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Effect of reinforcing fibres on the morphology of a toughened epoxy/amine system

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The effect of reinforcing fibres on the morphology of a thermoplastically toughened tri-functional epoxy resin cured with an aromatic hardener has been studied using optical microscopy. Single and multiple strands of different types of fibres were placed within curing resin matrices containing varying thermoplastic concentrations. The fibres appeared to encourage the development of large particles (significantly larger than would be found in the bulk matrix), which remained at the fibre surface. A plain weave glass fibre tape was also found to greatly affect the final morphology of the same system. The results indicate that the morphology of a thermoplastic modified epoxy/amine resin is significantly affected by reinforcing fibres. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: morphology; fibres; particle size)

INTRODUCTION

Epoxy resins are a class of high performance thermosetting polymers widely used as matrix resins for advanced composite materials for application in the automotive, construction and aerospace industries. These polymers have achieved widespread use due to their high modulus, corrosion resistance, thermal stability and low shrinkage upon cure. However, because of their generally highly crosslinked nature they tend to be brittle, which has limited their proliferation into many critical areas. Over the years there have been numerous studies aimed at the toughening (or increasing the resistance to impact) of epoxy resins, without compromising too many other properties; with some degree of success. Generally toughening has been achieved by adding a second rubbery component which is able to enhance various toughening mechanisms by dissipating the energy of impact. Some of the greatest toughening improvements have been achieved using reactive synthetic rubbers[2–4], although in recent times thermoplastic modifiers have also been used successfully, particularly for the more highly crosslinked epoxy resins[5–7]. There are many contributing factors which, added together, cause the toughness of an epoxy resin to increase. Some of the factors that have been considered particularly important for the toughening of epoxy resins are, the morphology of the cured material (this includes both the size of particle inclusions and the type of the multiphase structure), the concentration and the molecular weight of the toughener, the adhesion between the particles and matrix, and the chemical structure of the toughening phase.

Another factor that has not generally been considered in academic studies, but which is very important for practical purposes, is the relationship between the reinforcing fibre and the morphology of the matrix resin. Much of the work that has been reported in the literature focuses upon the multiphase structure of the neat resin system alone, and has ignored any effects that the reinforcing fibre might have on the development of resin morphology. It is obviously important to know what effects (if any) a reinforcing fibre will have on the properties of a toughened epoxy matrix resin in order to gain a more complete understanding of the relationship between toughness, morphology and cure in advanced composites.

The work presented here demonstrates some effects of reinforcing fibres on the morphology of a thermoplastically toughened epoxy resin system that has been extensively studied by ourselves[8,9] and others[10–12] as both a neat and thermoplastic modified, resin system. The

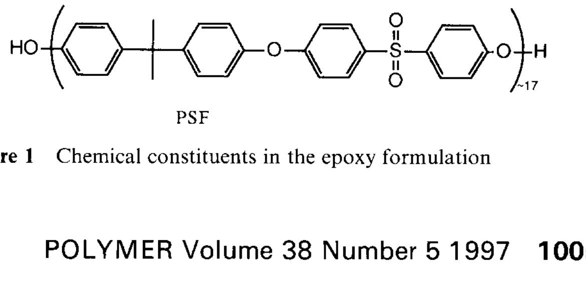

Figure 1 Chemical constituents in the epoxy formulation

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Table 1 Effect of fibre on particle sizes for the composition 10% PSF/TGAP/DDS

Fibre	Average *r* in bulk	Average *r* on fibre
Carbon	2.37	7.37
Carbon (desized)	2.84	6.93
Kevlar	3.02	16.34
Glass	2.46	6.53

system chosen was the trifunctional epoxy resin, tris glycidyl *p*-amino phenol (TGAP) using the aromatic amine hardener, diaminodiphenyl sulfone (DDS) and a hydroxy terminated polysulfone (PSF) as the thermoplastic toughening agent. The chemical structures of these compounds are shown in *Figure 1*.

