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Properties of Epoxy Based Hybrid Composites

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Epoxy resins have very important chemical and mechanical properties, however they have a small elongation at break, poor impact strength and resistance to crack propagation i.e. they exhibit a brittle behaviour. This study investigates the effects of inorganic and polymeric modifiers on the fracture toughness, thermal properties and creep modulus of epoxy resin. The obtained results show that a specific amount of kaolin and polyesters (Desmophen 1100 and Desmophen 1200) improved maximally the impact strength, the critical stress intensity factor as well as the flexural strength. As expected, creep modulus increased with addition of kaolin and decreased with polyesters modifiers. Similar results to those were obtained with the deflection temperature under load. Moreover, the results confirmed that hybrid composites had higher fracture toughness than unmodified epoxy resins or composites containing one modifier. No synergism effect was observed with the hybrid composites mechanical properties.

Keywords: epoxy resins, modification, fracture toughness, hybrid composites.

1. INTRODUCTION

Epoxy resins are widely used as matrices for high performance composite materials. However, these materials exhibit low impact strength, poor resistance to crack growth and small elongation at break, i.e. they are inherently brittle.

In the last few decades, a great deal of effort was devoted to the improvement of the fracture resistance and the ductility of brittle polymers such as epoxy and unsaturated polyester resins.

Approaches to improve the toughness of epoxy resins include mainly the incorporation of solid particles [1 – 3] and copolymers of butadiene and acrylonitrile terminated with reactive groups such as carboxyl (CTBN) [4 – 6], hydroxyl (HTBN) [7], amine (ATBN) [8, 9]. However, the reactive rubber toughening led to the deterioration of some mechanical and thermal properties of the epoxy resins.

To overcome the drawbacks of the loss of thermal properties of epoxy resins, other toughening methods are proposed. These latter include the addition of ductile, chemically and thermally stable tough thermoplastics such as polyethersulphones [10] or polyetherimide [11].

A great deal of literature has been devoted to the toughening of epoxy resins via polyurethanes incorporation as a second phase to form a grafted or ungrafted Interpenetrating Polymer Networks [12, 13]. It has been found that the mechanical properties are fairly superior to those of the base polymer matrix. More recently, Pascault et al. modified the epoxy resin with core-shell particles [14]. The Functionalised and reticulated polymethylmethacrylate constituted the shell whereas polybutylacrylate the core of the particles.

The aim of the present work is to investigate the effect of of polymeric modifiers and inorganic particles on the fracture toughness, thermal resistance and creep modulus of epoxy based resins.

2. EXPERIMENTAL

2.1. Materials

In the experiments the following materials were used:

– epoxy resin, Epidian 5 produced by “Organika – Sarzyna”, Nowa Sarzyna, Poland. Epidian 5 had an epoxy number of 0.49 mol/ 100g and a viscosity of 30000 mPa.s at 25°C;

– cycloaliphatic amine (trade name IDA) from “Organika – Sarzyna” was used as hardener;

– the modifiers used were Kaolin (Polarite 102 from Imerys) and polyesters (Desmophen 1100 and Desmophen 1200) from Bayer Company.

2.2. Preparation of composites

An appropriate amount of modifier was added to the epoxy resin and finally the hardener was added. The mixture was poured into teflon coated plates with adequate sample geometry ($60 \times 10 \times 4$ mm^3). The maximum amount of each modifier were dictated by the mixing efficiency and good wettability of the incorporated particles. The amount of added modifier giving the optimum properties was chosen to produce hybrid composites.

Curing was carried out at room temperature for 24 h then followed by a post-curing at 60 °C for 6 hours.

The prepared compositions were tested for their impact resistance according to Charpy method, critical stress intensity factor under three point bending mode, flexural strength according to Dynstat method as well as deflection temperature under load according to Martens method.

All compositions were based on 50 parts of epoxy resin and 26.5 parts of hardener.

2.3. Evaluation of mechanical properties

Impact strength was measured according to Charpy method on notched samples having the following geometry $15 \times 10 \times 4$ mm^3.

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The critical stress intensity factor (K_c) was estimated on samples 10 cm long, 1 cm wide and 4 mm thick having 1 mm of crack length according to the following equation :

$$K_c = \frac{3P \cdot L \cdot a^{1/2} \cdot Y}{2d \cdot w^2}, \quad (1)$$

where P is the load at fracture, N; L is the distance between the spans, mm; w is the sample width, mm; d is the sample thickness, mm; a is the crack length, mm; Y is the geometrical factor expressed by the following formula:

$$Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80(a/w)^4. \quad (2)$$

Five samples were used for each data of each composition.

