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# Compositional influence on toughness of structural acrylic adhesives

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The fracture behaviour and toughness of modified acrylic adhesives, based on mixtures of various acrylic monomers and rubbers polymerized by a radical mechanism have been investigated. The influence of the matrix and rubber composition on bulk morphology and mechanical properties is analysed by means of transmission and scanning electron microscopy, and dynamic–mechanical measurements. Both microtexture of the material and resin–rubber compatibility have been found to significantly influence the fracture behaviour in tension–impact tests.

## 1. Introduction

Toughness denotes the amount of total energy absorbed by a material before the initiation of a destructive fracture [1]. The transition from a maximum (ductile failure) to a minimum (brittle failure) fracture energy may be induced by an increase in the testing temperature which enhances the extensibility of the polymer segments. Fracture energy, however, is also influenced by the molecular weight distribution and the polymer structure morphology, such as the presence of side groups or polymer backbone flexibility. In the case of thermosetting polymers, a particularly relevant additional parameter is the distribution and density of the cross-links in the three-dimensional network. A non-homogeneous distribution of cross-links is usually associated with lower values of the fracture energy. Nonetheless, the addition of a rubber to brittle polymers, such as acrylics, has been described to enhance fracture resistance. As shown in a previous work [2], the added rubber separates in a second phase which is responsible for increased toughness [3]. The toughening process may be briefly described as follows. Rubber particles act as initiation points for the production of high-energy absorbing crazes, resulting in a considerable increase of the fracture resistance. A multimodal size distribution of such particles has been reported to improve toughness more than monodispersity [4]. Generally, the smaller particles preferentially induce failure by shear-band formation while the bigger ones favour localized crazing. The highest levels of toughening have been reported to occur by a combination of crazing and shear yielding [4] associated with the presence of bimodal size distribution. The visco-elastic properties of the rubber phase have also been recognized to contribute significantly to the toughening process. The resin–rubber compatibility, however, seems to be the key point in the formulation of a suitable tough system even in the absence of apparent phase separation.

Although highly cross-linked materials present interesting properties such as high modulus and low creep even at high temperatures, they are rather brittle and characterized by poor resistance to crack growth. Different methods proposed to improve their toughness, among them the addition of a rubber, so creating a biphasic system, have achieved great success. Some principal mechanisms have been invoked to explain the toughness increase.

1. The crack stopping capability of the dispersed rubber particles [5, 6]. Fracture, in fact, is considered to develop freely until it meets a rubber particle, which stops the crack, and then should first elongate and eventually tear before it can grow further.
2. Crazing. The matrix under strain develops a multitude of microcrazes which are localized around the larger particles (1 to 2 μm) [4, 7, 8].
3. Yielding. The rubber particles, especially those smaller than 0.5 μm, act as strain centres leading to a generalized yielding of the glassy matrix.

The latter failure mechanism does not increase significantly the toughness unless coupled with crazing. This event occurs when a bimodal distribution of the inclusion sizes is present [7]. Toughening may depend on the resin compatibility with the dispersed rubber rather than exclusively on the system texture morphology [9], because it has been observed to occur even

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when neither evident phase separation nor plasticization were present. This may be the case of interpenetrating networks (IPN) or semi-interpenetrating networks (SIPN). In some cases, even when the rubber–resin compatibility is low, a clear phase separation may not be detected, especially if the matrix polymerization rate is high and gelation readily occurs. At a molecular level, however, the two components tend, in any case, to form independent and not interacting networks. This interpretation explains the absence of plasticization.

In this work the fracture behaviour and morphology of adhesive systems, obtained from the same matrix resin (cyclohexylmethacrylate monomer) toughened with different elastomers, and from different acrylic monomers toughened with the same rubber (chlorosulphonated polyethylene) were examined. The tension–impact tests and the observation of the fracture surface morphologies could be useful to evince the failure mechanisms of the adhesive systems and, hence, the related micro-texture.

