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Effect of Kaolin and Polyurethane on the Fracture and Thermal Properties of Epoxy Based Compositions

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The present work investigates the mechanical and thermal properties of conventional and hybrid composites based on epoxy resin modified with kaolin and polyurethane. Hybrid composites are expected to exhibit better properties than heat resin due to positive deviation generated from the combination of two different toughening mechanisms. Diglicydyl ether of bisphenol A (Araldite 260 GY) was used as a matrix and polyamine Aradure 460 as crosslinking agent. Polyurethane was obtained with hydroxyl-terminated polyester Desmophen 1200 and toluene diisocyanate. The chain extender used in this work was 1,4-Butanediol. The impact strength, the critical stress intensity factor (K_C) and the deflection temperature under load (DTUL) were evaluated as function of modifiers content. It was shown that the impact strength of epoxy resin increased with polyurethane (PU) content significantly until it reached a maximum value of 5.8 kJ/m^2 at 20 phr kaolin and 6.9 kJ/m^2 with 20 phr of PU, which corresponds to respectively 150 % and more than 200 % improvement in comparison with IS of neat resin. The addition of 5 phr – 20 phr PU did not affect K_C but this latter decreased with 30 phr or 40 phr PU. However, K_C was maximally increased by approximately 60 % with 20 phr kaolin and 40 % with 20 phr PU. The thermal resistance of epoxy resin decreased by 40 % with the addition of 10 phr PU, however the addition of both modifier, i.e. 15 phr kaolin and 10 phr PU leads to an increase of DTUL the level of that of virgin epoxy resin.

Keywords: epoxy, polyurethane, kaolin, impact strength, fracture toughness, thermal properties.

1. INTRODUCTION

Epoxy resins are widely used as matrices for high performance composite materials, surface coatings and adhesive joints. However due to their highly cross-linked density, these materials exhibit a low impact strength, a poor resistance to crack propagation and a small elongation at break, i.e. they are inherently brittle.

A great deal of effort was devoted to the improvement of the fracture toughness of epoxy resins in the last few decades aiming at enlarging their field of applications. Approaches to improve the epoxy resins fracture toughness include the incorporation of solid particles [1 – 3] and copolymers of butadiene and acrylonitrile terminated with reactive groups such as carboxyl (CTBN) [4 – 6], amine (ATBN) [7 – 9], hydroxyl (HTBN) [10, 11] or epoxy (ETBN) [12, 13]. It was noticed that the rubber, which is in general soluble in the uncured epoxy resin, precipitates out from solution during the curing process forming thus a fine and homogeneous dispersion of rubber particles. However, the reactive rubber toughening leads to the deterioration of some mechanical and thermal properties of the epoxy resins.

In order to overcome the drawback of the loss of thermal properties, ductile thermoplastics such as polysulphones [14], polyethersulphones [15], polyetherimides [16], polycarbonate [17] and polyimide [18] have been used to toughen epoxy resins.

Moreover, the formation of epoxy based on interpenetrating polymer networks was also investigated as a toughening way for epoxy resins [19 – 21].

However, the addition of both solid and rubber polymer network seems to be a very interesting method for epoxy resin modification.

The aim of the present work is to investigate the effect of polyurethane and kaolin content on the fracture toughness and thermal properties of epoxy resin.

2. EXPERIMENTAL

2.1. Materials

The following ingredients were used in the present work:

- diglicydyl ether of bisphenol A: Araldite 260 GY, $Mw = 381$ g/mol from Ciba-Geigy;
- crosslinking agent: polyamine Aradure 460, from Ciba-Geigy;
- kaolin: Calcined Clay Polarite 102 A from Imerys .
- Desmophen 1200 slightly branched polyester with 5 % OH from Bayer;
- toluene diisocyanate (TDI);
- chain extender: 1,4-Butanediol (1,4-BD);
- crosslinking agent trimethylolpropane (TMP).

2.2. Synthesis of polyurethane prepolymer and preparation of epoxy- polyurethane compositions

Polyurethane prepolymer synthesis was carried out at 70 °C for one hour using 2 equivalents of TDI and 1 equivalent of Desmophen 1200. TDI was previously heated to 40 °C in a reaction kettle.

The preparation of IPN (epoxy-PU) was carried out using different amounts of PU (5, 10, 20, 30, 40 phr) to a constant amount of epoxy resin. Then, chain extender (1,4-

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BD) and second crosslinking agent (TMP) were added via the dropping funnel. After mechanical agitation PU prepolymer was added and agitation was continued for 45 min at 70 °C. Finally 60 phr of curing agent was added. The mixture was poured into teflon coated plates with adequate samples geometries (60 mm × 10 mm × 4 mm).

