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The toughness of syndiotactic polystyrene (sPS)/epoxy blends

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1. Introduction

When cured, thermosetting polymers such as epoxies, typically possess a high crosslink density. This property leads to such materials exhibiting good thermal stability, relatively high modulus and creep properties, and excellent adhesion properties. This combination of properties has led to their widespread use as engineering adhesives and matrices for fibre-composite materials. Unfortunately, the high crosslink density also leads to a low ductility and a poor fracture toughness being exhibited by the epoxy polymers.

In order to improve the toughness of thermosetting polymers, a most successful route is to form a blend with a low molecular-weight rubber, where the rubber undergoes phase separation upon curing the rubber-epoxy blend [e.g. 1-3]. The rubber-toughened epoxy often possesses outstanding fracture properties. However, the presence of the rubbery phase may somewhat decrease the modulus and thermal stability of the material, and increase the tendency for water absorption with an accompanying loss of properties at elevated temperatures. Whilst for adhesive applications such decreases in modulus and temperature resistance are usually of no significance, in fibre-composite applications these effects can lead to unacceptable decreases in the properties of the fibre-composite. Therefore, an alternative approach to toughening epoxy materials which are intended to be used as matrices for fibre-composites has been reported in the literature [e.g. 4-8]. This approach has been based upon blending the thermosetting resin with a thermoplastic polymer that phase separates upon curing of the resin, but where the thermoplastic phase has a relatively good thermal stability and a low water uptake compared to the rubbery phase in rubber-toughened thermosetting polymers. The thermoplastics employed have typically been functionalised poly(ether sulphone), poly(ether imides), polyesters - which are all amorphous polymers. The present paper describes the major increases in toughness that have been obtained from using a novel semi-crystalline thermoplastic/epoxy blend and demonstrates that, in contrast to the

previous studies such as those noted above, very significant increases in toughness may be obtained from using relatively low concentrations of the thermoplastic.

2. Experimental

The thermoplastic employed was syndiotactic polystyrene (sPS) which is a relatively new thermoplastic polymer, being first synthesised in 1985 by Ishihara et al. [9]. It has some excellent properties, namely: very low water absorption, a relatively high Young's modulus and high heat resistance. The sPS, "Dow Questra QA 101", was supplied by Buna Sow Leuna Olefinverbund GmbH, Schkopau, Germany, in the form of coarse granules. The glass transition temperature, T_g, and the crystalline melting temperature, T_m, of sPS are 95-100^{o}C and 270^{o}C, respectively. The sPS is an intractable polymer, which means that it has a melting temperature very close to its degradation temperature, making it very difficult to process. Sheets, 6 mm in thickness, of sPS were, however, successfully compression moulded by pressing granules at 300°C under 20 tons for 30 minutes to form 80 mm by 80 mm sheets. The heating pressure-platens were then switched off and the sheets of sPS were left to cool slowly overnight in the press.

The epoxy resin was a diglycidylether of bisphenol-A, "DER 330" supplied by Dow Chemicals, Texas, USA. The hardener used to cure the epoxy resin was an aromatic diamine 4,4-methylenebis(3-chloro-2,6-diethylaniline) and was supplied by Lonza, Germany. The resin and the hardener were mixed in the ratio of 2:1 by weight. Before being mixed with the resin, the hardener was melted by placing it in an oven at 220°C for five minutes. To form sheets, 6 mm in thickness, of the epoxy polymer, the resin-hardener mixture was stirred at room temperature for five minutes and poured into a preheated steel mould placed in an oven at 220°C. The resin-hardener mixture was cured for an hour at 220°C and left to cool slowly overnight in the oven. The resulting epoxy polymer possessed a T_g of 169±2^{o}C.

Sheets, 6 mm in thickness, of the sPS/epoxy blends were prepared with concentrations of sPS varying from 1%w/w to 10%w/w, essentially following the procedure recommended by Schut et al. [10]. The sPS and the epoxy resin were first mixed together and placed in an oven preheated at 290°C. (The sPS granules had previously been cryomilled to a fine powder, so that the sPS would melt relatively rapidly in the epoxy resin.) The sPS and resin were stirred in the oven using a mechanical stirrer for 15 to 35 minutes according to the quantity of sPS: the higher the concentration of sPS in the blend, the longer time it took to melt the sPS into the epoxy resin. However, the stirring time had to be kept as short as possible, since the high temperature being employed caused degradation of both the epoxy resin and sPS. (Indeed, no blend could be made with a concentration of sPS of more than 10%w/w since, after about 35 minutes spent at 290°C, the epoxy resin (which was initially transparent) became orange-brown in colour. This is a clear sign that significant thermal degradation had occurred.) As soon as all the sPS particles had melted in the resin the oven was switched off, and the amine hardener was placed in an

oven at 220°C for five minutes to melt. Once the hardener was molten, it was mixed with the sPS/resin blend and the mixture was stirred for a maximum of two minutes at 220°C. The sPS/resin-hardener blend was then poured into a mould preheated at 220°C, and the epoxy resin cured for an hour at 220°C. The oven was then switched off and the mould was left in the oven to cool slowly overnight, after which the sheet of sPS/epoxy was removed from the mould. It was noted that the sheet of pure epoxy polymer was transparent but the blends were all opaque materials. The resulting sPS/epoxy polymers possessed T_g values which were independent of the concentration of sPS and were in the range of 167±3°C. Since the T_g of the pure epoxy was 169±2°C, this reveals that all the sPS has indeed phase separated during the preparation of the sPS/epoxy blends.

