工程塑膠增韌環氧樹脂之破壞特性
THE FRACTURE PROPERTIES OF THERMOPLASTICS TOUGHENED EPOXY RESIN

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摘 要

本文主要探討工程塑膠PC, Phenoxy及blocked PU增韌環氧樹脂之破壞機構當改變工程塑膠含量時，會呈現不同之裂縫圖形；且增韌的程度受基材與環氧樹脂的相容性，形成之粒子大小及基材的特性等所影響。從動態實驗中，我們發現在環氧樹脂中含有10phr的blocked PU或10phr的Phenoxy展現較佳的增韌效果，而PC增韌環氧樹脂則無顯著的變化。從靜態實驗中，我們也觀察到15phr的blocked PU或10phr的PC展現較佳的增韌結果，但Phenoxy增韌環氧樹脂則無顯著的影響，此外，我們也藉SEM照片觀察增韌機構中的破壞形態。

ABSTRACT

The fracture properties of toughenes epoxy by Phenoxy, Polycarbonate and blocked NCO- terminated PU prepolymer were studied. The toughening mechanism of the system was investigated. Different crack patterns were observed on specimens of different plastic contents. The toughness of a toughened material is affected by the amount of particles, the miscibility of particle and matrix material, and the property of matrix material. Under dynamic condition, the epoxy resin containing 10 phr blocked NCO- terminated PU prepolymer or 10 phr Phenoxy showed good toughness. On the other hand, the effect of adding Polycarbonate on toughness of epoxy resin is insignificant. Under quasi-static condition, the best toughening result of resin by adding blocked NCO-terminated PU prepolymer and Polycarbonate was obtained at 15 phr and 10 phr separately, and the toughening effect is insignificant by adding Phenoxy in epoxy. The toughening mechanism was investigated by examining the fracture morphology with SEM photographs.
KEYWORDS: Epoxy, Toughening mechanism, fracture properties

INTRODUCTION

Toughened epoxy resins are widely studied, and several toughening mechanism have been proposed(1-8). The microstructure of toughened epoxy can be divided into homogenous and heterogeneous, according to the miscibility between resin and toughening material. In general, a heterogeneous microstucture may result in a better toughness, because the particles can impeded the propagation of crack(2).

Liquid rubber was used to toughen bi-functional epoxy resin, such as DGEBA type epoxy(1-2). However, when it was used in tri-functional or tetra-functional epoxy resin system, the result is not promised, since the crosslinking density of resin is too high(3). Thermoplastics was used to toughen these systems(4-8). In this study Phenoxy, Polycarbonate and

Blocked NCO-terminated PU prepolymer were used to modify the Epoxy/DICY system. The toughness of the modified materials and the toughening mechanism were studied.

EXPERIMENTAL

Materials :

The epoxy resin used in this study was DER 331, a DGEBA type epoxy with and average M.W. of 380 g/mole, produced by Dow Chemical Company, U.S.A. Dicyandiamide (DICY) was used as curing agent in this study.The accelerator was 3-pheny1-1, 1-dimethylurea (PMU). The materials used to toughen epoxy were Phenoxy (Mn=30000 g/mole), produced by the Union Carbide Company, U.S.A.; Polycarbonate (Mn=28000 g/mole), Lexan^R, supplied by the General Electric Company, U.S.A. and Blocked NCO-terminated Ployurethane prepolymer (BL1100, Mn-4300), produced by the Bayer Chemical Company, Germany.

Mechanical properties:

The ASTM D256-88 Izod impact test was conducted with an impact tester (type 43-01), manufactured by the Testing Machines Inc. K_{IC} test of three point bend type specimen with span-to-width ratio of 4 was carried according to ASTM E399−83. A razor blade was used to incise a sharp crack, and a tester (type 4201), produced by the Instron Company was used to test specimens with crosshead speed of 0.5 mm/min. The K_{IC} value is calculated by the equation(11):

$$K_{IC}= (P_QS/BW^{3/2}) \cdot f(a/W)$$

where:

$$f(a/W)=\frac{3(a/W)^{1/2}\,[\,1.99-(a/W)(1-a/W)(2.15)}{2(1+2a/W)(1-a/W)^{3/2}}$$

$$-3.93a/W+2.7a^2/W^2)\,]$$

PQ : maximum load in (kN) for our experiment

B : specimen thickness in (cm)

S : span distance in (cm)

W : specimen width in (cm)

a : crack length in (cm)

Morphology :

A scanning electronic microscope from the JEOL Company (type JSM-5300) was used to study the fracture surfaces.

