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A STUDY ON THE TOUGHENING MECHANISM OF RUBBER-MODIFIED POLYFUNCTIONAL EPOXY RESINS

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ABSTRACT

The toughening mechanism of CTBN rubber-toughened trifunctional epoxy resins was studied using a scanning electron microscope. The SEM micrographs show that the CTBN rubber-modified trifunctional epoxy resins are composite materials consisting of a continuous phase of epoxy resins and a CTBN rubbery disperse phase. The toughening mechanism is discussed mainly in terms of the initiation and propagation of secondary microcracks during or before propagation of the primary cracks, and the several important models of the secondary microcrack formation are discussed in more detail. Our task was to control the morphology of the composite, the structures of separate phases and the interfacial adhesion in such a way as to obtain the best balance of properties.

INTRODUCTION

Rubber-modified epoxy resins constitute an important class of adhesives used especially in the aeronautical and cosmonautical industries. They are characteried by a combination of high adhesion strength and toughness. One of the most important factors controlling the toughness of rubber-epoxy resins system is the size, distribution and structure of the rubber particles.

Recently, much attention has been paid to the fracture processes of rubber-modified epoxy resins [1-5]. However, very few works have been published in the literature concerning the effect of rubber/epoxy resin interfaces on toughness. Therefore, it has been difficult to know exactly the toughening mechanism in the above dual-phase system. This paper deals with the morphologies of fracture surfaces and the toughening mechanism of carbonyl terminated buta-

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diene-acrylonitrile(CTBN) rubber toughened trifunctional epoxy resins. The task in this paper is to control the morphology of the composite, the structure of the separate phase and the interfacial adhesion in such a way as to obtain the best balance of properties.

EXPERIMENTAL PROCEDURE

The original materials used in the present study were P-aminophenol epoxy resin, epoxy resin of bisphenol A, CTBN rubber, acid anhydride and 2-ethyl-4-methyl imidazole. Specimens for impact tests were cut from a casting piece into pieces of 55x6x4 mm. Impact tests were performed with a XCJ-40 type machine, made in China. The shear strength of the cohesion layer was determined with an Instron-type tensile machine operated at three temperatures, i.e., room temperature, 120°C and 150°C. The material bonded by the present adhesive was an aluminium alloy. The fracture modes were examined by using a scanning electron microscope(SEM) Hitachi S-550.

RESULTS AND DISCUSSION

Figure 1 and Table I show the effect of the CTBN content on the shear strength of the cohesion layer. As shown in Fig.1 and TableI, the shear strength greatly increases on increasing the CTBN content from 0% to 20%. There is a maximum at 18-20%, after which the shear strength decreases.

Table I. Effect of the CTBN content on shear strength

Shear strength,kg/cm^2	CTBN content, %				
	0	10	18	20	30
room temperature	164	227	245	248	219
120°C	170	185	218	203	121
150°C	123	135	133	158	115

Figure 2 shows the effect of the CTBN content on the impact strength of the rubber-epoxy resin casting piece. It can be seen that the impact strength increases correspondingly with increasing CTBN content.

Figure 3 shows the fracture surfaces of impact specimens with different CTBN contents. As shown in Fig.3, the rubber-modified trifunctional epoxy resins are composite materials, consisting of a rigid matrix and a rubbery disperse phase. In other words, the epoxy resins are the continuous phase, and CTBN rubbers are the

