Characterization of polypyrrole–fibre composites by time-of-flight secondary ion mass spectrometry and vibrational spectroscopy

M. J. Hearn and I. W. Fletcher
ICI Advanced Materials, PO Box 90, Wilton, Middlesbrough TS6 8JE, Cleveland, UK

and S. P. Church
Courtaulds Research, PO Box 111, Lockhurst Lane, Coventry CV6 5RS, UK

and S. P. Armes*
School of Chemistry and Molecular Sciences, University of Sussex, Falmer,
Brighton BN1 9QJ, Sussex, UK

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We have examined polypyrrole–polyester and polypyrrole–quartz fibre composite samples using time-of-flight secondary ion mass spectrometry (TOF-SIMS). This technique has allowed us to confirm that in each composite the conducting polymer overlayer of cationic polypyrrole chains is doped with 5-sulphosalicylate dopant anions, at least to a sampling depth of 10 Å. Surprisingly there is no detectable presence of the second aromatic sulphonate dopant anion utilized in the Milliken synthetic procedure (1,5-naphthalenedisulphonic acid, disodium salt). Our Fourier transform (*FT*) Raman spectra of these polypyrrole–fibre composite contain strong spectral bands due to the cationic polypyrrole chains, several weak features due to the underlying fibre substrate (particularly in the case of the polyester fibres), and no bands attributable to the dopant anions. These observations suggest that the Raman scattered light from the substrate component is largely reabsorbed by the polypyrrole overlayer. Thus we conclude that there must be extensive coverage of the fibre substrate by the conducting polymer with few, if any, 'bare' patches. Finally, our *FT*i.r. microscopy studies on these coated composites produced good quality spectra of the underlying substrate with few features attributable to the polypyrrole overlayers.

(Keywords: composites; fibre; polypyrrole)

INTRODUCTION

Polypyrrole has been recognized to be a reasonably air stable organic conducting polymer since its electrochemical synthesis in 1968[1,2]. It may be easily prepared as a bulk powder precipitate using various chemical oxidants in either aqueous or non-aqueous media[3–7].

It is well known that the electrical conductivity, molecular anisotropy and the environmental and thermal stabilities of polypyrrole can be significantly improved by the judicious choice of the dopant anions which are incorporated as counter ions for the oxidized, cationic polypyrrole chains[8–17]. For example, the chloride-doped material is markedly less air stable and has lower electrical conductivity than polypyrrole doped with aromatic sulphonate anions such as tosylate[15–17].

The main drawback of this material is its poor processability, since it is both infusible and also completely insoluble in all known solvents. In order to overcome this inherent intractability various groups have reported the preparation of composites of polypyrrole with other conventional polymers such as cellulose[18], nylon[19,20], poly(vinyl alcohol)[21], poly (methyl methacrylate)[22] or poly(4-vinyl pyridine)[23].

In 1989 Kuhn *et al.* of the Milliken Research Corporation reported that polypyrrole–textile composites could be easily fabricated by a remarkably efficient *in situ* solution deposition process[24–26]. The polypyrrole is formed *directly* on the textile fibres in a controlled surface polymerization which produces smooth, well-adhering overlayers of polypyrrole of submicrometre dimensions. The Milliken group utilized two different aromatic sulphonate dopant anions in their synthetic methodology: 5-sulphosalicylic acid (which forms a weak 1:1 complex with the $FeCl_3$ oxidant and thus reduces the rate of pyrrole polymerization) and a 1,5-naphthalenedisulphonic acid (disodium salt).

In collaboration with Milliken we have characterized such textile composites and also quartz fibre composites using various techniques such as thermogravimetry, Rutherford backscattering spectrometry, scanning electron microscopy and scanning tunnelling microscopy[27,28]. Our energy dispersive X-ray analyses (EDAX) confirmed the presence of sulphur in the textile composites, which

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*To whom correspondence should be addressed

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indicated the incorporation of aromatic sulphonate dopant anions into the polypyrrole chains as expected[27]. However, we were unable to distinguish between the two aromatic sulphonate anions in our EDAX studies and therefore could not assess the extent, if any, of preferential incorporation of one or other of these dopant anions into the polypyrrole overlayers.

In the present work, we have utilized time-of-flight secondary ion mass spectrometry (TOF-SIMS) to examine the nature of the aromatic sulphonate dopant anion(s) in polypyrrole overlayers deposited onto both polyester fibres and quartz fibres using the Milliken methodology. In addition we have examined these fibre composites by both Fourier transform (*FT*) Raman spectroscopy and *FT*i.r. microscopy.

EXPERIMENTAL

Chemicals

The 5-sulphosalicylic acid and the 1,5-naphthalenedisulphonic acid (disodium salt) were purchased from Aldrich and were used as received.