RESULTS AND DISCUSSION

I . Mechanical properties test:

Figures 1 and 2 show the Izod impact toughness and the critical stress intensity factor K_{IC} of materials with different contents of toughening agent. Blocked-PU of 10 phr and 15 phr shows the most significant effect on impact toughness and on K_{IC}. Phenoxy of 10 phr shows larger effect on impact toughness, but only little effect on K_{IC}. PC shows insignificant effect on impact toughness, and higher data of 10 phr on K_{IC} Comparing with Phenoxy and PC, blocked-PU shows better effect among these toughening agents on both impact toughness and K_{IC}.

II . Tg test

Table 1. shows the glass transition temperature of materials of different contents of toughening agent. It shows higher Tg of 10 phr

PU/Epoxy system than pure epoxy, which implies that the crosslinking density of 10 phr PU/Epoxy system is higher than pure epoxy and 20 phr blocked-PU shows lower Tg than pure epoxy for its softer backbone. The Tg of Phenoxy and PC decrease as the contents of toughening agent increased.

III. Morphological properties :

1. Epoxy resin :

Figures 3A and 3B are the SEM photographs of Izod impact specimen of pure epoxy resin. Clear river patterns were observed(9). It occurs when crack propagates to different planes, and joins together by secondary cleavage matrix or by shear matrix to minimize surface energy by exposing a minimum of extra free surface. It shows that the specimen broken under cleavage fracture(9).

2. Phenoxy toughen epoxy resin :

Figures 4A, 4B and 5A, 5B are the SEM photograghs of Izod impact fracture surface of 10 phr and 20 phr phenoxy toughen epoxy resin, respectively. Figures 4A and 5A show that the particles interfere crack propagation, and new crack formed, propagates to the back of particles. The paths on the back of particles show that crack propagates to different planes after interferred by particles, and it consumes more energy to propagate for more free surface. Figures 4B and 5B show clearly that particles were torn into pieces after impact test. It means that cohesive force between phenoxy particles and epoxy resin are rather good, meanwhile, it also consumes energy to tear particles. One can observe that Figure 4A shows more particles than in Figure 5A, while Figure 4A shows more river pattern than in Figure 5A. It means that the crosslinking density of 10 phr Phenoxy/Epoxy system is higher. It can also be confirmed by lower Tg of 20 phr Phenoxy/Epoxy system.

3. Polycarbonate toughen epoxy resin:

Figures 6A, 6B and 7A, 7B are the SEM photographs of Izod impact fracture surface of 10 phr and 20 phr polycarbonate toughen epoxy resin, respectively. Figures 6A and 7A show that the crack paths are shorter in length comparing with those showed in Figures 4A and 5A, some of them even have no crack path. It is attribute to the existance of polycarbonate which softens the matrix, hence the crack yielding matrix behind particles, and shows shorter crack paths. The bonding between polycarbonate nad epoxy is poor, hence most of the particles were pulled out completely when damage occurs, as shown in Figures 6B and 7B.Comparing Figures 6A 7A, Figure 7A shows shorter crack paths than in Figure 6A,it indicates that 20 phr PC toughen epoxy exhibits soft matrix, and lower crosslinking density. It can be confirmed again by Tg shifts to lower temperature as the PC content increased.