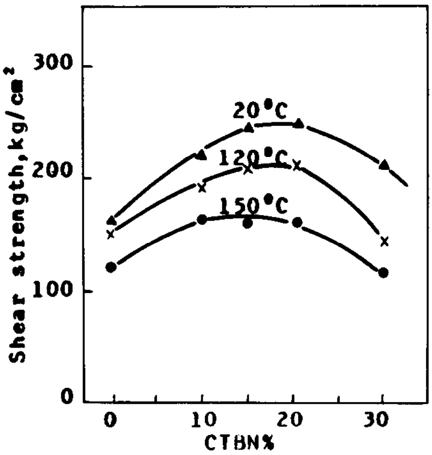

Fig.1. Influence of the CTBN content on shear strength

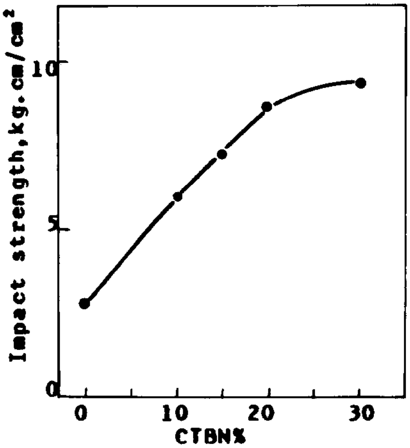

Fig.2. Influence of the CTBN content on impact strength

disperse phase. The higher the rubber content, the greater the particle size. As shown in Fig.3a, for the case of 0% CTBN, the fracture surface appears as a typical brittle fracture pattern which is extremely similar to the brittle river pattern found in the cleavage fracture of metals. As shown in Fig.3b, for the case of 10% CTBN, (in contrast with the small number of large cracks formed in the 0% CTBN specimen) a large number of small cracks was produced. The rubber particles both initiate and control crack propagation. Under stress, cracks are initiated at points of maximum principal strain, which are near the equators of rubber particles, and the crack pro-

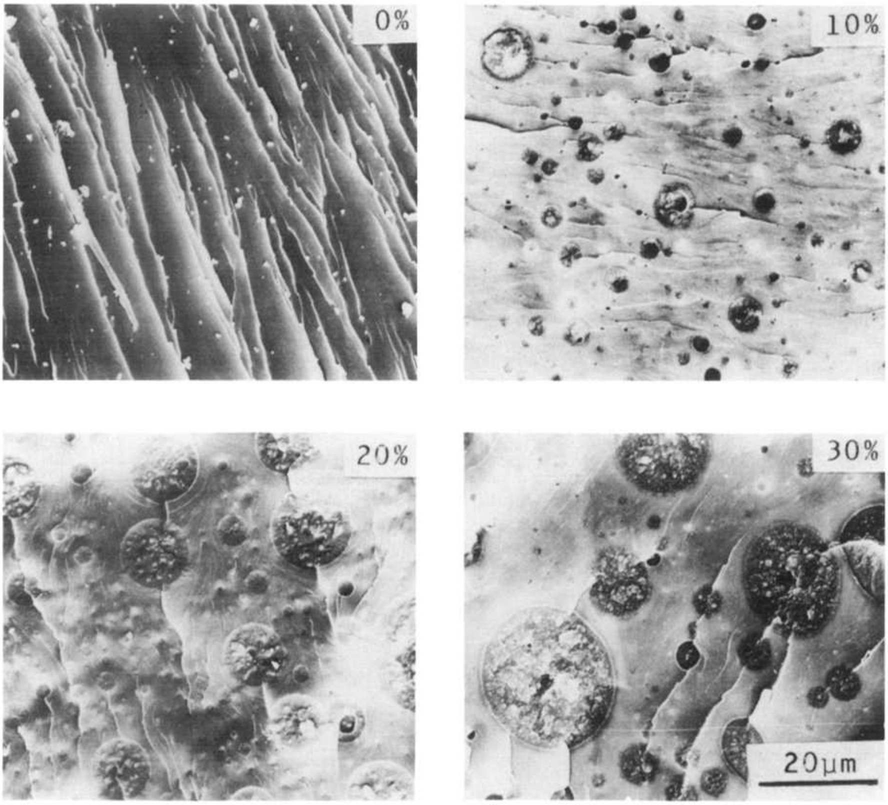

Fig.3. SEM fractographs of impact samples containing 0, 10, 20 and 30% CTBN, respectively.

pagation is terminated when a large rubber particle is encountered. As shown in Fig.3c, for the case of 20% CTBN, the rubber particles are relatively large and contain a high proportion of epoxy resins. Therefore, the rubber particles have a dual-phase structure, containing the appropriate amount of epoxy resin particles (also shown in Fig.4). This dual-phase structure is called a 'salami structure' [6,7]. As shown in Figs. 3c, 3d and Fig.4, a great number of microcracks in the sub-inclusion structures will be initiated at rubber/epoxy resin interfaces during impact testing. As shown in Fig.3d, for the case of 30% CTBN, the rubbery particles start to be partly out of shape after fracture, and the modulus and the strength of rubber/epoxy resins composite decrease, along with the adhesive properties.