To ascertain the toughness of the materials, compact-tension test specimens were machined from the sheets of materials and the critical stress-intensity factor, K_{Ic}, (also often termed the 'fracture toughness') for the onset of crack propagation measured according to the relevant standard [11] at a rate of displacement of 1mm/minute and at 21°C. To assist in identifying the morphology of the materials and the mechanisms of toughening, the fracture surfaces were examined using scanning electron microscopy.

3. Fracture studies

Four replicate specimens of sPS and nine replicate specimens of epoxy polymer were tested and the values of the critical stress-intensity factor, K_{Ic}, were found to be 338 (±72) $kNm^{-3/2}$ and 482 (±3) $kNm^{-3/2}$, respectively. Typically eight replicate specimens were tested for each blend composition and the results are shown in Figure 1. As may be seen, as the concentration of sPS in the blend is increased the corresponding value of K_{Ic} increased dramatically up to approximately 1100 $kNm^{-3/2}$ (for about 3 to 4%w/w sPS) and then slowly decreased to 600 $kNm^{-3/2}$ (for 10%w/w sPS). This increase in toughness at such very low concentrations of added thermoplastic has not to the authors' knowledge been previously reported and is most noteworthy. For example, previous work by one of the present authors [7] revealed an increase in the value of K_{Ic} from approximately 600 $kNm^{-3/2}$, for the pure epoxy polymer, to 1100 $kNm^{-3/2}$ for a thermoplastic/epoxy blend, but only after the addition of about 45%w/w of a functionalised poly(ether sulphone) copolymer.

4. Scanning electron microscopy studies

Scanning electron micrographs of the fracture surfaces of the pure materials and the sPS/epoxy blends are shown in Figure 2. The fracture surface of the pure epoxy is virtually flat and featureless, which is typical of a very brittle thermosetting polymer, see Figure 2a. The sPS/epoxy blends all show evidence of spherical particles of a second phase, which is the semi-crystalline sPS phase, see Figures 2b to 2e. The particles range in diameter from about 1 to 3μm, and this may be readily seen from Figure 3. However, clearly from Figures 2a to 2e, the spherical particles are most readily seen at the lower concentrations of sPS, although this may be due to the increased roughness of the fracture surfaces which

occurs at the higher concentrations of sPS obscuring the particles. However, when specimens were fractured in liquid nitrogen, under which test conditions all the specimens would be expected to be extremely brittle in nature, similar fracture surfaces were still observed.

These observations may be explained from previous work by one of the present authors [12,13]. It has been established that phase separation of the sPS from the epoxy may occur in these sPS/epoxy blends via two main routes. Firstly, by 'reaction-induced phase separation' (RIPS) where the curing reaction of the resin and hardener leads to the development of a three-dimensional epoxy-polymer network, and this leads to phase separation of the initially-soluble sPS. Secondly, however, if the sPS crystallises before the network has been developed sufficiently to force the sPS out of solution, then phase separation occurs 'prematurely' and is termed 'crystallisation-induced phase separation' (CIPS). (Note that the crystallisation temperature of the sPS is greatly reduced when it forms part of the blend composition.) From the present micrographs and the previous work [13], it appears in the present studies that at lower concentrations of sPS the phase-separation process may be occurring via RIPS, whilst at the higher concentrations of sPS it is occurring via CIPS. Further work is currently exploring these aspects in more detail in order to identify the phase-separation mechanisms which are operating, as a function of the concentration of sPS in the sPS/epoxy blends and their thermal history. Indeed, it may well be that the maximum in the relationship between K_{Ic} versus concentration of sPS in the blend, which was discussed above, might arise from different phase-separation mechanisms operating over the range of sPS concentrations employed.

