

STRUCTURES AND PROPERTIES OF A RUBBER-EPOXY RESIN DUAL-PHASE SYSTEM

W.F. YANG and S. LI

Department of High Polymer Materials, Harbin Institute of Technology, Harbin (China)

Received July 17, 1986; accepted August 25, 1986

ABSTRACT

The microstructures and the properties of a CTBN rubber toughened trifunctional glycidic ester (TGE) epoxy resin dual-phase system were studied. The SEM micrographs show that the CTBN rubber-modified TGE epoxy resins are composite materials consisting of a continuous phase of epoxy resins and a CTBN rubbery disperse phase. For the case of 120 °C pre-reacted 20% CTBN modified epoxy resins, the rubber particles have a dual-phase structure, containing an appropriate amount of epoxy resin particles, along with the best combination of strength and toughness.

INTRODUCTION

Rubber-modified epoxy resins constitute an important class of adhesives used especially in the aeronautical and cosmonautical industries. They are characterized 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 and the toughening mechanism of rubber-modified epoxy resins [1-6]. However, very few works have been published in the literature concerning the effect of structures of the rubber particles on the mechanical properties in the rubber-epoxy resin system.

This paper deals with the morphologies of the fracture surface and the effect of pre-reaction temperature on the structures and properties in carbonyl terminated butadiene-acrylonitrile (CTBN) rubber toughened trifunctional glycidic ester (TGE) 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 TGE epoxy resin, CTBN rubber, acid anhydride and 2-ethyl-4-methyl imidazole. The shear strength and the uneven pull strength of the cohesion layer were determined with an Instron-type tensile machine operated at three temperatures, *i.e.*, room temperature, 120°C and 150°C. The uneven pull strength is considered as the combination measurement of strength and toughness of the cohesion layer. The shape of the uneven pull specimens is shown in Fig.1.

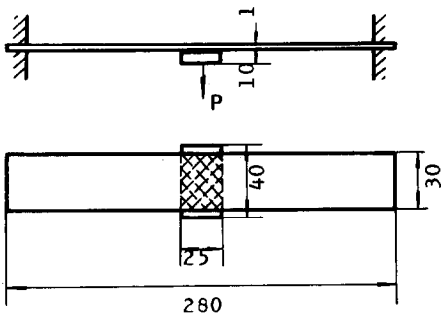


Fig.1. Uneven pull specimen.

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

Figures 2 and 3 show the effect of the CTBN content on the shear strength and the uneven pull strength of the cohesion layer. As shown in Fig.2, when the testing temperature is relatively lower (room temperature), the shear strength increases on increasing the CTBN content from 0% to 20%, and when the testing temperature is relatively higher (120°C and 150°C), the shear strength almost remains constant, indicating that the shear strength changes little with CTBN content. As shown in Fig.3, the uneven pull strength greatly increases on increasing the CTBN content from 0% to 20%.

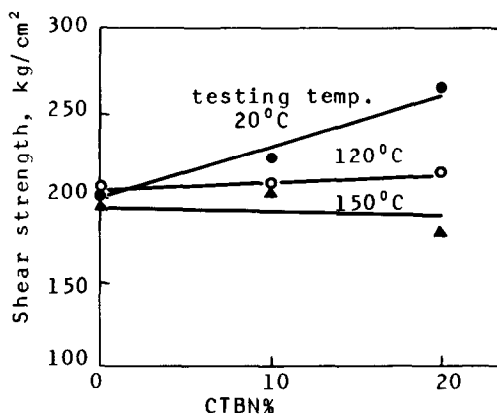


Fig.2. Influence of the CTBN content on shear strength.

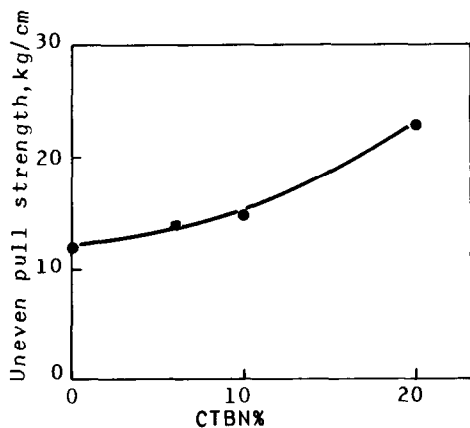


Fig.3. Influence of the CTBN content on uneven pull strength.