Preparation of the polypyrrole-coated fibre composites

The samples were obtained from Dr H. H. Kuhn of the Milliken Research Corporation and were prepared as previously described[24–26]. For the polypyrrole–polyester composite the initial concentrations of the two dopant anions in the reaction solution are typically 12 and 4 $\mathrm{g\,l^{-1}}$ for the 5-sulphosalicylate and 1,5-naphthalenedisulphonate species, respectively. This corresponds to an initial molar ratio (5-sulphosalicylate:1,5-naphthalenedisulphonate) of 4:1. For the preparation of the polypyrrole–quartz composite this initial molar ratio was ~11:1. The polypyrrole loading on these fibre composites is in the range of 2–5 wt% and their surface resistance is of the order of 100 Ω per square (ref. 29).

TOF-SIMS experiments

The VG IX23S instrument and charge compensation technique used in this work have been described elsewhere[30,31]. Experimental details were as follows: static SIMS conditions (i.e. a total ion dose of $< 1 \times 10^{12}$ ions $\mathrm{cm^{-2}}$ during the analysis) were employed using a pulsed 30 keV $^{69}\mathrm{Ga}^+$ primary ion beam rastered at TV rate over an area of $0.2 \times 0.2\ \mathrm{mm^2}$. A mass range of 5–500 was covered for both positive and negative secondary ions. Individual samples were prepared by placing the materials onto double-sided adhesive tape on a sample holder; any loose or excess material was subsequently removed.

FT *Raman spectroscopy*

These measurements were carried out using a Bruker IFS 66 spectrometer in conjunction with an FRA 106 *FT* Raman module and a diode-pumped Nd/YAG laser (operating wavelength 1.064 μm). *FT* Raman spectra of the 5-sulphosalicylic acid and 1,5-naphthalenedisulphonic acid (disodium salt) control samples and the uncoated polyester and quartz substrate samples were measured under standard conditions using a laser power of 300 mW. Measurements from the polypyrrole–polyester and polypyrrole–quartz fibre composites were hampered by a high heating background. Satisfactory *FT* Raman spectra could only be obtained by fine adjustment of the laser power in order to minimize this heating effect. Thus, these latter two spectra were recorded using powers of 30 and 40 mW, respectively. All spectra were recorded at 4 $\mathrm{cm^{-1}}$ resolution.

FT*i.r. microscopy*

These measurements were carried out using a Spectra-Tech IR-PLAN i.r. microscope coupled to a Nicolet 740 *FT*i.r. spectrometer. The samples were rolled flat onto NaCl supports prior to analysis. Both the fibre substrates and the fibre composite samples were recorded from single flattened filaments. Spectra from a range of filaments within a given sample indicated a uniform chemical composition. All i.r. spectra were recorded at 8 $\mathrm{cm^{-1}}$ resolution.

U.v. spectroscopy

All u.v. spectra were recorded in the range 200–400 nm (referenced to water) using a 10 mm quartz cell with a Philips PU 8720 instrument.

RESULTS AND DISCUSSION

As far as we are aware, there have been relatively few SIMS studies on conducting polymers reported in the literature. Chan *et al.* have recently examined polyaniline samples by static SIMS[32], but we were unable to find any publications focusing on SIMS analysis of polypyrrole samples.

The fibre composite samples were both heavily contaminated with the usual extraneous impurities (fatty acids, oils, etc.) and it was very difficult to obtain any useful structural information on the polypyrrole overlayers using the TOF-SIMS technique. However, utilizing the negative ion mode of this instrument allowed us to focus on the nature of the aromatic sulphonate dopant anions rather than the cationic polypyrrole chains. The TOF-SIMS spectra of our control samples, 5-sulphosalicyclic acid dihydrate and 1,5-naphthalenedisulphonic acid (disodium salt) in the mass range 100–300 are shown in *Figure 1*. The 5-sulphosalicylic acid spectrum exhibits a large parent ion peak at 217 and smaller peaks at 199, 172 and 137 due to loss of water, COOH and $\mathrm{SO_3H}$, respectively. The peak at 297 is probably due to substitution of the OH proton in the parent ion by $\mathrm{SO_3H}$. The 1,5-naphthalenedisulphonic acid (disodium salt) spectrum exhibits no parent ion peak at 286 since this would be doubly charged, but there is a peak at 143 due to the symmetric break-up of this parent ion. There are also two major peaks at 206 and 207 which are probably due to loss of $\mathrm{SO_3}$ (giving $\mathrm{C_{10}H_6SO_3}$-; 206), and addition of H to this latter fragment (i.e. $\mathrm{C_{10}H_7SO_3}$-; 207).