With respect to the underlying toughening mechanisms which are involved, then from Figures 2b to 2e and Figure 3 there is no evidence of any plastically-drawn fibrils of the thermoplastic sPS phase; such evidence of plastic yielding of the sPS phase might have readily explained the significant increases in toughness seen in the sPS blends. However, such plastic yielding of the thermoplastic phase is in fact rarely seen [7,14,15]. Nevertheless, significant features may be seen from Figure 3, where cavities are visible around the spherical sPS particles and the particles have therefore clearly debonded from the epoxy polymer. The presence of such cavities around particles on the fracture surfaces of multiphase crosslinked polymers has been previously ascribed [16] to the triaxial stresses at the crack tip causing the particle to debond as the crack advances. This debonding of the particles then enables plastic hole growth of the epoxy polymer to occur. Thus, we observe the second-phase particles with the cavities surrounding them. Hence, it appears that the increase in toughness in the sPS/blends arises from the energy dissipated by debonding of the particles and the associated plastic hole growth in the epoxy polymer, although the toughening mechanisms of crack pinning and crack-path deflection around the relatively rigid sPS particles may also play a secondary role [16,17].

5. Conclusions

Finally, we would wish to emphasise the novel nature of these semi-crystalline sPS/epoxy blends and the major increases in toughness that have, most unusually, been obtained from using a very low concentration of the thermoplastic sPS in the sPS/epoxy blend.

Acknowledgements

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Figure 1. Variation of the critical stress-intensity factor, K_{Ic}, with the concentration of sPS in the sPS/epoxy blend.

Figure 2. Scanning electron micrographs of the fracture surfaces. (The direction of crack growth is from the bottom of the micrograph upwards.)

(a) Pure epoxy polymer.

(b) 1%w/w sPS/epoxy blend.

(c) 3%w/w sPS/epoxy blend.

(d) 5%w/w sPS/epoxy blend.

(e) 8%w/w sPS/epoxy blend.

(f) Pure sPS.

Figure 3. Higher-magnification scanning electron micrograph of the fracture surface of the 5%w/w sPS/epoxy blend. (The direction of crack growth is from the bottom of the micrograph upwards.)