## 2. Experimental procedure

### 2.1. Materials

Adhesive formulations were obtained from acrylic monomers, such as cyclohexylmethacrylate (CEMA, Fluka) for systems A, B and C, ethylmethacrylate (EMA, Fluka) for system D, *n*-butylmethacrylate (*n*-BMA, Fluka) for system E, isobutylmethacrylate (IBMA, Fluka) for system F, methylmethacrylate (MMA, Fluka) for system G, and tetrahydrofurfurylmethacrylate (THFMA, Sartomer) for system H. The methacrylic moiety is cross-linked with 5% by weight of ethyleneglycoldimethacrylate (EGDMA, Fluka), and activated by 0·5% cumene hydroperoxide radical initiator (CHP, Fluka). The elastomeric moieties were 20% butadiene–acrylonitrile rubber (Elaprim S3360, Enichem) for system B, 30% fluorinated rubber (Tecnoflon NML, Montefluos) for system C, and 30% chlorosulphonated polyethylene (Hypalon 20, DuPont) for the other systems. A mixture of condensation products between butanal and anyline (Vamax 808, DuPont) was used as accelerator.

### 2.2. Tension–impact tests

A tension–impact tester was used to evaluate the energy required to fracture the specimens. The bulk adhesive samples were prepared by mixing the acrylic paste and accelerator in the proportion 10:1 and polymerizing the system for (a) 24 h at room temperature, (b) 24 h at 6 °C, and (c) 3 h at 50 °C. A post-cure of 1 h at 100 °C was also carried out in order to ensure complete polymerization. Tests were carried out according to ASTM D1822 by using a Zwick pendulum with a modified hammer operating at an impact rate of 0.68 m sec$^{-1}$.

### 2.3. Transmission electron microscopy (TEM)

The bulk adhesives polymerized at room temperature were examined by TEM. Ultrathin sections of about 100 nm were cut from the hardened materials using a LKB ultramicrotome with a diamond knife. All bright-field micrographs were obtained using a 100 kV electron microscope Philips EM 300.

### 2.4. Scanning electron microscopy (SEM)

The fracture surfaces of the impact tested samples were examined using a Cambridge Stereoscan 604 scanning electron microscope.

### 2.5. Dynamic–mechanical analysis

The dynamic–mechanical measurements were carried out on a freely oscillating Brabender torsion pendulum (Torsion Automat). Measurements were performed in a nitrogen atmosphere from −180 to 200 °C at a heating rate of 1 °C min$^{-1}$ according to the standard method ISO-R537 B.

## 3. Results and discussion

Fracture energies calculated from the tension–impact tests of cyclohexylmethacrylate toughened with different elastomers and polymerized in various conditions are reported in Table I. Even if data suffer for some dispersion, some considerations are straightforward. The fracture energy value is low for the system toughened with the chlorosulphonated polyethylene rubber and cured with cycle a, while the three systems behave similarly when prepared at 6 and 50 °C. The bulk texture morphologies of these systems were presented in a previous work [2]. The fracture energies cannot be simply related to the bulk morphologies because they do not seem to depend on the resin–rubber compatibility rather than on a well-defined phase separation. The fracture behaviour of specimens prepared at room temperature, the most important considering a practical application, has been examined.

Unmodified and modified epoxies were reported to fail as a result of three basic types of crack growth [10]: (1) ductile–stable; (2) brittle–unstable; (3) brittle–stable. Fig. 1 shows the force–displacement diagrams obtained from the tension–impact measurements of our systems. Considering the CEMA-based systems A, B and C, the character of the fracture was found to be a combination of brittle–unstable and brittle–stable failure. The fracture surfaces of these systems were examined by SEM. The Hypalon rubber addition (system A) does not produce a significant increase of the fracture energy as indicated by the

TABLE I Influence of elastomer nature and cure cycle on fracture energies

| Material | Fracture energy, $U_f$ (J cm$^{-2}$) | | |
|---|---|---|---|
| | Cure cycle a | Cure cycle b | Cure cycle c |
| A | 0.12 ± 0.04 | 0.20 ± 0.04 | 0.15 ± 0.03 |
| B | 0.26 ± 0.06 | 0.06 ± 0.01 | 0.14 ± 0.04 |
| C | 0.18 ± 0.07 | 0.12 ± 0.02 | 0.08 ± 0.03 |