The curing of the formulations was carried out at 80 °C for 1 h and at 120 °C for 3 h. Upon removal from the mold samples were kept in a dessicator of a minimum period of 3 days.

2.3. Preparation of epoxy-kaolin and epoxy-PU- kaolin compositions

The compositions of epoxy-kaolin were obtained with different amounts of kaolin. Epoxy resin and kaolin was poured into reaction kettle and heated at 45 °C. After mechanical agitation, the curing agent was added and agitation was continued for 5 min. Curing was achieved under the same conditions as above. Epoxy compositions containing both PU and kaolin were prepared with constant amount of PU (10 phr and 20 phr) and different amounts of kaolin.

The same procedure, as above presented, was followed for PU-kaolin samples preparation.

2.4. Properties evaluation

Impact strength was measured according to Izod method on samples having the following geometry 80 mm × 10 mm × 4 mm. Tests were performed at room temperature using Zwick 5012 impact tester using the Polish Norm PN-85/C-89050.

The critical stress intensity factor K_C was estimated under three point bending mode on samples 8 cm long, 1 cm wide, 4 mm thick and having 1 mm of crack length. The tests were performed at room temperature using an Instron tensile machine type 5566 at a crosshead speed of 5 mm/min according to ASTM E-399 using the following relationship [22]:

$$K_C = \frac{3PL\,a^{1/2}}{2t\,w^2}Y\,, \qquad (1)$$

where P is the critical load for crack propagation [N]; L is the distance between the spans [m]; a is the precrack length [m]; w is the specimen width [m]; t is the specimen thickness [m]; Y the geometrical factor expressed by the following equation [22]:

$$Y = 1.93 - 3.07\left(\frac{a}{w}\right) + 14.53\left(\frac{a}{w}\right)^2 - 25.11\left(\frac{a}{w}\right)^3 + 25.80\left(\frac{a}{w}\right)^4. \qquad (2)$$

Five samples were used for K_C and impact strength evaluations with 95 % confidence limit.

The deflection temperature under load (DTUL) was estimated according to the Martens method using the Polish Norm PN – 90/C-89025-1 with a heating rate of 50 °C/h. Three samples were tested for each composition.

3. RESULTS AND DISCUSSIONS

Figure 1 represents the impact strength (IS) of epoxy resin modified with kaolin and polyurethane (PU). It can be seen that IS increases and then decreases as the modifier content increases. The maximum improvement is attained with 20 phr of either kaolin or PU, and represents respectively 150 % and more than 200 % in comparison with IS of neat resin. The IS enhancement through the addition of solid particles of kaolin can be explained by the crack pinning mechanisms [1]. However, in the case of PU, the impact strength enhancement can be explained by the increase of the elasticity of the tested compositions induced by PU chains flexibility due the presence of chain extender. Polybutadiene may also contribute to some extent to the impact strength improvement .

The maximum impact strength improvement has already been reported in literature with different modifiers [1 – 3, 19, 20].

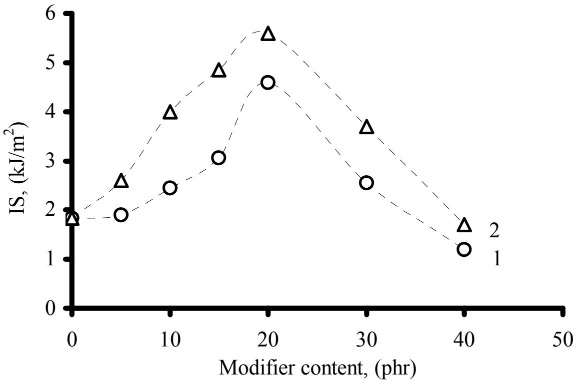

Fig. 1. Effect of kaolin and polyurethane content on the impact strength of epoxy based compositions: 1 – kaolin; 2 – PU

As it is shown in Fig. 2, the critical stress intensity factor (K_C) slightly increases then decreases with increasing amount of kaolin or PU but one can observe a more significant decrease with 30 phr and 40 phr PU. This confirms the the impact strength results (Fig. 1). At higher concentration PU acts as a plasticizer, that is more free volume is provided to the systems leading to more flexible compositions. Similarly to impact strength results, K_C was maximally increased (approximately 60 %) with 20 phr kaolin and 40 % with 20 phr PU.