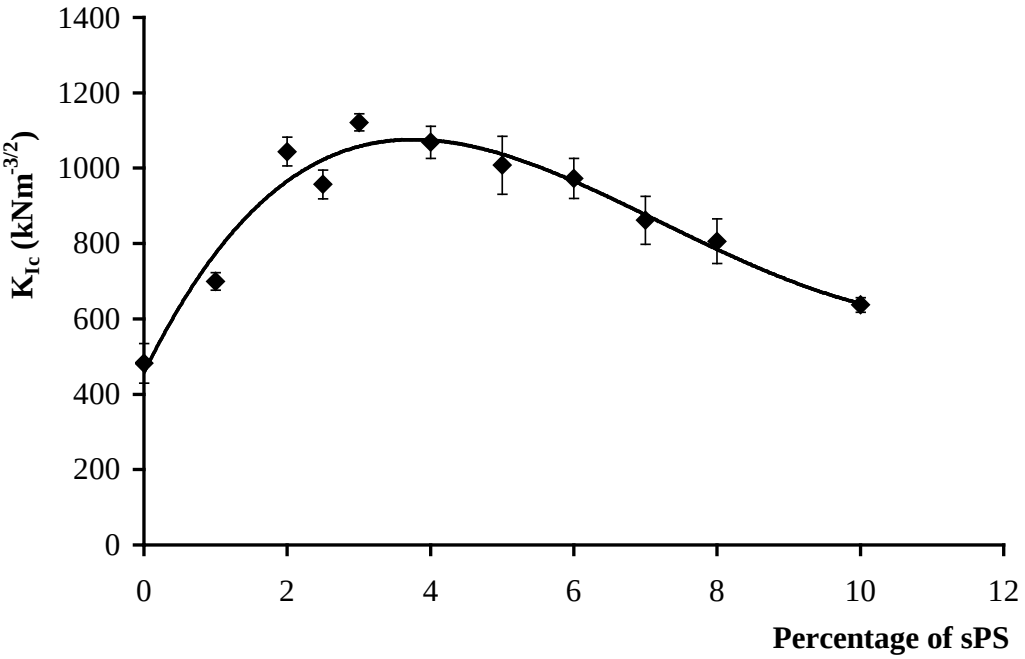
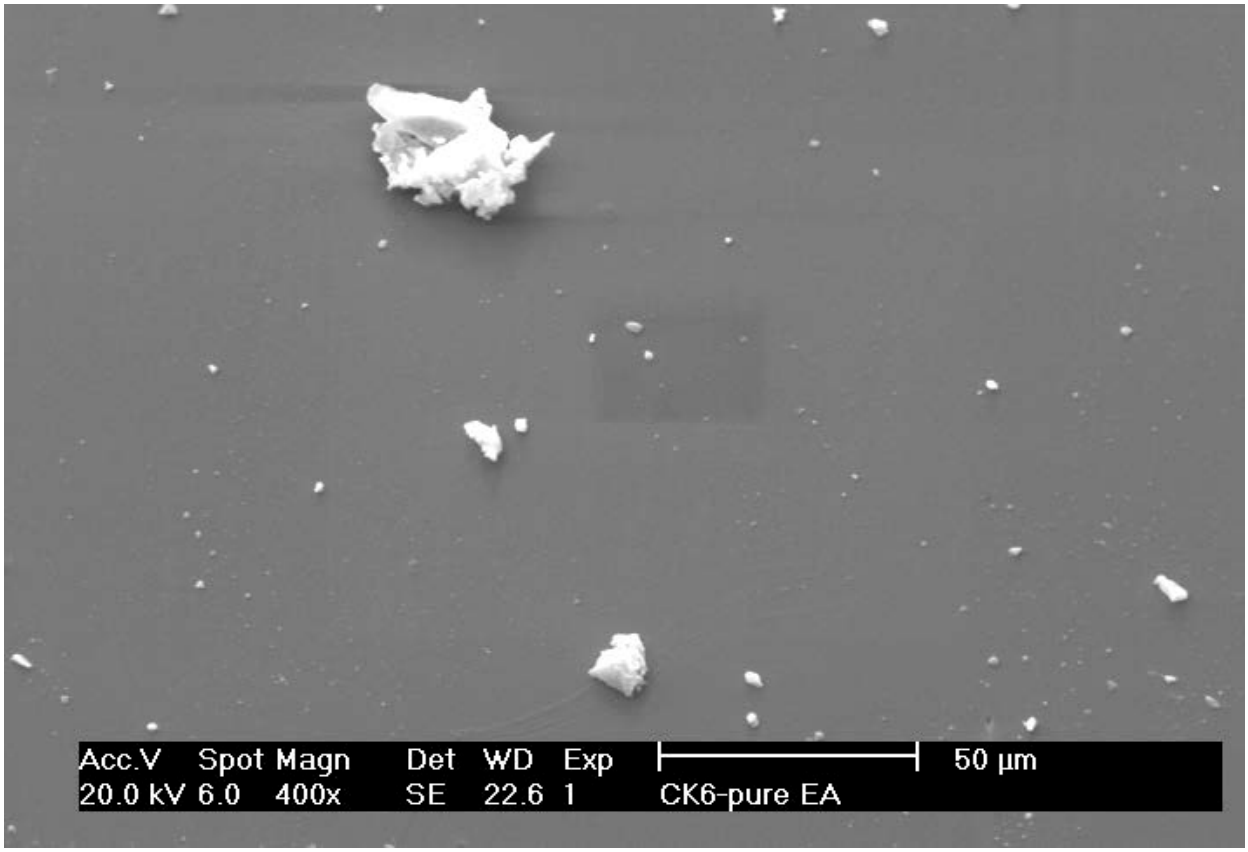
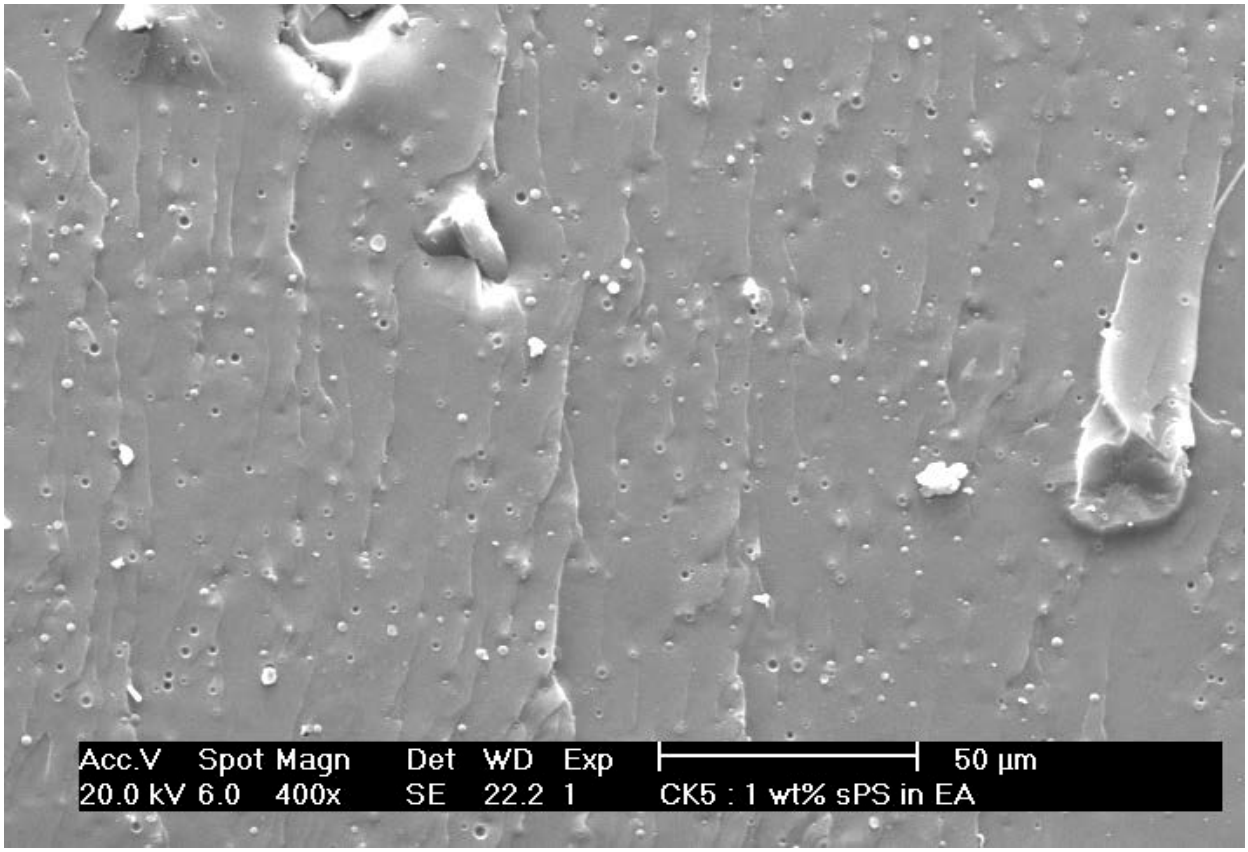