EXPERIMENTAL

Materials and samples preparation

The epoxy resin, TGAP (Ciba Geigy MY0510) and the hardener DDS (Ciba Geigy HT976), were used as received. TGAP was found to have an epoxy equivalent weight of 9.41 mmol epoxy g^{-1} as determined by titration. The thermoplastic modifier used was a hydroxyl terminated polysulfone synthesized from bisphenol A and dichlorodiphenyl sulfone monomers using the method described elsewhere by Merriam and coworkers[13]. Gel permeation chromatography (g.p.c.), infra-red (i.r.) spectroscopy and nuclear magnetic resonance (n.m.r.) were all used in the characterization of the final thermoplastic polymer. Both g.p.c. and n.m.r. measurements were used to confirm the number average molecular weight of the PSF to be 7800 g mol^{-1}.

Matrix resin samples were prepared by mixing the TGAP and PSF together in a rotary evaporator in an oil bath at about 130°C until the latter had fully dissolved, then the DDS was added and the total stirred under vacuum until homogeneous. Samples containing 10%, 15%, and 20% w/w PSF were prepared in this fashion.

The single fibres used in this work included carbon (ICI, Fiberite T300; used 'as is' as well as desized by heating at 400°C for 30 min), Kevlar, and a common, sized glass. Another material system that was used with analysis work was a glass braid tape. A 15% w/w PSF/TGAP/DDS sample was impregnated onto the tape and cured beyond gelation at 180°C in an oven in order to ensure that complete phase separation and morphological development had occurred.