2.4. Thermal analysis

The deflection temperature under load was estimated according to Martens method using a stress of 5 MPa and a heating rate 50 °C / hr.

3. RESULTS AND DISCUSSIONS

Fig. 1 represents the impact strength (IS) results of compositions containing one modifier. It can be seen that IS attained maximum values with 30 % Desmophen 1100 (De1100) and 20 % Desmophen 1200 (De1200) or kaolin. The improvements were 235 %, 245 % and 105 % respectively as compared with unmodified resin.

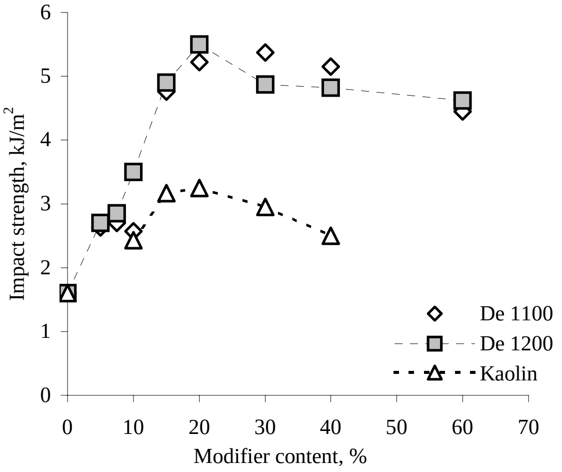

Fig. 1. Effect of modifier content on the impact strength

The improvement of impact strength of composites containing kaolin is generally explained by the so called crack-pinning mechanism [1]. Similar results to those were obtained with flexural strength. Flexural resistance exhibited maximum improvement (which represented 65 % when compared with unmodified resin) with 7.5 % De1100 or De1200 and 30 % enhancement with 10 % kaolin. The impact strength improvement with kaolin is less pronounced than with polyesters and this might be attributed to the poor adhesion between epoxy resins and the fillers and/or filler agglomeration.

In Fig. 2 the impact strength of the hybrid composites are shown. All hybrid composites exhibited better impact strength as well as flexural resistance than unmodified epoxy resin. Hybrid composites containing 8 % of kaolin and 12 % of Desmophen 1100 exhibited the best impact strength in comparison with neat resin or any composition with one modifier.

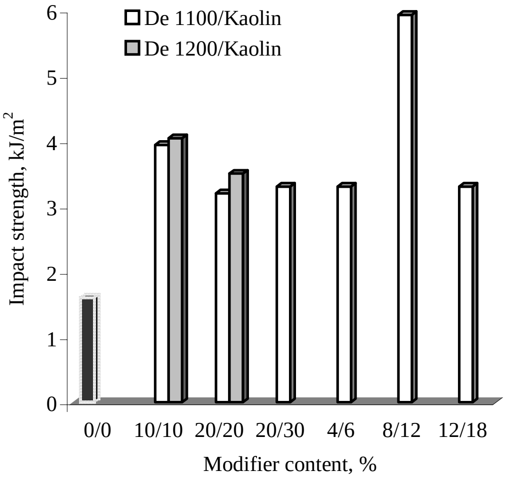

Fig. 2. Effect of modifiers on the impact strength of hybrid composites

However no synergism effect was observed for hybrid composites. The lack of synergism might be due to the particles agglomeration and the poor adhesion between epoxy resin and the inorganic particles.

The critical stress intensity factor (i.e. the fracture toughness parameter, K_c) is represented in Fig. 3 as function of modifier content.