4. Polyurethane toughen epoxy resin:

Figures 8A, 8B and 9A, 9B, 10A are the SEM photographs of Izod impact fracture surface of 10 phr and 20 phr blocked NCO- terminated PU prepolymer toughen epoxy resin, respectively. Figures 8A and 9A show shorter crack paths after interferred by particles, which indicated that PU can soften epoxy matrix and it may conclude that three kinds of toughen mechanism of PU/Epoxy system existed. The first is that PU particles were pulled out completely. The second is the PU particles wee torn into pieces, as show in Figures 8B and

9B. The third mechanism shows that the crack by-pass the particles. The effect on the interfere crack propagation is larger than the other kinds of mechanism, since the crack lines around are bold and branching, as can be seen in Figure 10A.

5. comparison among Phenoxy, PC and PU:

PC/Epoxy system shows lower toughness under dynamic condition. It means that poor impact toughness may be caused by poor bonding between particles and matrix. Phenoxy/Epoxy system shows lower data in K_{IC} test, indicates that the softness of matrix exhibit larger dffect under quasi-static condition. The measurement of Tg gives a coincident conclusion. Comparing PU/Epoxy system with other system, better bonding between particles and matrix was observed, a softer backbone, and the by-pass toughen mechanism was also observed. Hence,PU/Epoxy system shows the best toughenss among them under both dynamic and quasi-static condition.

CONCLUSIONS

1. The toughening effect of adding thermoplastics in epoxy shows the most significance by the incorporation of PU. This is consistent with the observation of fracture morphology which shows that the cohesion of the PU particle matrix interface is better than PC or Phenoxy particles.
2. The PC particles are easily pulled out from the matrix in crack propagation, which count for the low toughening ability.
3. The lowering of Tg is most significant by adding PC which implies a lower crosslinking density and thus a soften matrix. This is possibly the reason of its higher K_{IC} value than the material modified by Phenoxy.

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ture mechanics", 4th edition, Martinus Nijhoff Publishers, 1986.
10.ASTM E399-83.
11.ASTM D256-88.

Table.1 Effect of plastics content on the glass transition temperature

Tg(℃) (pure epoxy 127.8℃)		
	10phr	20phr
Phenoxy	126.3	115.9
PC	114.1	101.7
PU	129.6	122.8

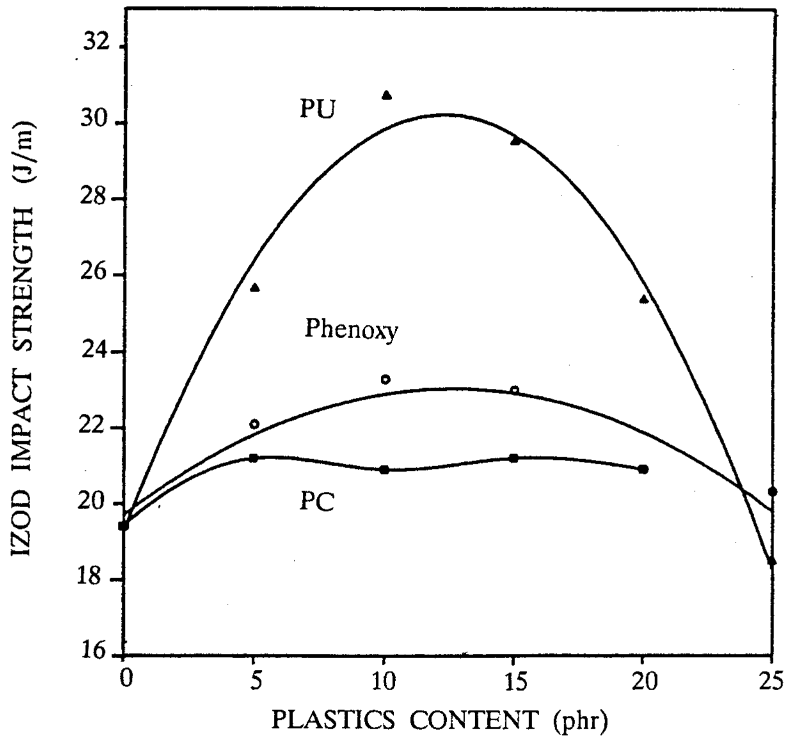

Fig.1 Izod impact strength (J/m) versus different contents of toughen agent (phr)