Figure 4 shows the effect of testing temperature on the shear strength of the cohesion layer. As shown in Fig.4, when the CTBN content is relatively higher (20%), the shear strength greatly decreases on increasing the testing temperature from room temperature to 150°C, and when the CTBN content is relatively lower (0%), the shear strengths almost remain constant, indicating that the shear strength changes little with testing temperature from room temperature to 150°C.

Figures 5 and 6 show the effect of the pre-reaction temperature on the shear strength and the uneven pull strength of the cohesion layer. It can be seen that the shear strength and the uneven pull strength increase on increasing the pre-reaction temperature from room temperature to 120°C. There is a maximum at 120°C, after which

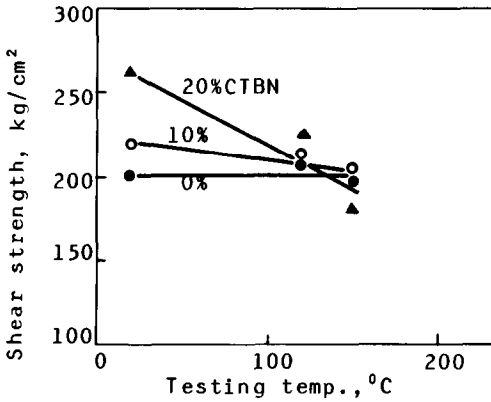


Fig.4. Influence of testing temperature on shear strength.

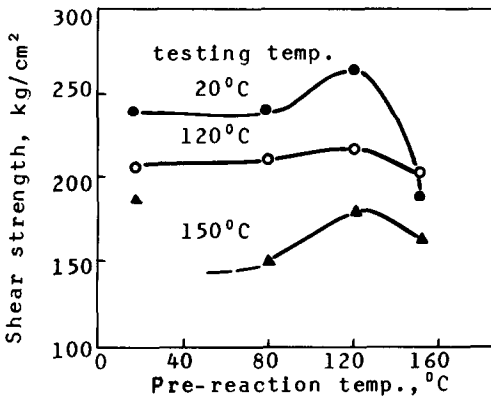


Fig.5. Influence of pre-reaction temperature on shear strength.

the shear strength and the uneven pull strength decrease. Therefore, it can be considered that the optimum pre-reaction temperature is 120°C.

Figure 7 shows the fracture surfaces of impact specimens with different CTBN contents. As shown in Fig.7, the rubber-modified TGE 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 disperse phase. The higher the rubber content, the greater the rubber particle size.

As shown in Fig.7a, for the case of 0% CTBN, the fracture surface appears as a typical brittle fracture pattern which is extremely

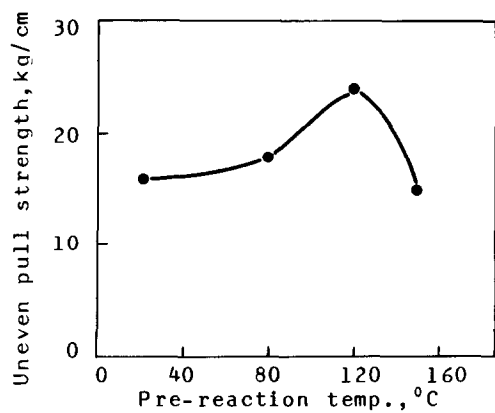


Fig.6. Influence of pre-reaction temperature on uneven pull strength.