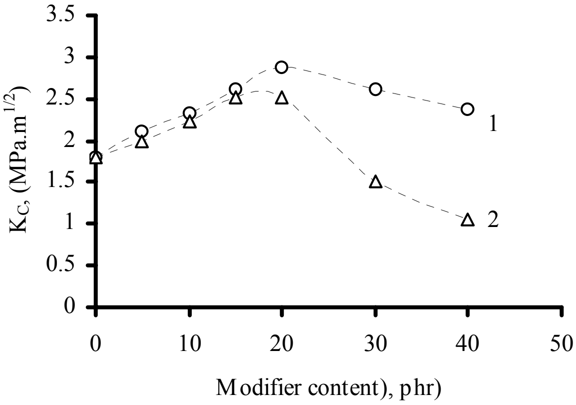

Fig. 2. Effect of modifier content on the critical stress intensity factor (K_C) of epoxy based compositions: 1 – kaolin; 2 – PU

As represented in Figure 3, the impact strength also increases as kaolin content increases for epoxy compositions containing 10 phr and 20 phr polyurethane. The impact strength (IS) reaches a maximum value of 6.9 kJ/m^2 for the composition with 20 phr PU and 20 phr kaolin, which corresponds to respectively 275 % and 50 % improvement in comparison with IS of neat resin and composition with only 10 phr kaolin.

Figure 4 presents the effect of kaolin content on the fracture toughness expressed by K_C of epoxy compositions with and without polyurethane. We can notice that hybrid composition containing 10 phr of PU and 15 phr of kaolin exhibits the highest resistance to crack propagation demonstrated by highest K_C.

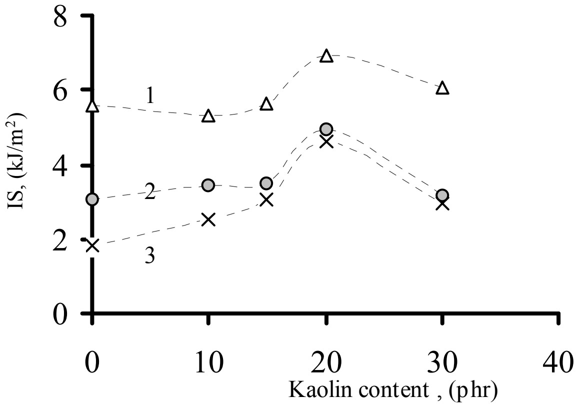

Fig. 3. Effect of kaolin content on the impact strength: 1 – 0 phr PU + kaolin; 2 – 10 phr PU + kaolin; 3 – 20 phr PU + kaolin

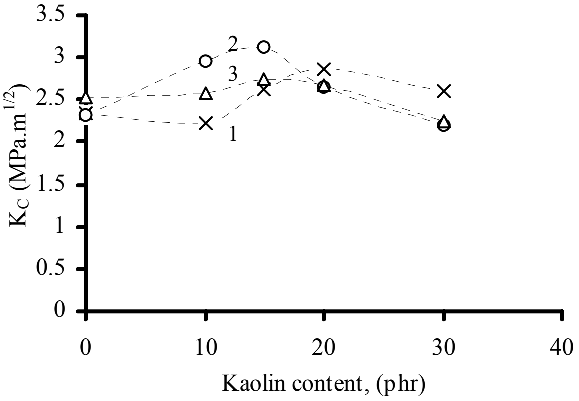

Fig. 4. Effect of kaolin content on the critical stress intensity factor (K_C): 1 – 0 phr PU + kaolin; 2 – 10 phr PU + kaolin; 3 – 20 phr PU + kaolin

Since the concepts of G_C (the critical strain energy release rate parameter) and K_C are exclusively applied for linear elastic fracture behaviour, they are not recommended for the elasto-plastic behaviour evaluation, that is for the compositions containing modifiers such as polyurethane and exhibiting non linear behaviour. Therefore, the energy needed to create new surfaces (designated the fracture energy) was evaluated from the load-extension curve that was obtained during the sample crack propagation. The fracture energy is presented in Figure 5 as function of polyurethane content.

It can seen that the fracture toughness enhancement (expressed by the fracture energy) pronounced than the critical stress intensity factor, but is comparable to IS results, and represents more than 110 % with 20 phr PU in comparison with the unmodified epoxy resin.

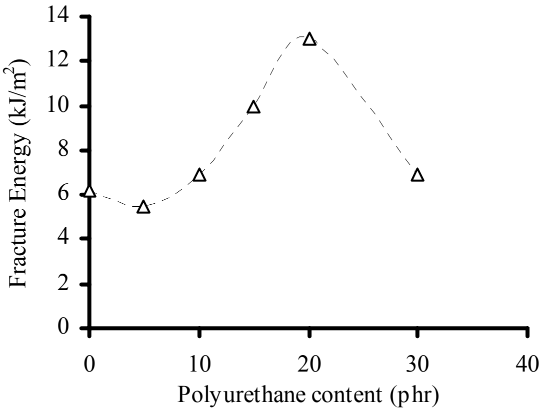

Fig. 5. Effect of polyurethane content on the fracture energy of epoxy resin

Figure 6 represents the evolution of deflection temperature under load (DTUL) as function of modifier content. We observe a linear decrease with 10 phr of polyurethane, which represents about 30 % decrease in comparison with DTUL of the virgin epoxy resin, followed by a level off with higher PU content.