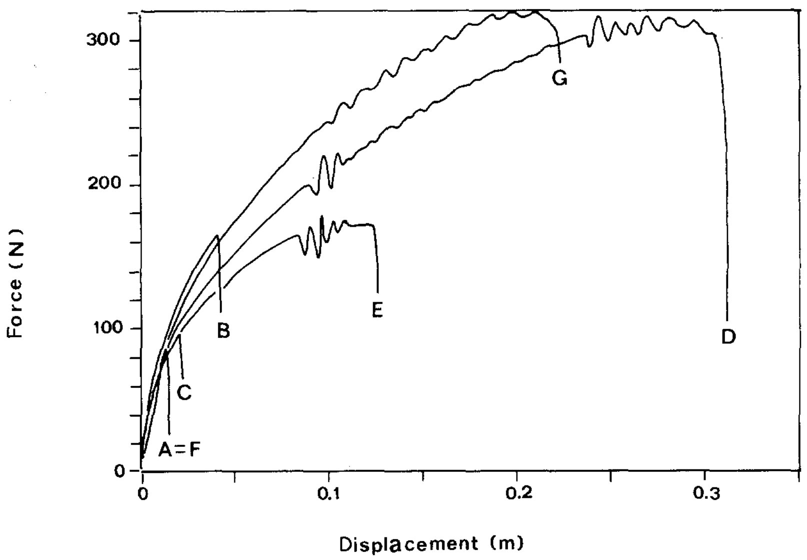

*Figure 1* Load–displacement curves obtained from impact–tension tests, for specimens of materials A to G.

impact–tensile diagram of Fig. 1 and the corresponding scanning electron micrograph of the fracture surface (Fig. 2a and b). A characteristic large mirror-like region indicates the location of the initiation point of the brittle fracture which propagates in brittle–unstable and in brittle–stable modes producing a rough region. A further magnification shows the presence of the brittle–unstable river markings often observed also in embrittled aged polycarbonate [11]. The fracture surface in Fig. 3a of the slightly tougher material B, according to the values in Table I, containing butadiene acrylonitrile rubber, also shows a large mirror region and a rough region. Again, the magnification (Fig. 3b) shows the presence of river markings and a large number of cleavages perpendicular to the crack direction (Fig. 3c). This material probably fails more by localized craze than by yielding, leading to a fracture behaviour intermediate between ductile–stable and brittle–unstable. Along these fracture lines, however, significant localized plastic deformation, due to the localized matrix yielding, is also evident. The fracture energy, even if still low, is, in fact, higher than in the previous case.

In the fracture surface of system C (Fig. 4a), mirror-like regions are absent and a generalized yielding seems to occur. In fact, the whole surface appears rough and magnification (Fig. 4b) shows evident plastic deformation associated with the yielding. As previously discussed, the fracture generated only by the matrix yielding should not lead to a significant increase in toughness as experimentally observed.

TEM observations reported previously [2] indicated the presence of well-defined, almost monodispersed rubber particles of about 2 μm only in the case of the chlorosulphonated polyethylene rubber system A, while adhesives containing fluorinated and butadiene–acrylonitrile rubbers showed a wide distribution of smaller particles. Therefore, due to the relationship between fracture mechanism and toughening, high improvements for these systems are not expected.

The values of the fracture energy measured in the tension–impact tests shown in Fig. 1 for systems D to G are reported in Table II. Most of them are significantly higher than those previously presented. For systems D, E and G, they are about ten times higher than those prepared with CEMA, while only the fracture energy of the formulation with isobutylmethacrylate (F) is almost equivalent to the latter. The adhesive H was too brittle to be tested. TEM observations reported in Fig. 5a and d show well-defined rubber domains dispersed in a bimodal distribution with smaller particles for system D containing EMA than for system G containing MMA. The corresponding fracture energies measured are the highest in

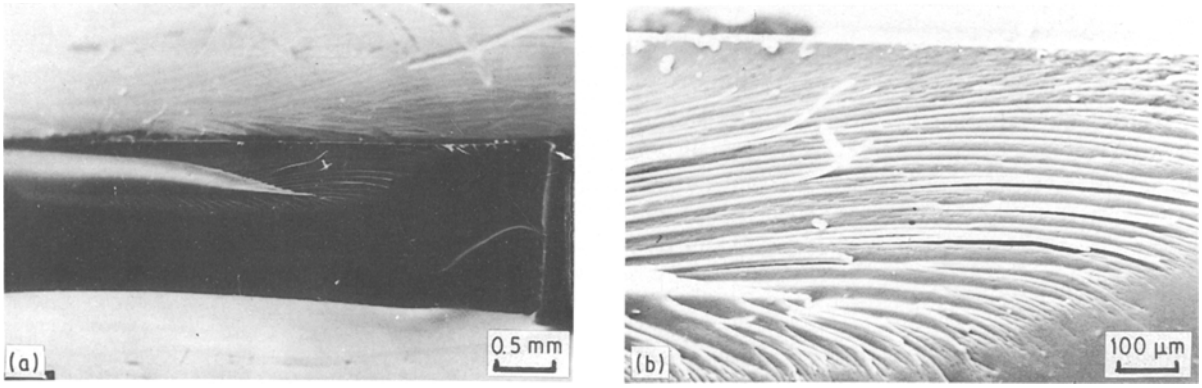

*Figure 2* Scanning electron micrographs of the fracture surface of material A: (a) the whole fracture surface; (b) higher magnification of the rough region.