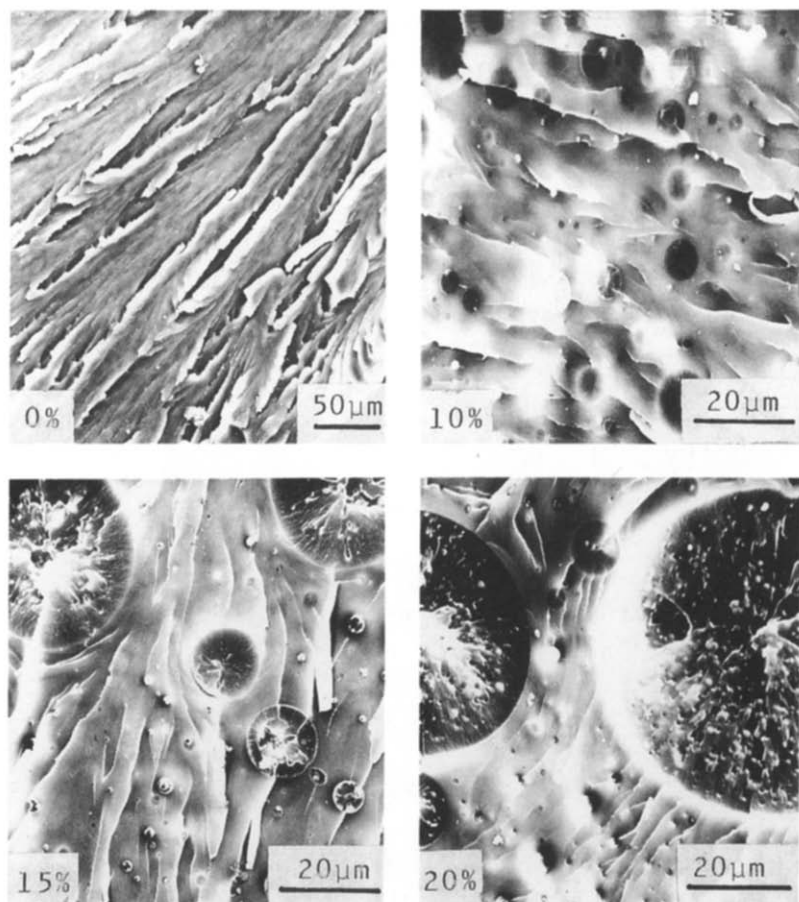


Fig.7. SEM fractographs of impact samples containing 0, 10, 15 and 20% CTBN, respectively.

similar to the brittle river pattern found in the cleavage fracture of metals. As shown in Fig.7c, for the case of 15% 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 propagation is terminated when a large rubber particle is encountered. As shown in Fig.7d, 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. This dual-phase structure is called a 'salami structure' [6]. As shown in Figs.7c, 7d and Fig.8, a great number of microcracks in the sub-inclusion structures will be initiated at rubber/epoxy resin interfaces during impact testing. It may be that the interface binding strength exerts a tremendous influence on the toughness of the dual-phase system during fracture. Consequently, when a great number of microcracks in the sub-inclusion structures will be initiated at rubber/epoxy resin interfaces during impact testing, 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 uneven pull testing or shear tests.

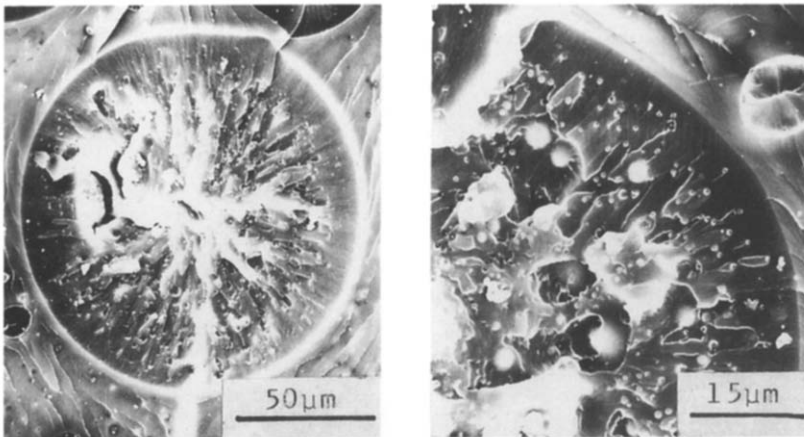


Fig.8. SEM fractographs of 20% CTBN impact sample showing the typical sub-inclusion structure of a rubber particle with 'salami structure'.

Figure 9 shows the fracture surfaces of impact specimens treated upon different pre-reaction temperatures. As shown in Fig.9a, for the case of room temperature, the rubber particle size is relatively small, and the sub-inclusion structures are not obtained. As shown in Fig.9c, for the case of 120°C, the rubber particle size is relatively large, and the 'salami structures' are obtained, that is to say, the rubber particles have a dual-phase structure, containing the appropriate amount of epoxy resin particles.