Figure 1. Variation of the critical stress-intensity factor, K_{Ic}, with the concentration of sPS in the sPS/epoxy blend.

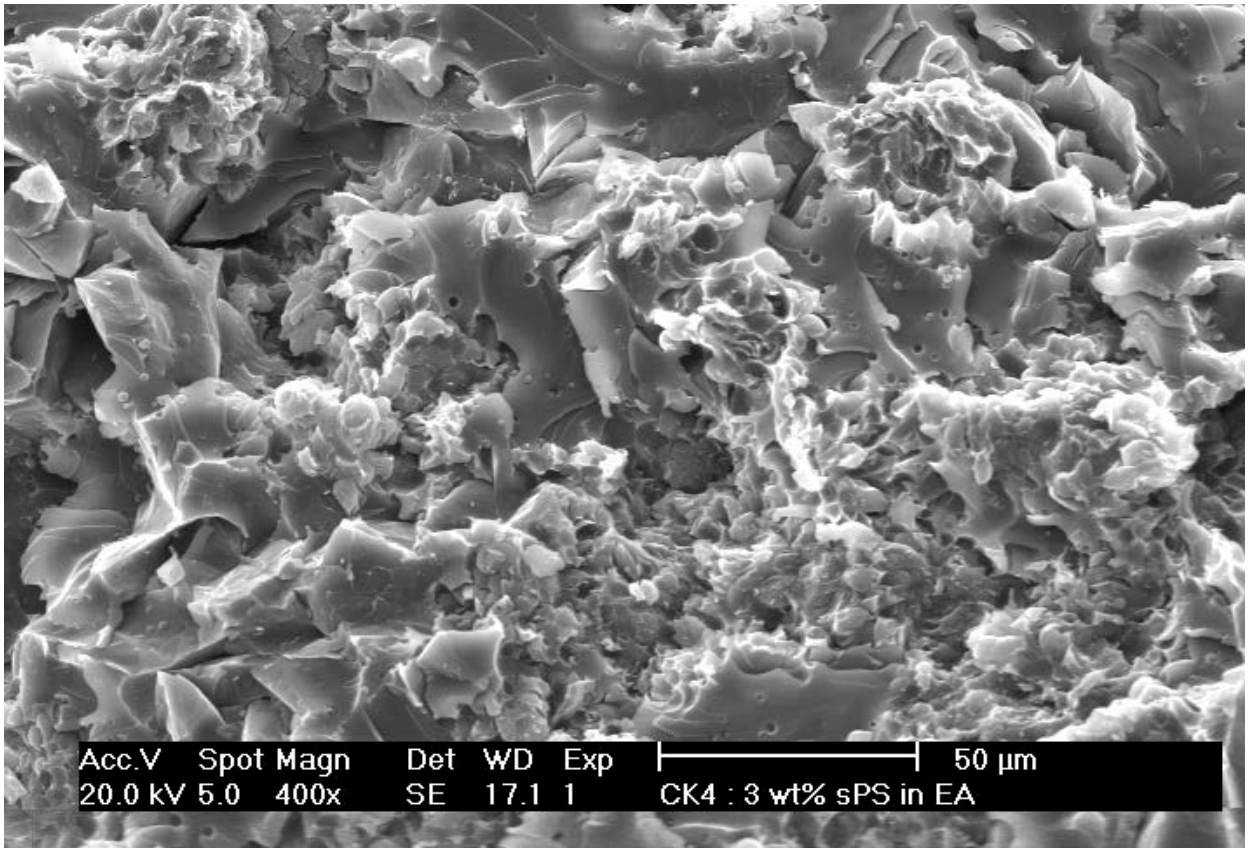


(a) Pure epoxy polymer.