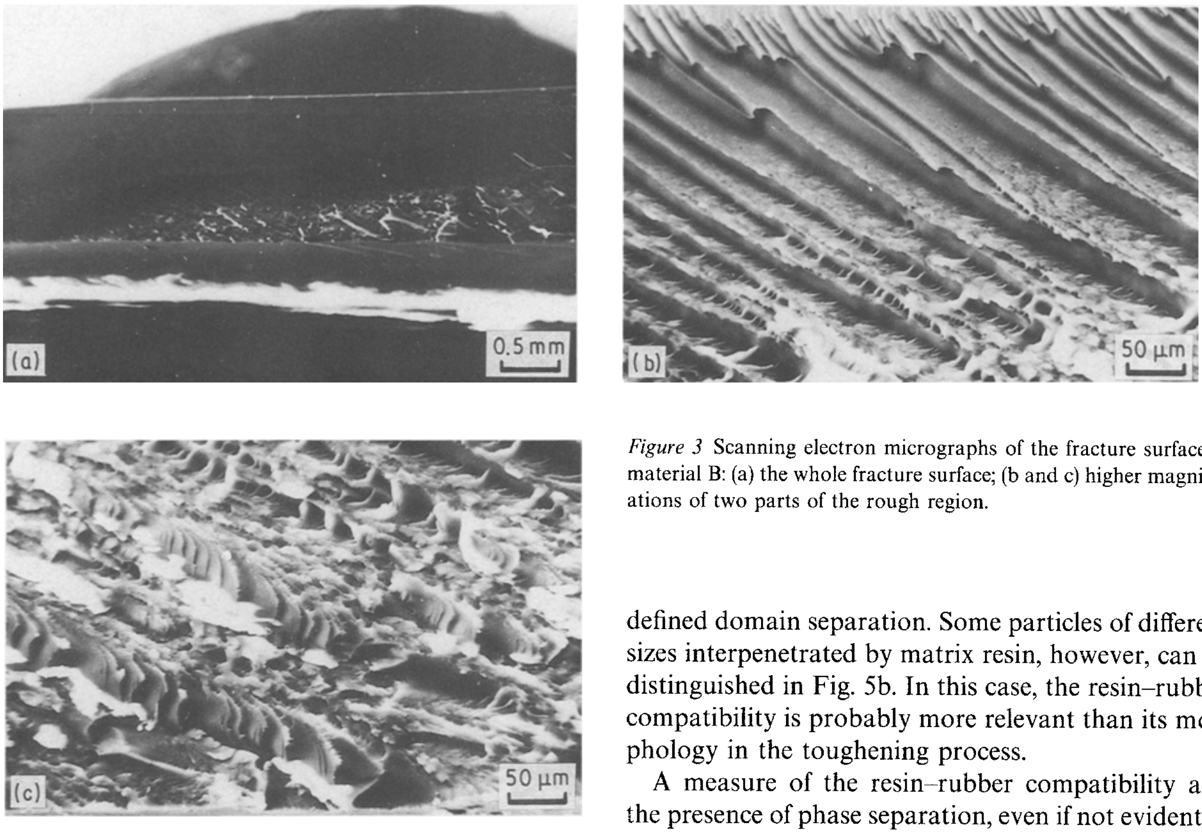

*Figure 3* Scanning electron micrographs of the fracture surface of material B: (a) the whole fracture surface; (b and c) higher magnifications of two parts of the rough region.

Table II. The hypothesis of the enhancement of fracture resistance in systems characterized by different failure modes, namely a combination of crazing and yielding, seems to be supported by the morphological observations. The multimodal particle size distribution, in fact, should favour different modes of failure. The SEM observations of the fracture surfaces of sample D tested in the tension–impact tests are reported in Fig. 6. Fracture planes are located on different levels, indicating crack branching coupled with massive yielding and crazing. The higher magnification (Fig. 6b) shows the initiation points of the fractures which generate from the crazed regions surrounding the rubber particles. The rubber particles were probably ablated during fracture propagation. Analogous results have been observed for system G (micrographs not reported).