Optical microscopy

The samples containing mixtures of the resin and a

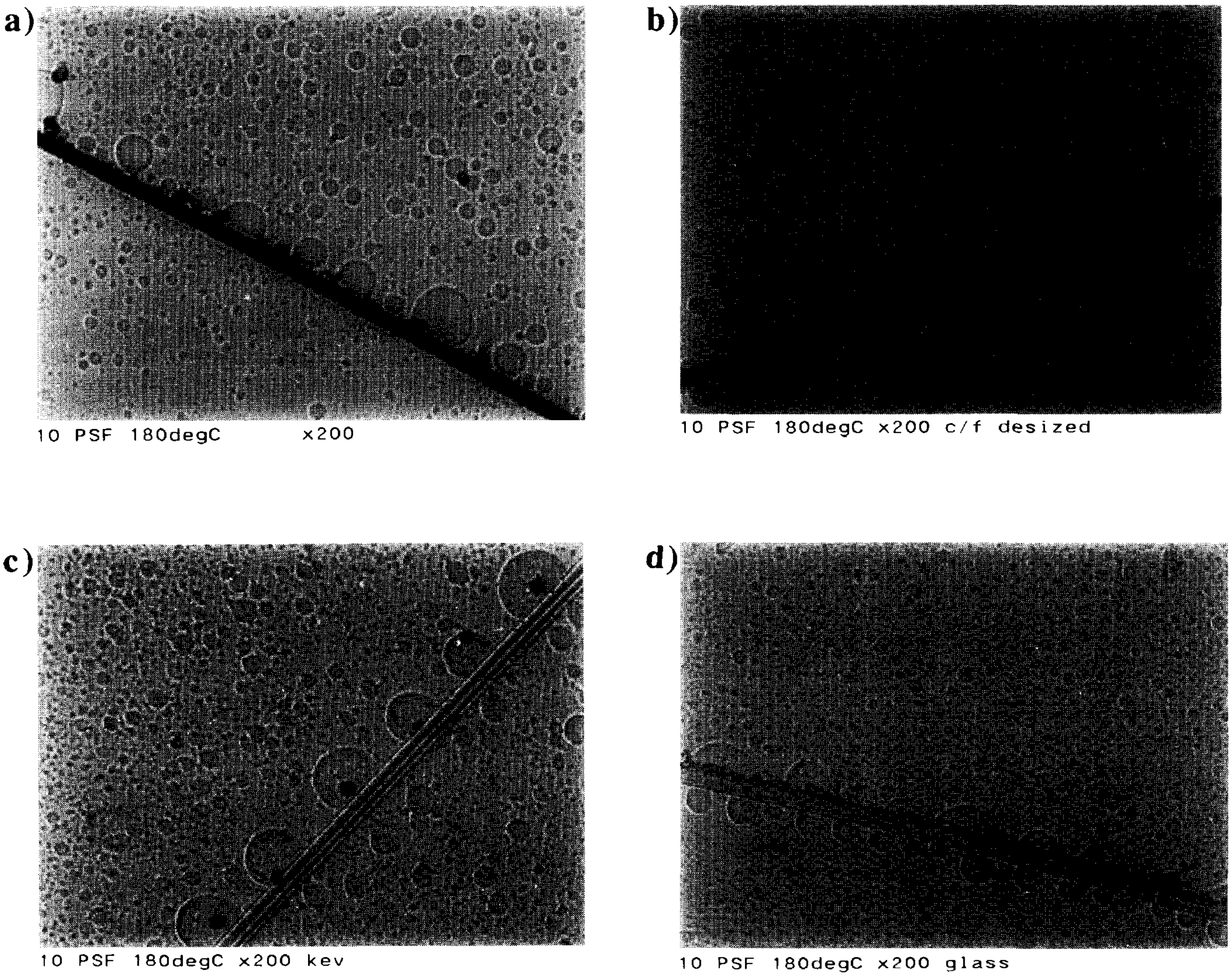


Figure 2 Effect of fibres on the morphology of 10% w/w PSF/TGAP/DDS, (a) carbon fibre, (b) desized carbon fibre, (c) Kevlar and (d) glass

small number of fibres were placed between two microscope slides and fitted into a Mettler FP82HT hot stage attachment which was held at 180°C by the Mettler FP90 central processor. The phase separation and morphological development of the multiphase system in the presence of different types of fibres was continuously observed by placing the hot stage under a Nikon Labophot 2 optical microscope. Photographs were obtained using a Mavigraph, Sony Colour Video Printer UP-2200P. Bubbles were often observed, particularly at higher PSF concentrations but were kept to a minimum by only using samples that had been freshly prepared. The composition of the PSF phase was confirmed by solvent etching the material with dichloromethane, as describe by Min *et al.*[14]. Scanning electron microscopy (SEM) was seen to clearly identify the thermoplastic phase by showing the large effect on the materials surface of extraction with dichloromethane since the crosslinked epoxy resin phase remains largely unaffected by solvent. SEM exhibited many areas of pitting for lower PSF concentrations as well as extensive dissolution of the continuous matrix for phase inverted morphologies at higher PSF contents.

RESULTS

Extensive previous studies of morphology[15–17] development in this particular epoxy system have shown that the morphology changes are very complex and depend greatly on the concentration of the thermoplastic. A concentration level of around 20% thermoplastic has been found to be the critical level for the initiation of complex morphology development in neat resin systems.

Single and multi fibres

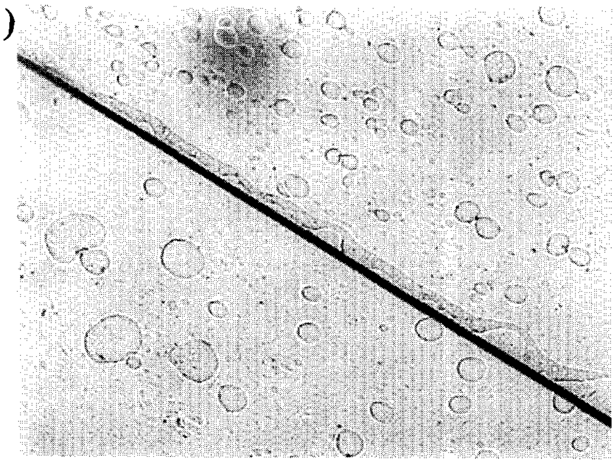
A number of new and interesting observations were made from the experimental work carried out in the presence of fibres. The most noticeable initial effect of the fibre is evident from *Figure 2*, which details the influence of all fibres, carbon (normal and desized), Kevlar and glass at an early stage in the cure. The formulation used in this instance was a 10% w/w PSF/TGAP/DDS. It could be seen that the fibre caused very large particles of thermoplastic to form along the fibre almost immediately after phase separation, and these remained there during the entire cure. As the whole resin melted and flowed across the glass slide (due to thermal currents) the non-polar thermoplastic particles were also seen to flow. When they came in contact with the fibre they were either, unable to pass through (under or over) and were held up significantly on the fibre. This flow caused other thermoplastic particles to collide and coalesce with the ones already at the fibre surface, forming much larger particles at the surface of the fibre than those remaining in the bulk matrix. The results shown in *Table 1*, indicate the degree to which the particles sizes were affected by the fibre in this particular formulation.