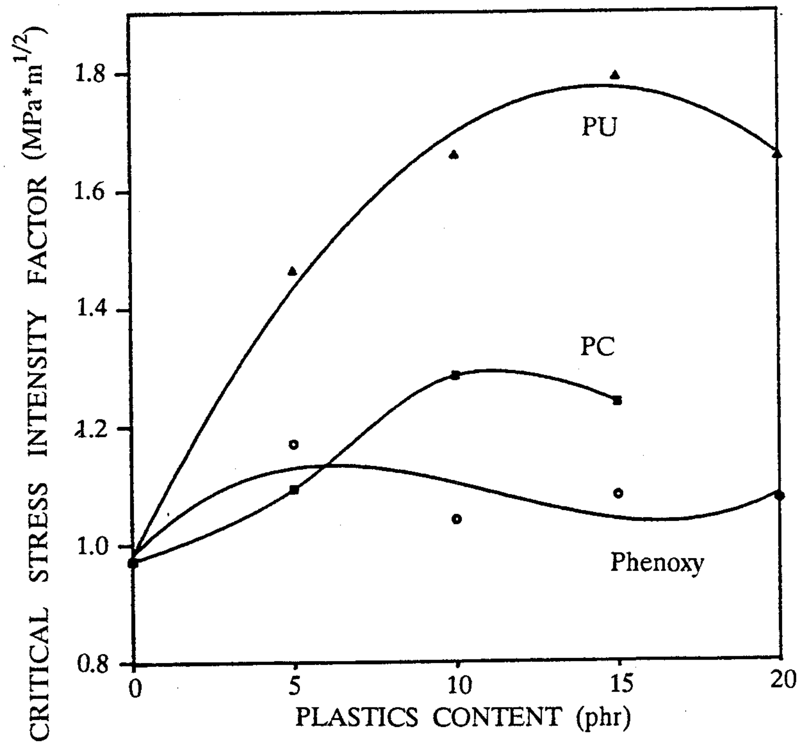

Fig.2 Critical stress intensity factor K_{IC} (MPa-$m^{1/2}$) versus different contents of toughen agent (phr)

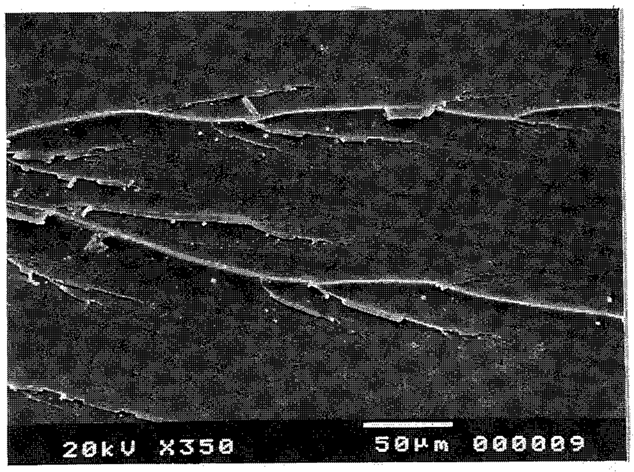

Fig.3A SEM photograph of pure Epoxy.(350X)

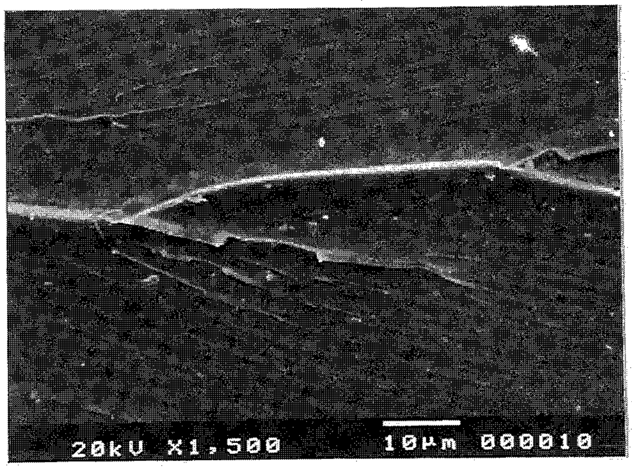

Fig.3B SEM photograph of pure Epoxy.(1500X)