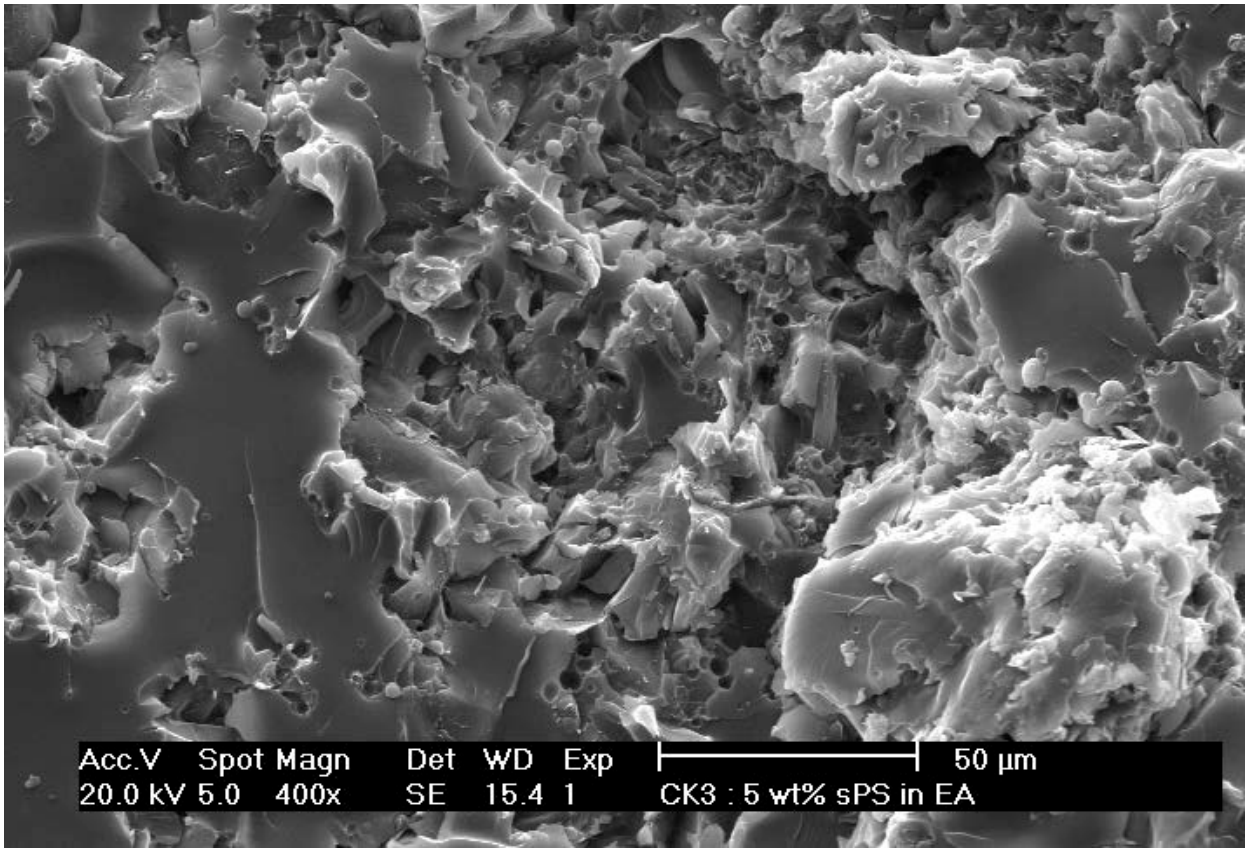
Figure 2. Scanning electron micrographs of the fracture surfaces. (The direction of crack growth is from the bottom of the micrograph upwards.)