It could be seen from both the optical microscope photographs and the particle size measurements that the type of fibre did not have any great morphological effect on this phenomenon, indicating that the fibres are simply acting as a nucleating site and a flow barrier more than anything else. Whilst the general effect of particle nucleation and growth did not appear to be dependent on the type of fibre there does seem to be some effect on the degree of adhesion of the thermoplastic particle to the fibre. The particles attached to the carbon fibre (sized and de-sized) generally appear to be fairly circular and the contact angle is relatively small (*Figures 2a* and *b*) while the glass fibre which presumably has a greater functionality (*Figure 2d*) has a much larger contact angle with the thermoplastic particles as evidenced by their semi-circular shape. The Kevlar fibre (*Figure 2c*) appears to have an intermediate behaviour. While our experimental system of a few fibres between glass surfaces is artificial it may well be similar to the flow barriers provided by bundles of fibres in more realistic composite materials.

Another related but unusual phenomenon was observed at higher concentrations of PSF, as seen in *Figure 3*. These photographs show two formulations containing 15% PSF cured at 180°C in the presence of carbon fibre. It can be seen that due to the nucleating effect of the fibre and the higher concentration of the thermoplastic, this phase was able to coalesce to form long lines of continuous thermoplastic along the fibre (*Figure 3a*). In *Figure 3b* this effect manifests itself by the formation of a massive globule with its own internal multiphase structure.

When the concentration of the thermoplastic was

a)



b)

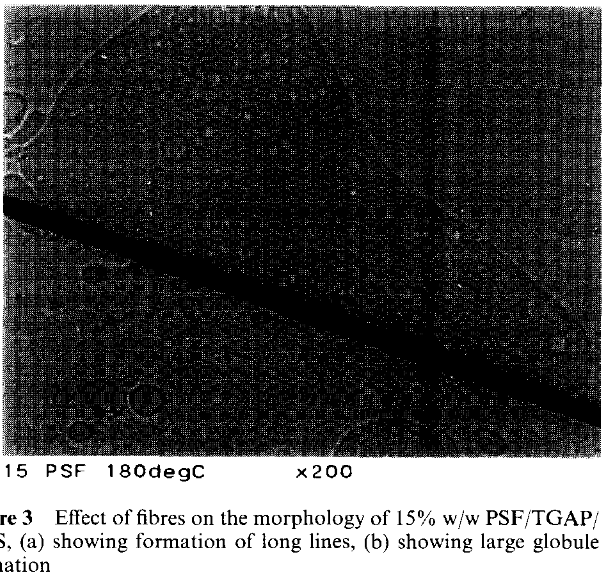


Figure 3 Effect of fibres on the morphology of 15% w/w PSF/TGAP/DDS, (a) showing formation of long lines, (b) showing large globule formation

increased to 20% the morphology of the system without any fibre exhibited a complex mixture of particulate and co-continuous phases. This morphology was further complicated by the introduction of fibres as shown in *Figure 4* which contains optical photographs for two different areas of the same cured carbon fibre formulation. Here it can be seen that on one side of the fibre there is an example of co-continuous type morphology with the non-polar thermoplastic forming a large ribbon like finger along the fibre, while on the other side of the fibre the co-continuous region is interrupted and appears as standard particulate morphology in the region immediately next to the fibre. At some further distance away from the fibre the co-continuous structure is once again resumed. This effect, shown in both *Figures 4a* and *b* was similar but not identical for both of the photographs shown.