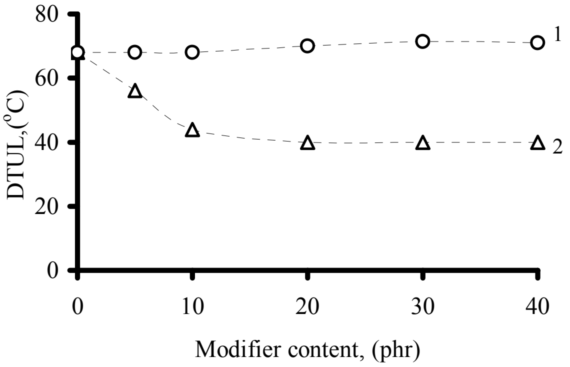

Fig. 6. Effect of polyurethane and kaolin content on the deflection temperature under load (DTUL) of epoxy resin compositions: 1 – kaolin; 2 – PU

Polyurethane acts as plasticizer promoting more free volume and therefore inducing an increase in flexibility of the tested compositions. The addition of 5 phr – 40 phr of kaolin did not affect the deflection temperature under load.

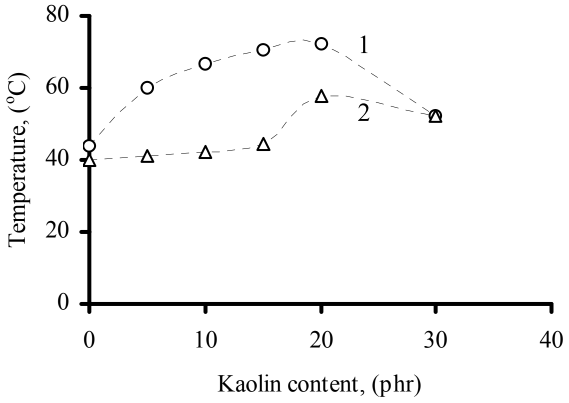

Fig. 7. Effect of kaolin content on the deflection temperature under load (1 – 10 phr PU + kaolin; 2 – 20 phr PU + kaolin)

Figure 7 represents the effect of kaolin on DTUL of rubber modified epoxy resin. For the composition modified with 20 phr of PU, a slight increase is observed with 20 phr and 30 phr of kaolin but the thermal resistance is lower than that of neat resin (Fig. 6). However DTUL of the composition modified with 10 phr of PU increased as the amount of kaolin increases until it attained a maximum value with 20 phr of kaolin which is at the level of DTUL of neat epoxy resin and seems to be the optimum amount of kaolin to be added to epoxy resin without causing DTUL decrease.

CONCLUSIONS

Based on the following results we can conclude that:

1. The addition of polyurethane modifier improved the impact strength as well as the resistance to crack propagation expressed by the critical stress intensity factor. Maximum values of impact strength and K_C were obtained with 20 phr of PU. The fracture toughness enhancement can be attributed mainly to the high modifier elasticity but a lesser extent also to polybuatediene which acts as plasticizer.

As expected, the thermal resistance of epoxy resin based compositions decreased with the addition of PU and remains almost constant with kaolin.

2. The addition of kaolin caused the increase of the impact strength, the critical stress intensity factor due to crack pinning mechanism. The thermal resistance of epoxy resin was also enhanced by kaolin addition.

3. The addition of both modifiers (PU and kaolin) leaded to an improvement of the fracture toughness of epoxy resin. However, the addition of both modifiers resulted in an increase of DTUL to the level of DTUL of virgin epoxy resin.