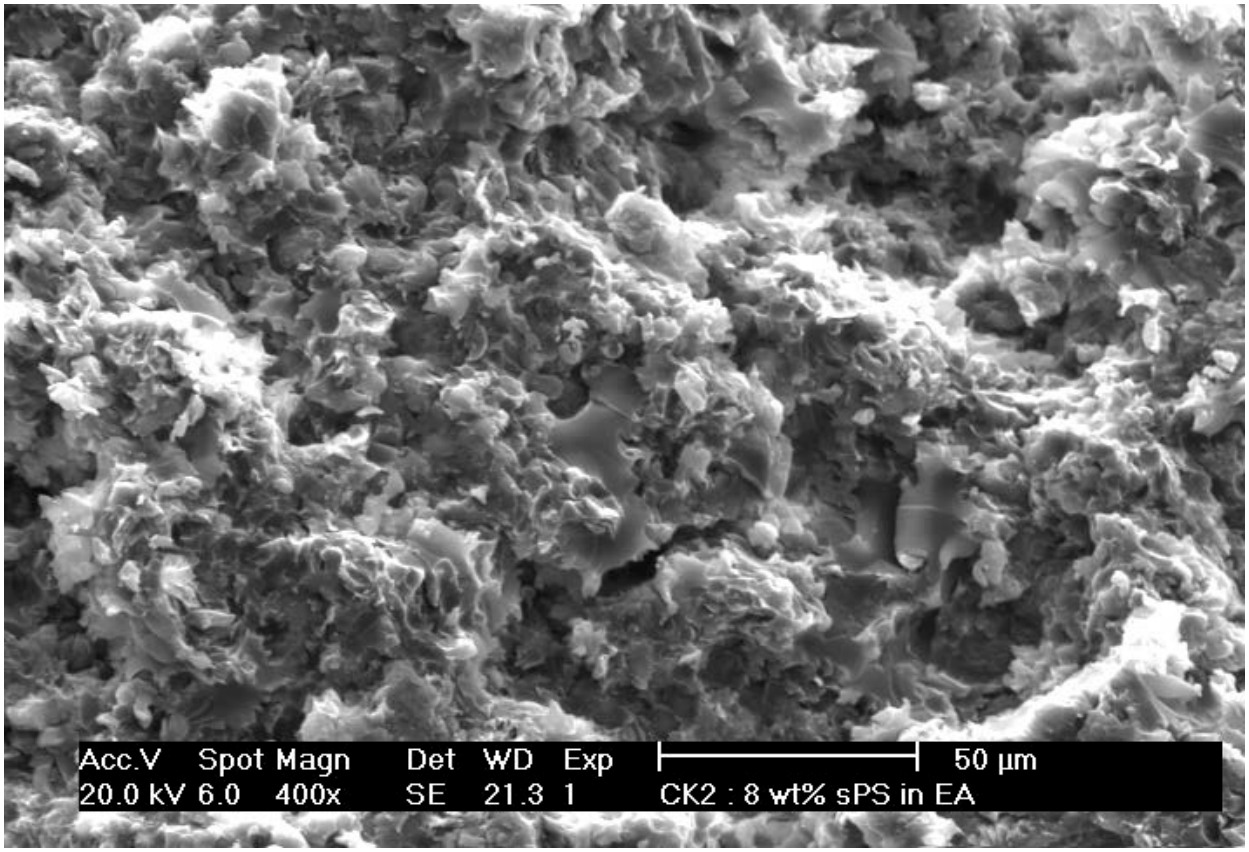
(b) 1%w/w sPS/epoxy blend.



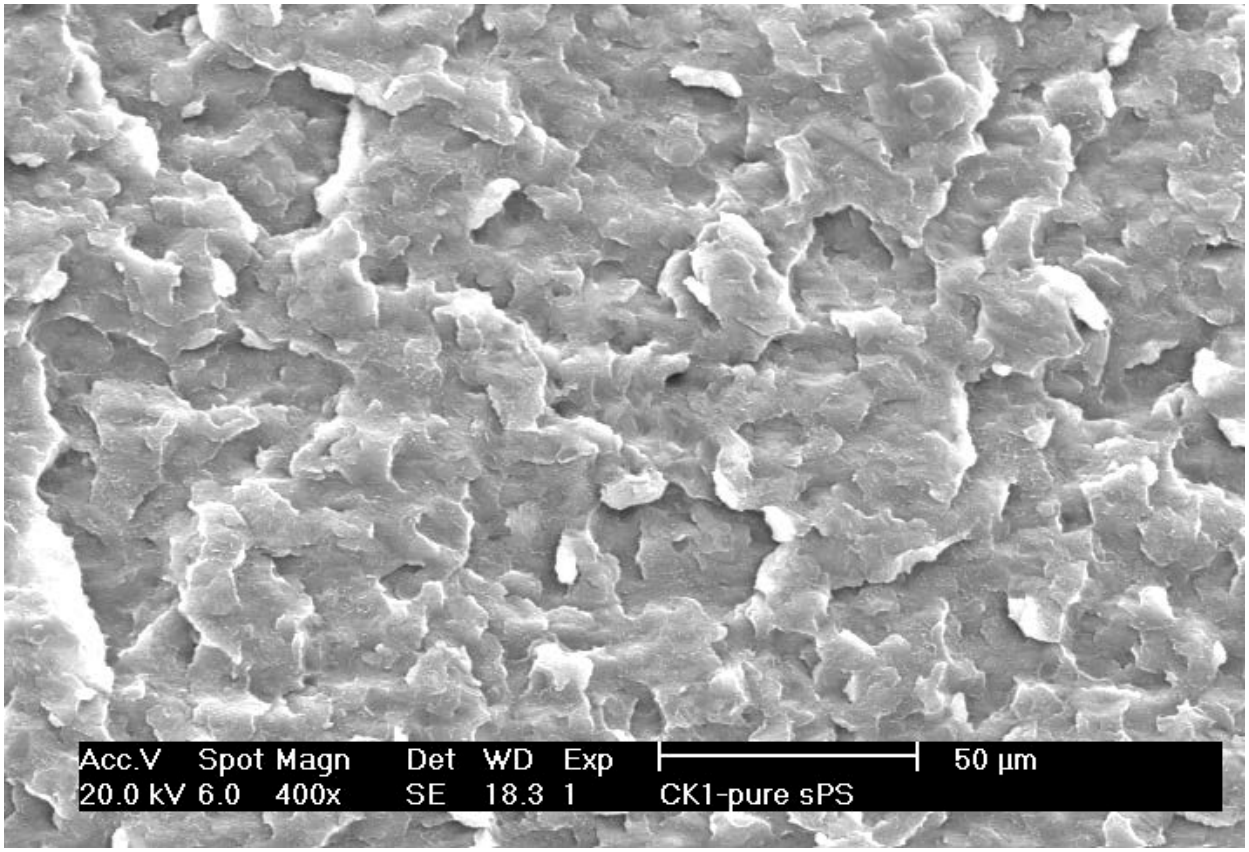
(c) 3%w/w sPS/epoxy blend.