The adhesive E, even if characterized by a high value of the fracture energy, does not present a well-defined domain separation. Some particles of different sizes interpenetrated by matrix resin, however, can be distinguished in Fig. 5b. In this case, the resin–rubber compatibility is probably more relevant than its morphology in the toughening process.

A measure of the resin–rubber compatibility and the presence of phase separation, even if not evident in the microscopy observation, can be obtained from dynamic–mechanical measurements. Fig. 7 reports the storage modulus, $G'$, and the loss factor, $\tan\delta$, of the systems toughened with the chlorosulphonated polyethylene rubber. The presence of the glass transitions (primary transitions) of the rubber and the acrylic matrix may be considered to be experimental evidence of the resin–rubber separation. Rubber-containing glassy polymers exhibit a low-temperature loss peak at the glass transition of the rubber, the magnitude of

TABLE II Influence of the nature of the methacrylic monomer on fracture energies

| Material | Fracture energy, $U_f$ (J cm$^{-2}$) |
|---|---|
| D | 2.20 ± 0.55 |
| E | 1.84 ± 0.52 |
| F | 0.16 ± 0.07 |
| G | 2.24 ± 0.31 |
| H | No results |

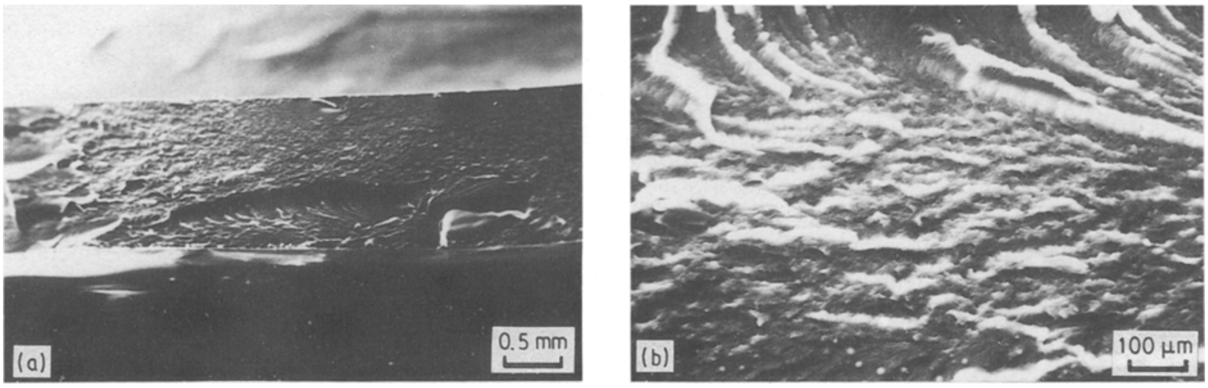

*Figure 4* Scanning electron micrographs of the fracture surface of material C: (a) the whole fracture surface; (b) higher magnification.