Of course, the most practical point of interest in the composite area is the morphological development effects of large bundles of closely packed fibres. While this is difficult to study directly, an intermediate condition with a number of fibres is shown in *Figure 5*. This shows two optical photographs using carbon fibres which have a loading of 10% PSF and demonstrate clearly the unusual effect that many fibres can have. The first one, *Figure 5a* shows how they can act as barriers as we have discussed previously, but in doing so they can promote different morphologies in different areas. As can be seen here, in between the two fibres the particle sizes are considerably larger than those on the outside of the fibres. Another effect, as shown in *Figure 5b* with even more fibres, shows how the particle sizes can be built up even more to massive proportion than would be normally expected. These structures are not the regular fine thermoplastic particles normally seen in neat resin bars at this PSF concentration. It can also be seen that the fibres have encouraged the precipitation of epoxy particles within the thermoplastic domain. This behaviour has never been observed for 10% PSF levels in the absence of fibres.

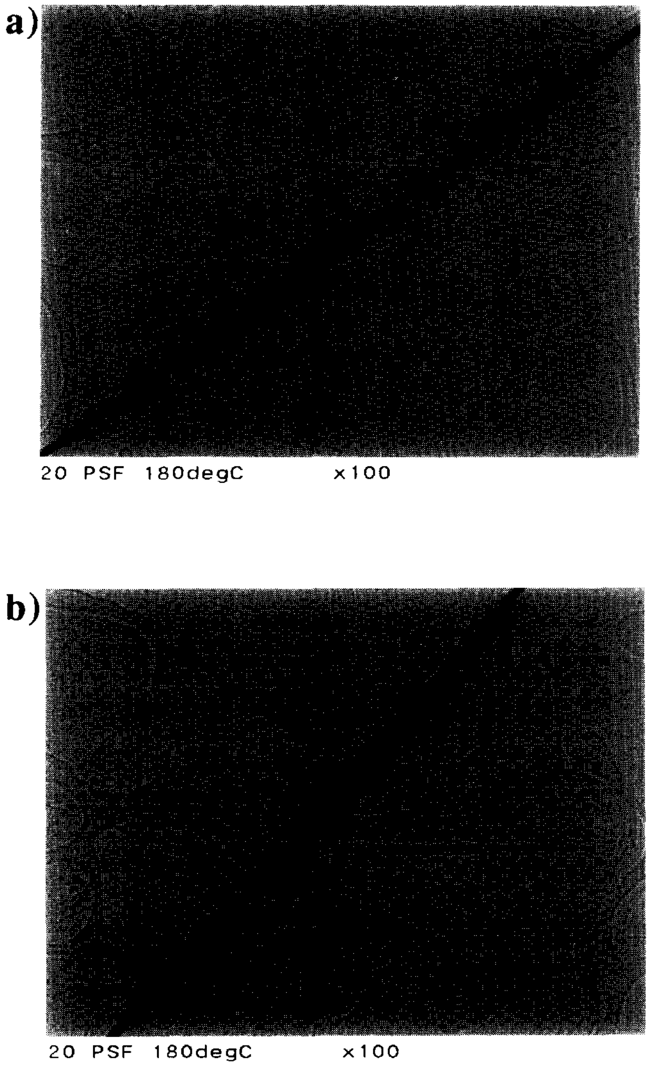


Figure 4 (a, b) Effect of fibres on the morphology of 20% w/w PSF/TGAP/DDS

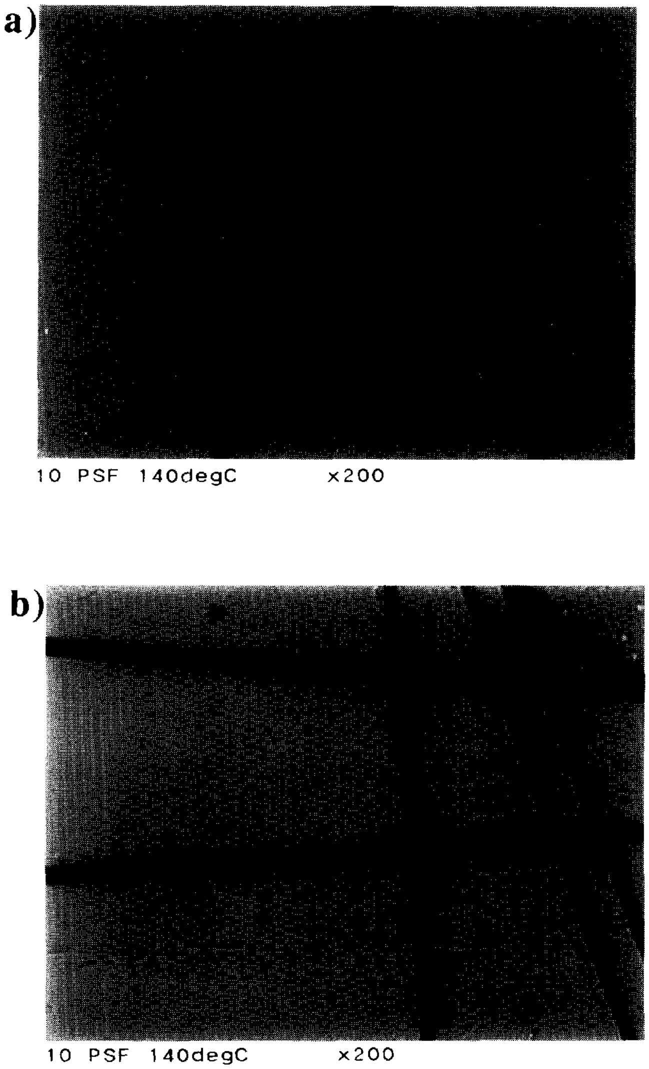


Figure 5 (a, b) Effect of many fibres on the morphology of 10% w/w PSF/TGAP/DDS

Plain weave glass tape

As a further step towards the true composite situation, studies were carried out on the morphology development on a glass braid. The 15% PSF sample cured on glass tape could only be observed under the microscope by using reflectance techniques. The photographs as shown a)