(d) 5%w/w sPS/epoxy blend.



(e) 8%w/w sPS/epoxy blend.


Acc.V Spot Magn Det WD Exp
20.0 kV 6.0 400x SE 18.3 1
50 µm
CK1-pure sPS

(f) Pure sPS.

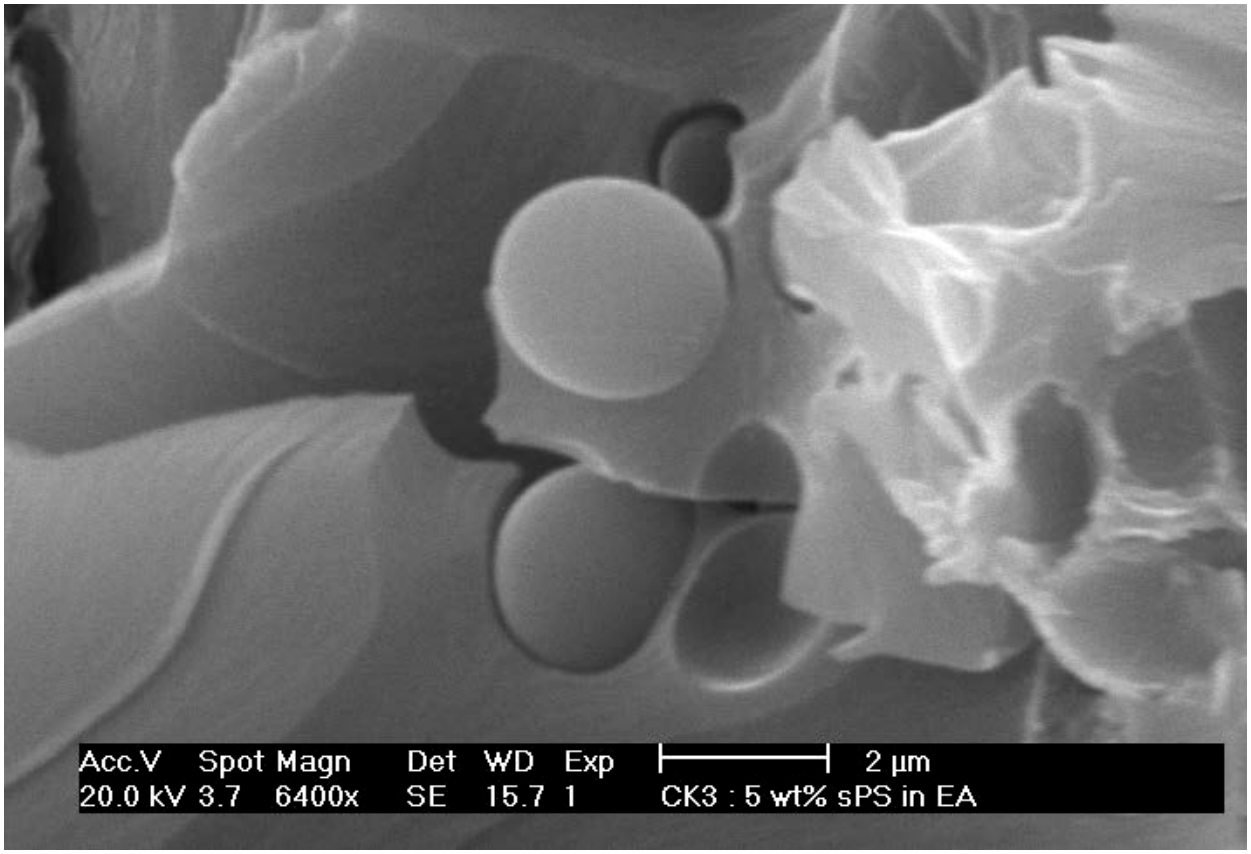


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