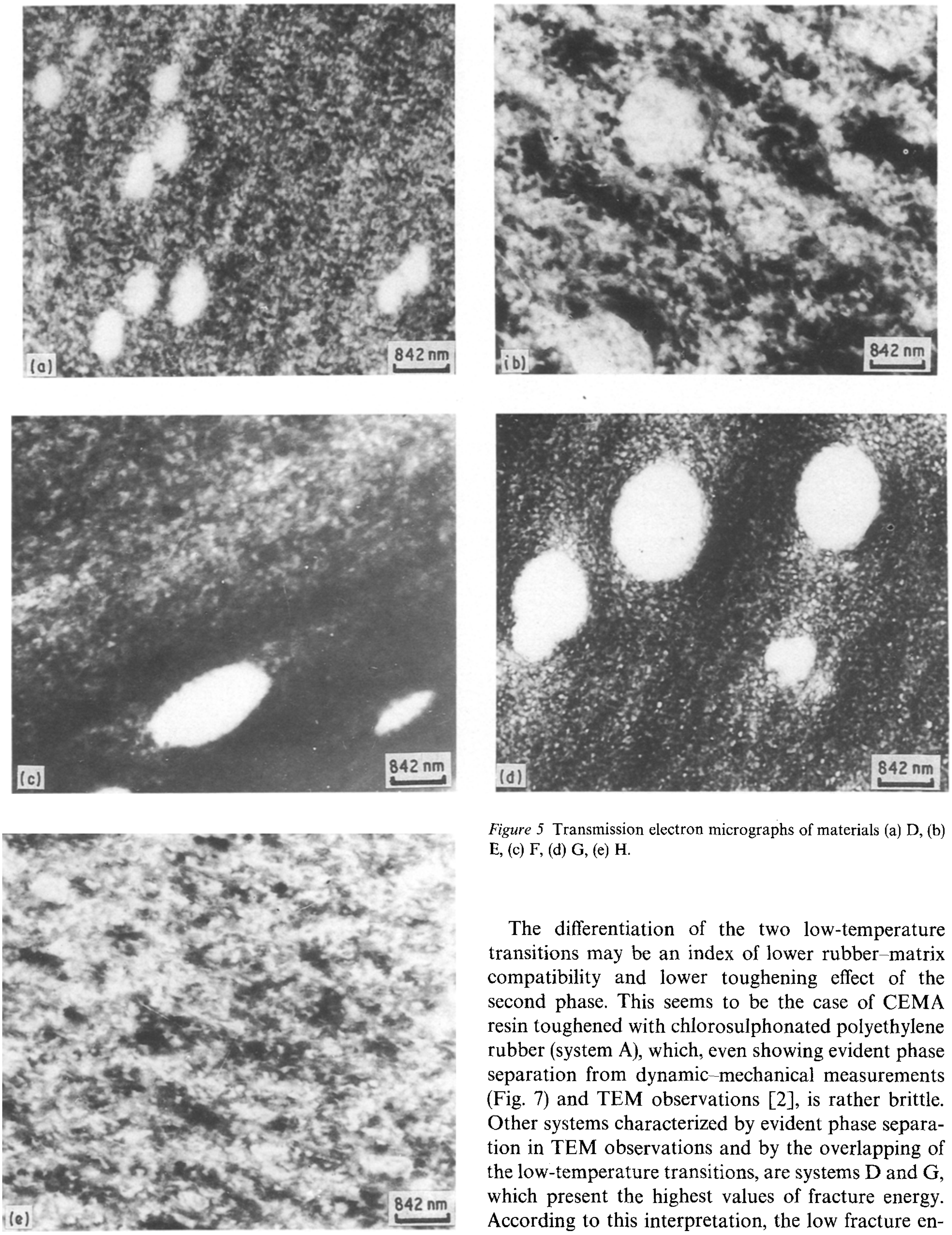

*Figure 5* Transmission electron micrographs of materials (a) D, (b) E, (c) F, (d) G, (e) H.

the peak being determined by the level of phase separation. The secondary loss process of the glassy matrix, however, may overlap the primary rubber transition. The matrix secondary transition is associated with the mobility of side groups or particular chain segments. The temperature activation of the mobility of the main rubber chains and of some of the glassy matrix side groups increases, at a molecular level, the compatibility of the two phases finally leading to an increase in toughness.

The differentiation of the two low-temperature transitions may be an index of lower rubber–matrix compatibility and lower toughening effect of the second phase. This seems to be the case of CEMA resin toughened with chlorosulphonated polyethylene rubber (system A), which, even showing evident phase separation from dynamic–mechanical measurements (Fig. 7) and TEM observations [2], is rather brittle. Other systems characterized by evident phase separation in TEM observations and by the overlapping of the low-temperature transitions, are systems D and G, which present the highest values of fracture energy. According to this interpretation, the low fracture energy of the system based on isobutylmethacrylate should be attributed more to the insufficient phase separation than to resin–rubber compatibility.

## 4. Conclusions

The morphology of toughened glassy polymers is a critical factor in adhesive formulation, because it is responsible for the fracture modes and, hence, for the material fracture resistance. A fracture generated by crazes nucleated on the surfaces of the larger inclusions ( $>$ 1 to 3 μm), coupled with generalized yielding