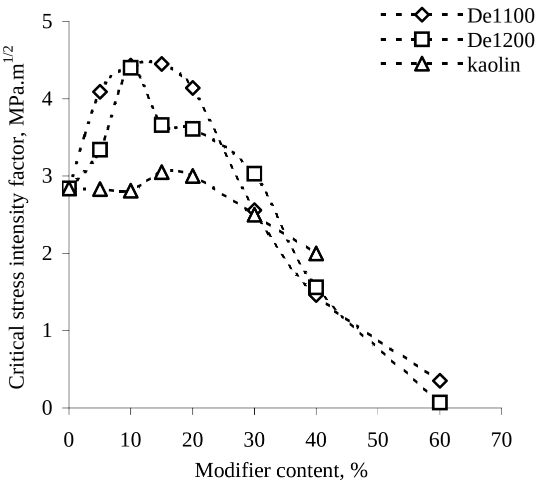

Fig. 3. Effect of modifier content on the fracture toughness of epoxy resin

It can be seen that K_c increases to a maximum value then decreases as the polyester amount increases. Similar results to those were obtained with impact strength. The fracture toughness parameter was maximally enhanced by about 55 % with either De1100 or De1200 and 7.5 % with 20 % kaolin respectively.

Moreover, one can notice that kaolin (up to 20 %) has no significant effect on K_c and higher amounts lead to its decrease. This can be explained essentially by the particles agglomeration and/or a poor adhesion between kaolin and the matrix. The enhancement of the fracture toughness with the polymeric modifiers may arise from their plasticization effect. Phase segregation may occur leading to more energy absorption during the crack propagation of the samples.

In Fig. 4 the evolution of K_c for selected hybrid compositions is shown. Similarly to impact strength results, K_c values of hybrid composites were higher for than that of unmodified resin.

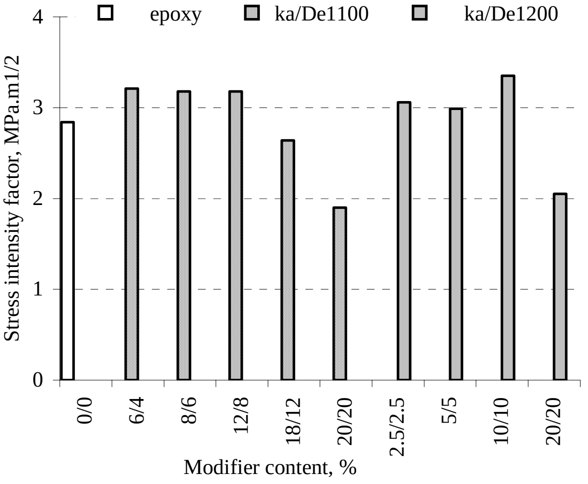

Fig. 4. Critical stress intensity factor of hybrid composites

The evolution of the instantaneous creep modulus is represented in Fig. 5 and 6 for composites containing respectively one and two modifiers.

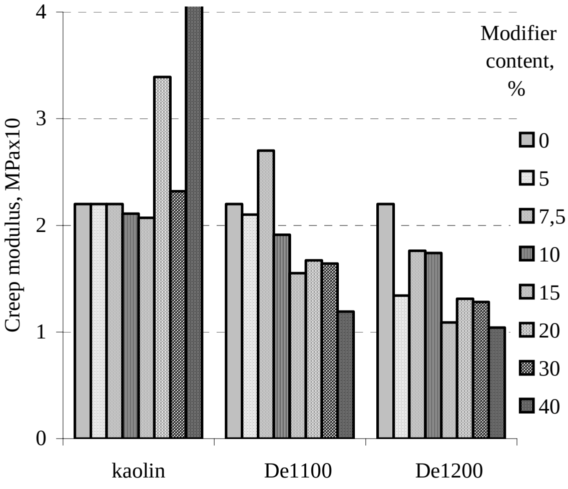

Fig. 5. Instantaneous creep modulus of composites with one modifier

From Fig. 5, one can notice that as the amount of kaolin increases the creep modulus increases until it reaches a maximum value which corresponds to 40 % of kaolin. The maximum creep modulus improvement represents 90 % in comparison with the creep modulus of epoxy resin without modifier. The creep modulus enhancement with kaolin is as one can expect with inorganic fillers.

In the case of polymeric modifiers, the creep modulus decreases as the amount of modifiers increases expect for compositions with 7.5 % of Desmophen 1100 or Desmophen 1200. It has to be mentioned that polymeric modifiers act as plasticizers which lower the creep resistance of the modified polymers. Similar results are obtained with hybrid composites.