Based on the results obtained in SEM observations, the toughening mechanism of rubber-toughened trifunctional epoxy resins is discussed mainly in terms of the secondary microcrack initiation and propagation during or before propagation of the primary cracks.

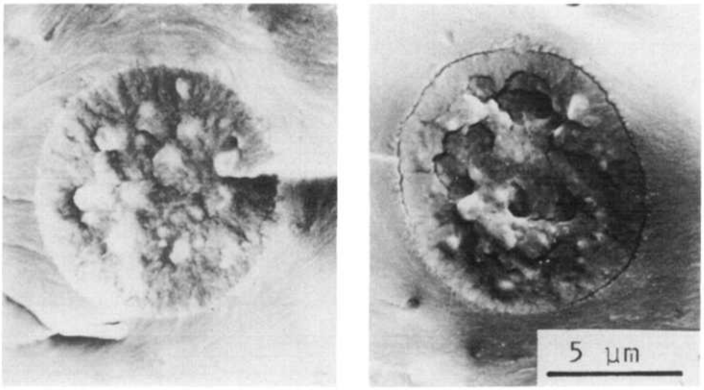

Fig.4. SEM fractographs of 20% CTBN impact sample showing the typical sub-inclusion structure of a rubber particle with <salami structure>.

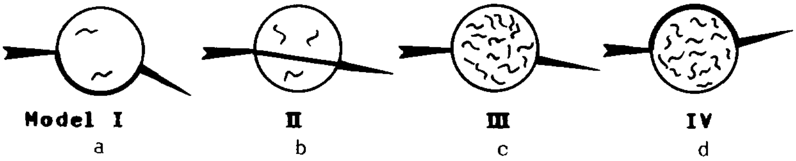

Fig.5. The models of secondary microcracks formation in a rubber-toughened epoxy resins system.

There are several important models of the secondary microcrack formation. As shown in Fig.5a (model I), when the epoxy resin content in the rubber particle is smaller, the primary crack propagates along the rubber particle/resin matrix interface, which induces a smaller number of secondary microcracks in the rubber particle. As shown in Fig.5b (model II), when both the content and the size of the epoxy resin phase in the rubber particle are large, the primary crack propagates mainly through the particle and along the dual-phase interfaces in it. This also induces a smaller number of secondary microcracks in the rubber particle. As shown in Fig.5c and 5d (model III and IV), when the content of the epoxy resin phase in the rubber particle is appropriate, the size of the epoxy resin phase is relatively smaller and well-distributed, the primary crack propagates through the particle (model Ⅲ) or along the rubber particle/epoxy resin matrix interface, and induces a greater number of secondary microcracks in the rubber particle.

Figures 5c and 5d show the typical fracture models of a 'salami structure'. The fracture models, whether the type I, Ⅱ or the type Ⅲ, Ⅳ, are part of the interface fracture models. It may be that the interface binding strength exerts a tremendous influence on the toughness of the dual-phase system during fracture. Consequently, the material can absorb a much higher strain energy before fracture. Dense cracking throughout a comparatively large volume of material accounts for the high energy absorption in impact or tensile tests.

CONCLUSION

The toughening mechanism of CTBN modified trifunctional epoxy resins was studied by using a scanning electron microscope. The results obtained are as follows:

1. The CTBN modified trifunctional epoxy resins are composite materials, consisting of a rigid epoxy resin matrix and a rubbery disperse phase.
2. For the case of 20% CTBN, the rubber particles have a dual-phase structure, containing an appropriate amount of epoxy resin particles, along with the best impact and shear properties.
3. The toughening mechanism was discussed mainly in terms of the secondary microcrack initiation and propagation during or before propagation of the primary cracks. Several important models of the secondary microcrack formation were also discussed in more detail.

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