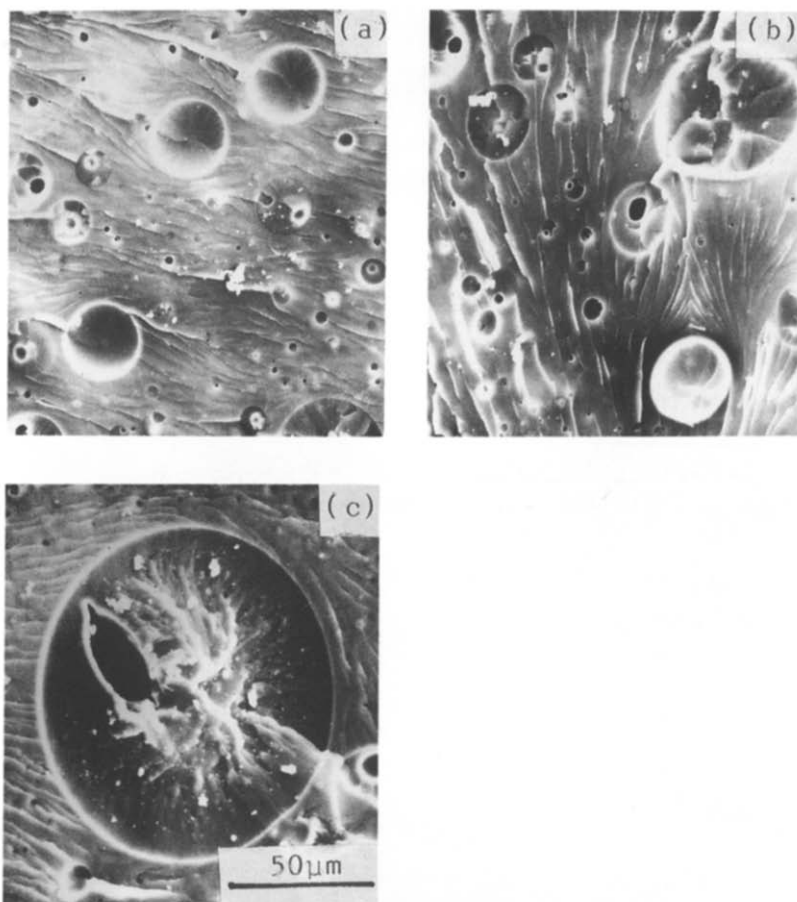


Fig.9. SEM fractographs of 20% CTBN impact samples treated upon different pre-reaction temperatures. a-room temperature, b-80°C, c-120°C.

The toughening mechanism was discussed in literature [6] mainly in terms of the secondary microcrack initiation and propagation during or before propagation of the primary crack, and several important models of the secondary microcrack formation were discussed.

On Yang's assumption [6] the 'salami structure' of rubber particles can absorb a much higher strain energy before fracture, along with the best combination of strength and toughness. As shown in Figs. 7, 8 and 9, Yang's assumption is also true for the rubber-modified TGE epoxy resins.

#### SUMMARY

The microstructures and properties of a rubber-epoxy resin dual-phase system were studied. The results obtained are as follows:

1. The CTBN modified TGE epoxy resins are composite materials, consisting of a rigid epoxy resin matrix and a rubbery disperse phase.
2. The optimum pre-reaction temperature is 120°C. For the case of 120°C pre-reacted 20% CTBN modified epoxy resins, the rubber particles have a dual-phase structure, containing an appropriate amount of epoxy resin particles, along with the best combination of strength and toughness.

#### REFERENCES

- 1 E.H. Rowe, A.R. Siebert and R.S. Dreke, Modern Plastics, 8 (1970) 110.
- 2 R.S. Dreke and J.M. Lipiec, Design and Process, 15 (1975) 14.
- 3 N.C. Paul, Adhesion, 3 (1979) 65.
- 4 C.B. Bucknall, Toughened Plastics, 1977, 188.
- 5 R.E. Lavengood, L. Nicolais and M. Narkis, J. Appl. Polymer Sci., 17 (1973) 1173.
- 6 W.F. Yang and Y.Z. We, Mater. Chem. Phy., 15 (1986) 505.