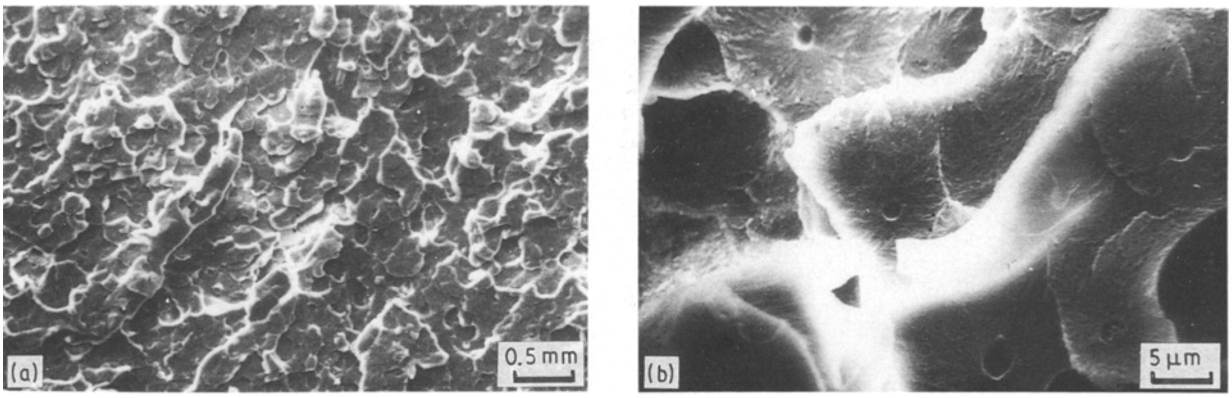

*Figure 6* Scanning electron micrographs of the fracture surface of material D.

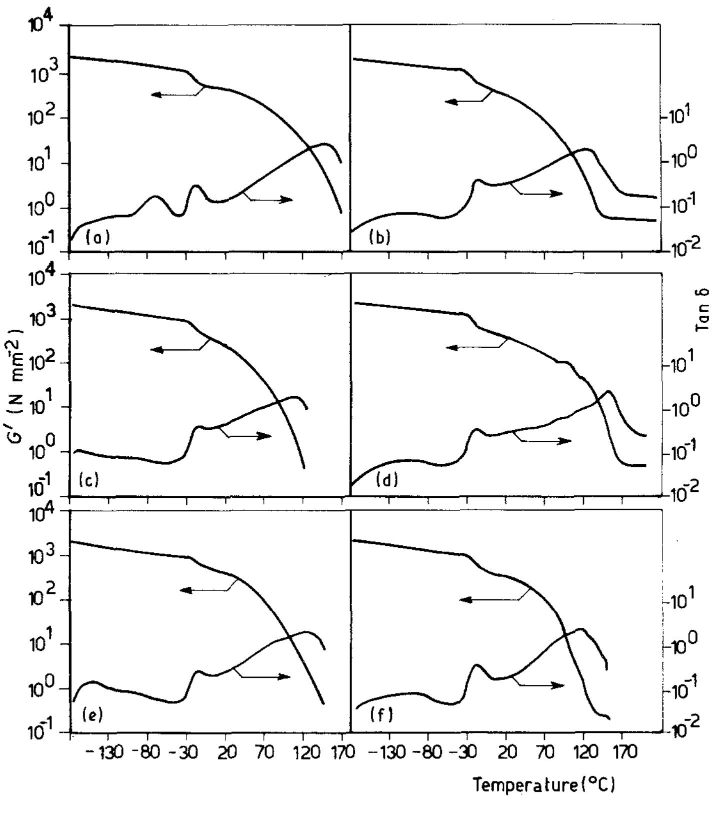

*Figure 7* Dynamic-mechanical spectra of materials (a) A, (b) D, (c) E, (d) F, (e) G, (f) H.

induced by the smaller particles, propagates with the adsorption of a large amount of energy. A bimodal distribution of the particle sizes favours this type of failure. A well-defined bimodal phase separation, however, is not sufficient to ensure high toughness. The degree of compatibility at a molecular level, as evinced by the dynamic–mechanical tests, seems to be relevant in the toughening process.

The acrylic systems, characterized by evident phase separation in TEM observations and very distinct dynamic–mechanical primary transitions, present high values of fracture energy especially when the secondary low-temperature transition of the glassy matrix is superimposed on the primary rubber transition, as in the case of EMA- and MMA-based systems. On the other hand, CEMA, toughened with chlorosulphonated polyethylene rubber, even if showing evident phase separation by TEM [2] but not coincident low-temperature transitions, has, in fact, a lower fracture energy. Phase separation may become prominent when there is a good compatibility at a molecular level between glassy matrix and rubber inclusions, as for the system based on IBMA.

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