b)

Figure 6 (a, b) Effect of plain weave braid on the morphology of 15% w/w PSF TGAP/DDS showing complex morphology

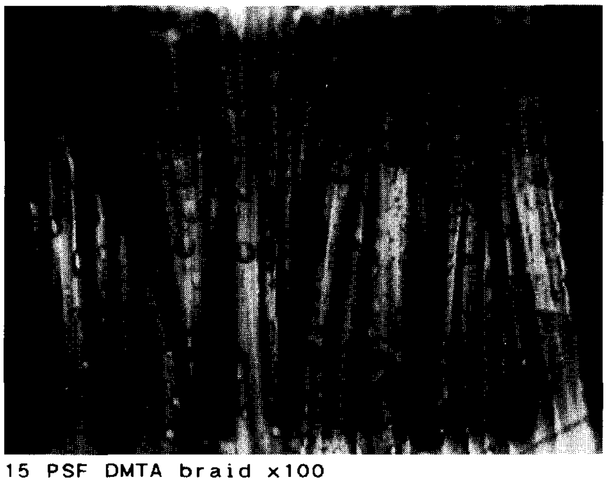


Figure 7 Effect of plain weave braid on the morphology of 15% w/w PSF TGAP/DDS showing standard particulate morphology

in *Figure 6* demonstrate again the way in which the morphology is affected by the fibre reinforcement. The thermoplastic material appears to have aggregated at the edges of the braid weaves. The initial particles settled here and in a similar fashion to the work described above appear to have become larger and larger. Once they have grown beyond a certain point the epoxy resin is precipitated within the thermoplastic matrix forming a large phase inverted structure around the square edges of the braid weave.

In between these fibre areas the morphology appeared to be as one would expect, which is a particulate structure of thermoplastic embedded in an epoxy matrix, as shown in *Figure 7*.

CONCLUSION

In conclusion, our results indicate that the less polar thermoplastic PSF phase is attracted to fibre surfaces as soon as phase separation commences. This encourages nucleation and agglomeration and hence the formation of very different morphologies than those seen in the same formulation in a neat resin specimen.

While there is not a major difference between the different fibres ranging from carbon to Kevlar and glass there have been small but noticeable changes in morphology with these different materials in particular the degree of contact with the fibre which are presumably due to surface chemical differences.

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