REFERENCES

1. **Lange, F. F., Radford, K. C.** Fracture Energy of an Epoxy Composite System *Journal of Materials Science* 6 1971: pp. 1197 – 1203.
2. **Spanoudakis, J., Young, R. J.** Crack Propagation in a Glass Particle-Filled Resin *Journal of Materials Science* 19 1984: pp. 487 – 496.
3. **Chikhi, N. Fellahi, S., Bakar, M.** Modification of Epoxy Resin with Kaolin *European Polymer Journal* 38 2002: pp. 251 – 264.
4. **Kinloch, A. J., Shaw, S. J., Tod, D. A., Hunston, D. L.** Deformation and Fracture Behaviour of a Rubber-Toughened Epoxy. I. Microstructure and Fracture Studies *Polymer* 24 1983: pp. 1341 – 1354.
5. **Sanjana, Z. N., Kupchella, L.** Dynamic Mechanical Analysis of Rubber Toughened Epoxy Resins *Polymer Engineering and Science* 25 1985: pp. 1148 – 1154.
6. **Wise, C. W., Cook, W. D., Goodwin, A. A.** CTBN Rubber Phase Separation in Model Epoxy Resins *Polymer* 41 2000: pp. 4625 – 4633.
7. **Kunz, S. C., Sayre, J. A., Assink, R. A.** Morphology and Toughness Characterization of Epoxy Resins Modified with Amine and Carboxyl Terminated Rubbers *Polymer* 23 1982: pp. 1897 – 1906.
8. **Levita, G., Marchetti, A. Butta, E.** Influence of the Temperature of Cure on the Mechanical Properties of ATBN/Epoxy Blends *Polymer* 26 1985: pp. 1110 – 1116.
9. **Chikhi, N., Fellahi, S., Bakar, M.** Modification of Epoxy Resin using Reactive Liquid (ATBN) Rubber *European Polymer Journal* 38 2002: pp. 251 – 264.
10. **Sankaran, S., Chanda, M.** Chemical Toughening of Epoxies. II. Mechanical, Thermal and Microscopic Studies of Epoxies Toughened with Hydroxyl-Terminated Po(butadiene-co-acrylonitrile) *Journal of Applied Polymer Science* 39 1990: pp. 1635 – 1647.
11. **Ozturk, A.**, **Kaynak, C., Tincer, T.** Effects of Liquid Rubber Modification on the Behaviour of Epoxy Resin *European Polymer Journal* 37 2001: pp. 2353 – 2363.
12. **Verchere, D., Pascault, J. P., Sautereau, H., Moschiar, S. M., Riccardi, C. C., Williams, R. J. J.** Rubber-Modified Epoxies. IV. Influence of Morphology on Mechanical Properties *Journal of Applied Polymer Science* 43 1991: pp. 293 – 304.
13. **Hwang, J. F., Manson, J. A., Hertzberg, R. W., Miller, G. A., Sperling, J. H.** Structure-Property Relationships in Rubber Toughened Epoxies *Polymer Engineering and Science* 29 1989: pp. 1466 – 1476.
14. **Hedrick, J. L., Yilgor, I., Wilkes, G. L., McGrath, J. E.** Chemical Modification of Matrix Resin Networks with Engineering Thermoplastics *Polymer Bulletin* 13 1985: pp. 201 – 208.
15. **Bucknal, C. B., Partridge, I. K.** Phase Separation in Epoxy Resins Containing Polyethersulphone *Polymer* 24 1983: pp. 639 – 644.
16. **Hourston, D. J., Lane, J. M., MacBeath, N. A.** Toughening of Epoxy Resins with Thermoplastics II. Tetrafunctional Epoxy-Polyetherimide Blends *Polymer International* 26 1991: pp. 17 – 21.
17. **Rong, M., Zeng, H.** Polycarbonate-Epoxy Semi-Interpenetrating Polymer Network. 2. Phase Separation and Morphology *Polymer* 38 1997: pp. 269 – 277.
18. **Li, S., Hsu, B.-L., Li, F., Li, C. Y., Harris, F. W., Cheng, S. Z. D.** A Study of Polyimide Thermoplastics Used as Tougheners in Epoxy Resins – Structure, Property and Solubility Relationships *Thermochimica Acta* 340 – 341 1999: pp. 221 – 229.
19. **Hsieh, K. H., Han, J. L.** Graft Interpenetrating Polymer Networks of Polyurethane and Epoxy. I. Mechanical Behavior *Journal of Polymer Science: Part B*: *Polymer Physics* 28 1990: pp. 623 – 630.
20. **Chern, Y. C., Tseng, S. M., Hsieh, K. H.** Damping Properties of Interpenetrating Polymer Networks of Polyurethane – Modified Epoxy and Polyurethanes *Journal of Applied Polymer Science* 74 1999: pp. 328 – 335.
21. **Harani, H., Fellahi, S., Bakar, M.** Toughening of Epoxy Resin using Synthesized Polyurethane Prepolymer based on Hydroxyl-Terminated Polyesters *Journal of Applied Polymer Science* 70 1998: pp. 2603 – 2626.
22. **Kinloch, A. J., Young, R. J.** Fracture Behaviour of Polymers. Applied Science Publishers, London, 1983.