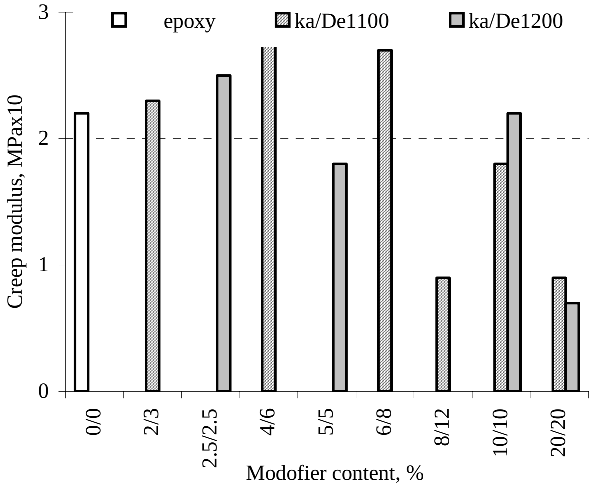

Fig. 6. Creep modulus of hybrid composites

The plasticization effect of polymeric modifiers and the poor compatibility between modifiers may explain the lack of creep resistance improvement for hybrid composites.

In Fig. 7 is shown the effect of modifiers content on the composites deflection temperature under load according to Martens method.

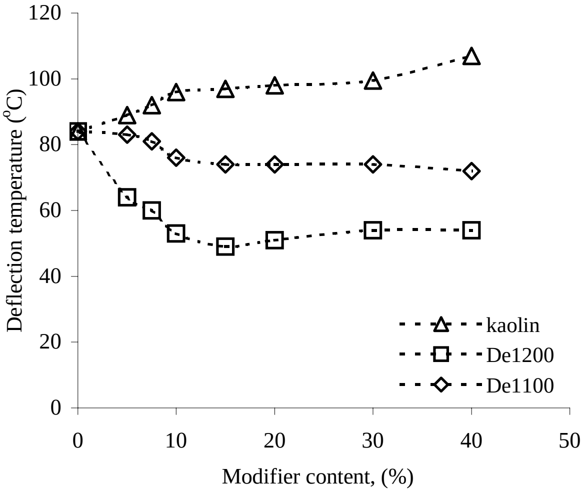

Fig. 7. Effect of modifier content on the deflection temperature under load

It can be seen that the temperature decreases with increasing amount of polymeric modifiers but increases as the kaolin content increases. Moreover, it has to be mentioned that the deflection temperature is higher for the composite containing Desmophen 1100 in comparison with that with Desmophen 1200. This might be due to the high level of branching of Desmophen 1100. The improvement of the composite thermal resistance with kaolin is mainly related to the high resistance of the modifier itself.

Fig. 8 illustrates the evolution of the deflection temperature under load of hybrid composites according to Martens method.

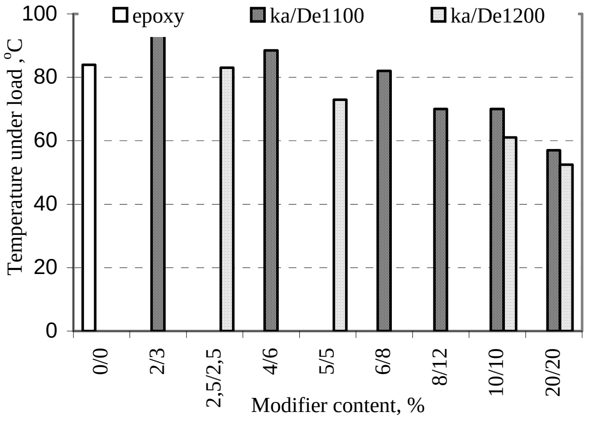

Fig. 8. Deflection temperature under load of hybrid composites

From Fig. 8, one can notice that only two formulations containing 2 % kaolin / 3 % De1100 and 4 % kaolin / 6 % De1100 have higher deflection temperatures under load when compared to neat resin. The lowering of the hybrid composite deflection temperature might be explained by the conjugated effects of the lack of compatibility between the polymeric modifiers and kaolin as well as the plasticizing character of polyesters

CONCLUSIONS

Based on the following results we can conclude that:

– the addition of kaolin and polymeric modifiers improved the impact strength and resistance to crack propagation as well the flexural resistance of the epoxy resin;

– properties enhancement was obtained with an optimum amount of either kaolin, Desmophen 1100 or Desmophen 1200;

– hybrid composites had better mechanical properties than unmodified epoxy resin, however no synergism was observed;

– the incorporated modifiers did not have any significant effect on the temperature under load according to Martens method.

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