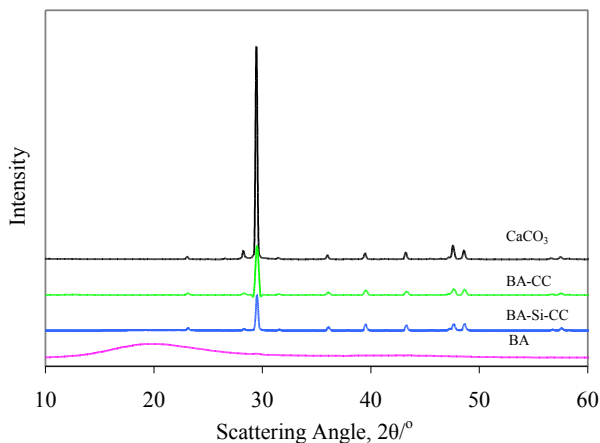
Table 1: Composites composition from TGA analysis

Meanwhile, the first stage of weight loss in the composites is attributed to the degradation of the polymer matrix and the second weight loss is mainly due to the loss of CO_2 from the filler. The residue remained at 850 °C is mainly contain CaO (BA-CC) or CaO and silica (BA-Si-CC). Hence, the first weight loss was used to determine the weight fraction of filler in the composites. Results indicate that the composition of the composites are influenced by the compaction techniques and filler type. Centrifuging is more effective in compacting the composites than the hot compression technique. Centrifuging $CaCO_3$ dispersion produced a highly compacted composite (BA-CC) with

81 % filler content. Whilst composite that compacted by hot compression technique (BA-CC hp) only content 77.3 % filler. Combination of microsized $CaCO_3$ and nanosilica efficiently compacted the composites. The filler content in composite prepared by centrifuging (BA-Si-CC) and hot compaction technique (BA-Si-CC hp) are 86.4 % and 81.5 % respectively.

Thermal stability of the cured resin and its composites were measured as the decomposition at temperature of 10 % weight loss ($T_{d,\,10\%}$). The high $T_{d,\,10\%}$ observed for the composites is considered to be related to the tortuous path of degradation products, which is strongly related to the distribution of fillers particles in the resin. In addition, this increase in the thermal stability, could be attributed to the high thermal stability of the $CaCO_3$ and the interaction between the filler and polymer matrix. The fillers were considered to be acting as a thermal barrier, thereby protecting the polymer from degradation.
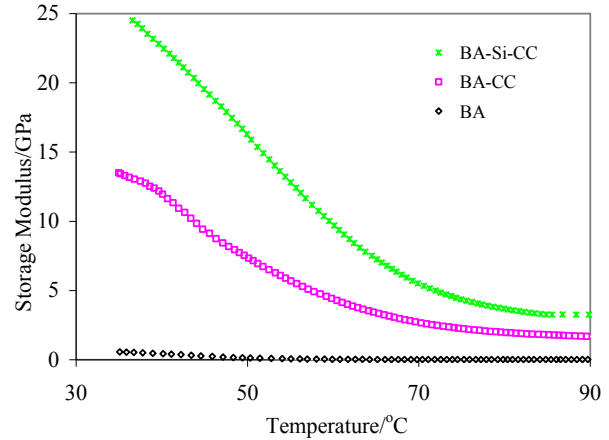
Figure 3 shows the WAXD patterns of the BA, $CaCO_3$ and the composites. A large halo obtained in BA pattern at around $2\theta = 20°$ indicates the amorphous state of the BA polymer. The relatively high intensity of the Bragg reflections is presented at the (104) plane ($2\theta = 29.5°$) for $CaCO_3$, BA-CC and BA-Si-CC, which indicates that the $CaCO_3$ is in the calcite form. The position of the peaks in BA-Si-CC did not change, indicating the structure of the $CaCO_3$ crystal was maintained in composite, with or without nanosilica.
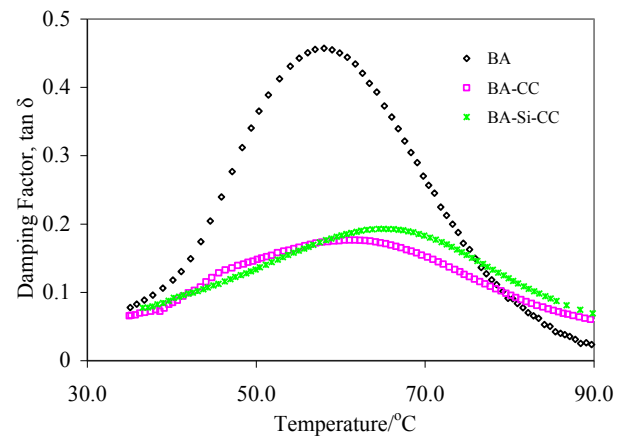