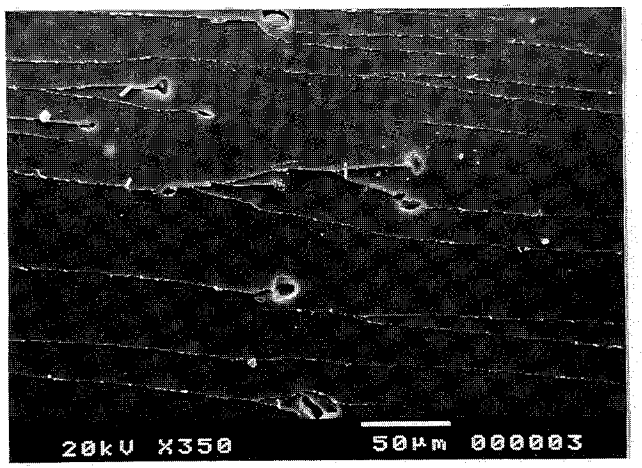

Fig.4A SEM photograph of 10 phr Phenoxy toughen epoxy.(350X)

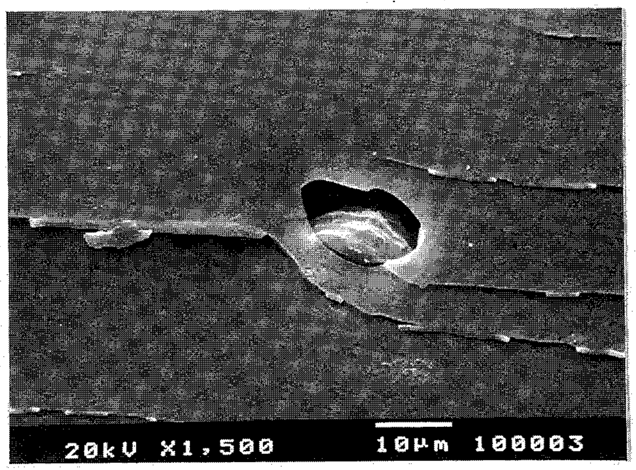

Fig.4B SEM photograph of 10 phr Phenoxy toughen epoxy.(1500X)

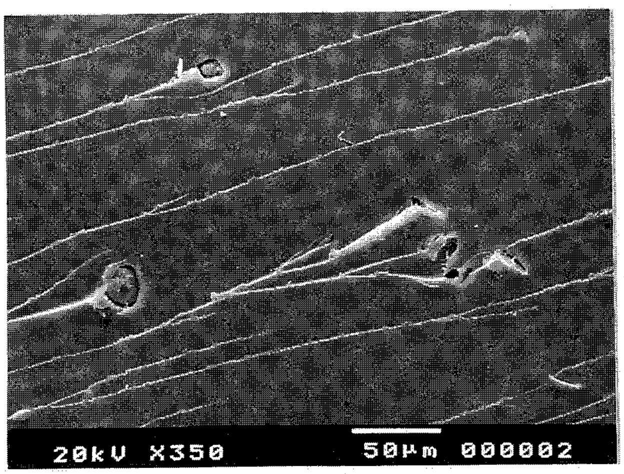

Fig.5A SEM photograph of 20 phr Phenoxy toughen epoxy.(350X)

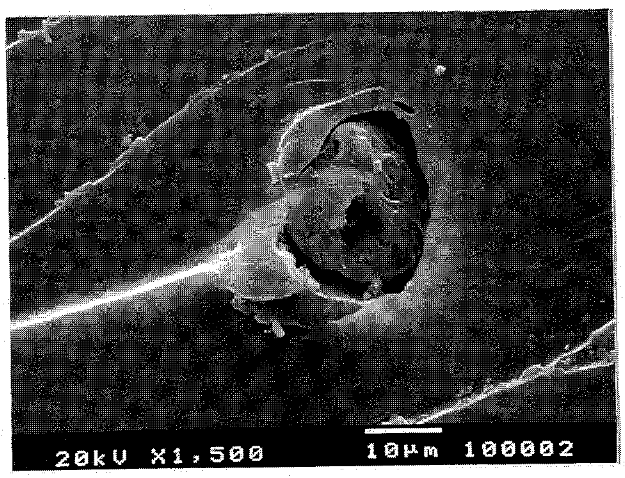

Fig.5B SEM photograph of 20 phr Phenoxy toughen epoxy.(1500X)