Figures 3: WAXD pattern of BA, $CaCO_3$ and its composites

The dynamic mechanical behaviour of BA and the composites are shown in Figure 4 (storage modulus, $E^{'}$) and Figure 5 (damping factor, tan δ). As expected, the storage modulus of the polymer increase significantly with addition of $CaCO_3$, from 0.57 GPa in cured BA to 13.5 GPA for BA-CC composite. The $CaCO_3$ introduces a rigid phase in the polymer, and the bulk modulus of the composite is a function of the filler volume fraction. Further, the polymer chains surrounding the filler particles may have a reduced mobility, which also leads to a higher modulus. Whilst the

E' of BA increased substantially with addition of $CaCO_3$, it was found that reinforcing effect of nanosilica is more prominent. E' of BA-Si-CC composite is 24.5 GPa, almost 2 times than that of BA-CC. Addition of nanosilica was found to have a reinforcing effect on composite, consistent with other polymers containing fillers of nanometer size [8,9].

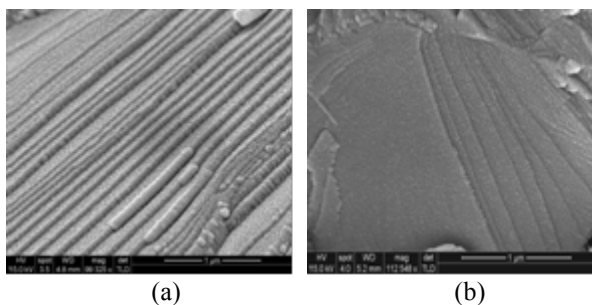Figures 4: Storage modulus of BA and its composites

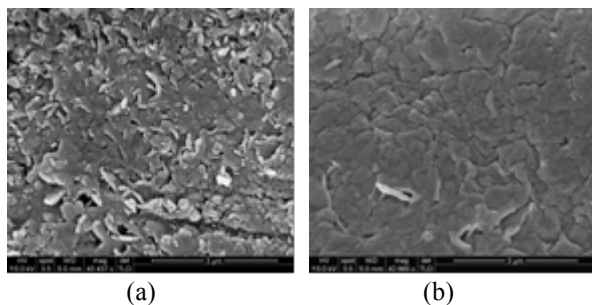Figures 5: Tan δ as a function of temperature of BA and its composites

The glass transition (T_g), which is the viscoelastic transition of a material, is obtain from the peak of tan δ curve as shown in Figure 5. It has been reported that in composite system, the addition of rigid fillers in matrix made it difficult to move the polymer chain and therefore damping decrease and T_g were shifted to higher temperature [8,9]. Consistently, in this study, the composites have higher T_g than the cured resin. The T_g of the cured BA was approximately 58.0 °C, whilst for BA-CC and BA-Si-CC were 60.4 °C and 65.1 °C respectively. The increase in T_g is attributed to a decrease in mobility of the polymer chains, due to the optimum cohesion in compacted composites.

Figure 5 also shown that damping (tan δ) is reduced substantially with the addition of fillers, indicating that fillers restricted the mobility of polymer chain. However, the tan δ is slighly higher in the BA-Si-CC composite than observed in BA-CC. Due to very high surface area of the nanosilica in the BA-Si-CC composite, the applied stress was expected to be transferred from the matrix onto the silica particles, resulting in an enhancement of the mechanical properties [9].

For SEM observation, two sample were prepared, fractured and etched surface composites. The fractured samples were prepared by submerging it in liquid nitrogen for 1 min and then break it down transversely with a small hammer. For the etched samples, the cross-sections of the composites were cut, polished and then etched by a solvent mixture of 8 mol·L^{-1} NAOH and methanol (3:2 volume ratio) and stirred for 2 h. All samples were gold-coated prior to scanning. The distribution of the nanosilica and/or $CaCO_3$ in BA are shown in Figure 6 and Figure 7.

(a) (b)

Figures 6: SEM images of the fractured surface composites: (a) Eb-$CaCO_3$ and (b) Eb-Si-$CaCO_3$

(a) (b)

Figures 7 : SEM images of the etched surface composites: (a) Eb-$CaCO_3$ and (b) Eb-Si-$CaCO_3$

SEM images of the fractured surface composites show that the dispersion of the particles in the BA matrix were fairly good (Figure 6). The surface fractured of BA-Si-CC composite was smoother and less steps than BA-CC. Further, the etched surface of the composites (Figure 7) revealed that the BA-Si-CC composite has smooth surface and less holes than that of BA-CC composite. This results indicate that BA-Si-CC composite is more compacted than BA-CC. As expected, the empty space between $CaCO_3$

particles are fillled with nanosilica, hence effectively compacted the composites.

4   CONCLUSION

Combination of nano and micrometer fillers efficiently compacted the composites. The compacted methods used indicate that centrifugation produced more compacted composites than hot compression technique. The dynamic mechanical properties revealed that nanosilica and $CaCO_3$ fillers had a reinforcing effect on the bisphenol-A ethoxy diacrylate resin. The SEM images indicate that fillers are well disperse in the BA-Si-CC composite and *in situ* polymerisation produced a better wetting of the fillers by the polymer matrix.

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