Fig.6A SEM photograph of 10 phr PC toughen epoxy.(350X)

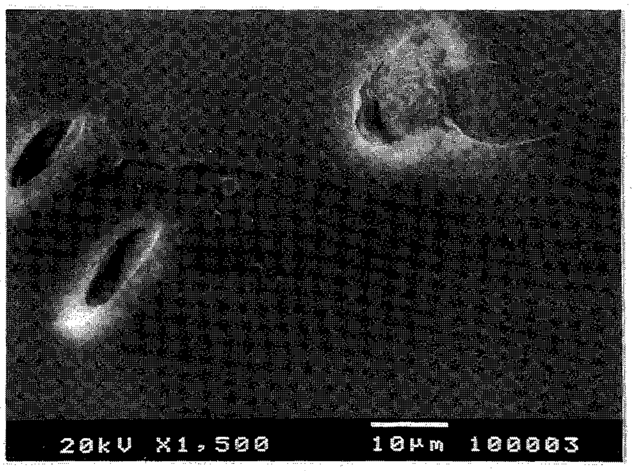

Fig.6B SEM photograph of 10 phr PC toughen epoxy.(1150X)

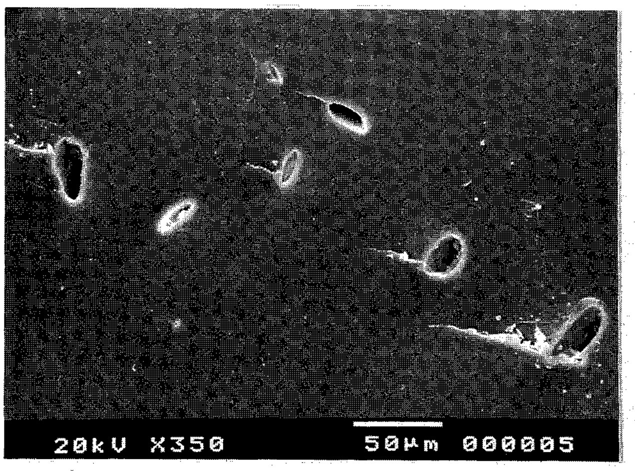

Fig.7A SEM photograph of 20 phr PC toughen epoxy.(350X)

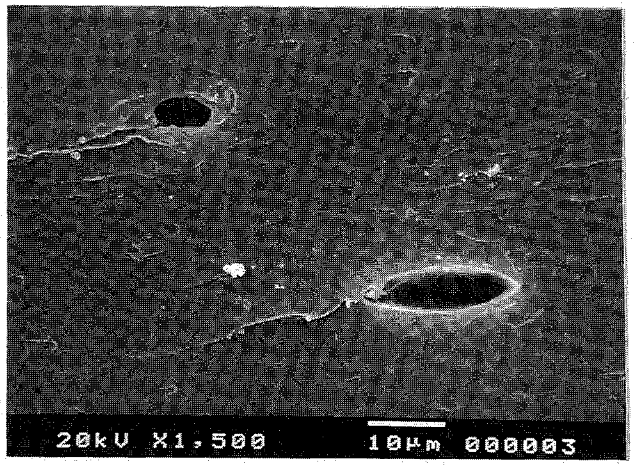

Fig.7B SEM photograph of 20 phr PC toughen epoxy.(1150X)

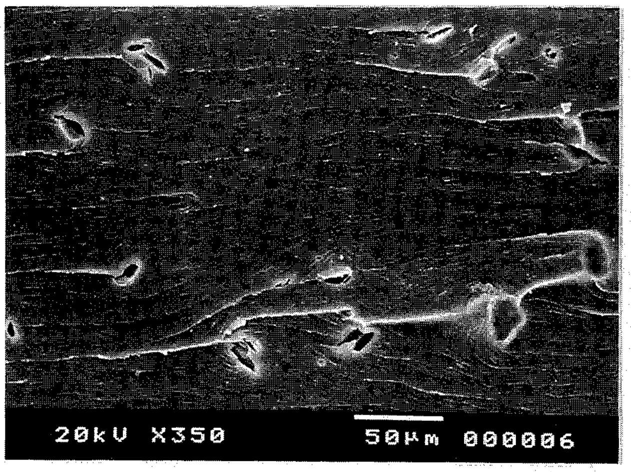

Fig.8A SEM photograph of 10 phr PU toughen epoxy.(350X)

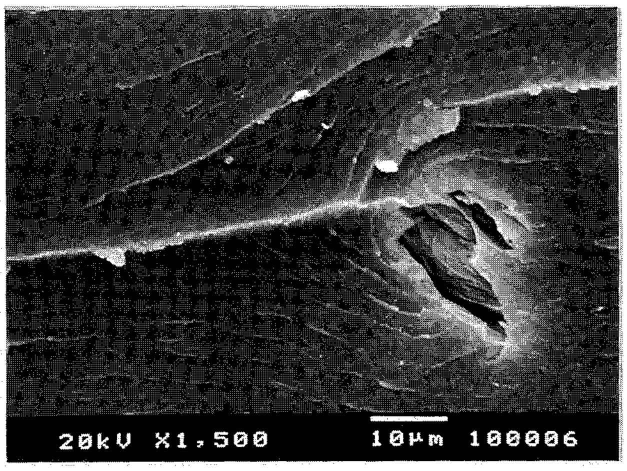

Fig.8B SEM photograph of 10 phr PU toughen epoxy.(1150X)

Fig.9A SEM photograph of 20 phr PU toughen epoxy.(350X)

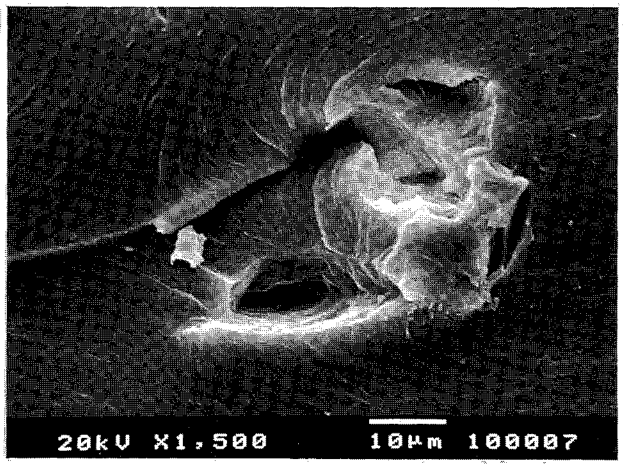

Fig.9B SEM photograph of 20 phr PU toughen epoxy.(1150X)

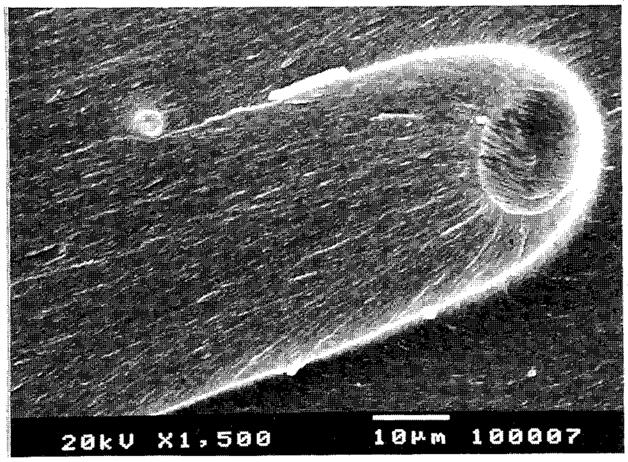

Fig.10A SEM photograph of the by-pass toughening mechanism in PU/Epoxy system.(1500X)