The TOF-SIMS spectra of both the polypyrrole–textile composite and the polypyrrole–quartz composite over the same 100–300 mass range clearly show all four peaks at 217, 199, 172 and 137 expected for the 5-sulphosalicylate dopant ion (see *Figure 2*). However, there is no evidence for the peaks at 206 and 207 expected for the 1,5-naphthalenedisulphonate dopant anion (the peaks between 240 and 290 are due to surface contaminants, e.g. fatty acids, esters, etc.). Thus the TOF-SIMS analyses unambiguously confirm the presence of the 5-sulphosalicylate anion in our polypyrrole–fibre composites but do not provide any evidence for the

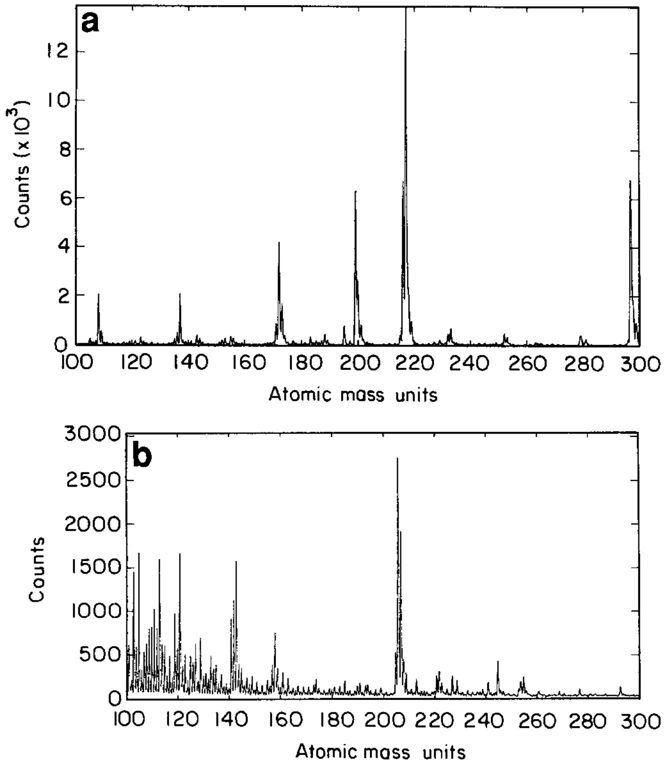

Figure 1 TOF-SIMS spectra of the control samples (a) 5-sulphosalicyclic acid and (b) 1,5-naphthalenedisulphonic acid (disodium salt)

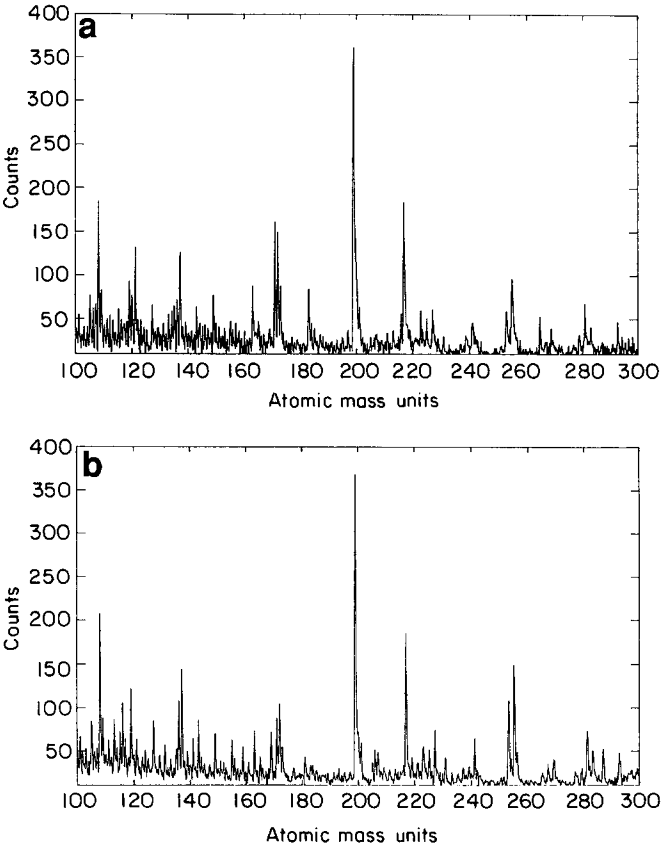

Figure 2 TOF-SIMS spectra of (a) the polypyrrole–polyester textile composite and (b) the polypyrrole–quartz textile composite

presence of the 1,5-naphthalenedisulphonate anion. It is true that the 1,5-naphthalenedisulphonate anion is present at a lower initial concentration than the 5-sulphosalicylate anion in the pyrrole polymerization procedures described by the Milliken group (see Experimental section), but nevertheless we were rather surprised to find no evidence for the former species in our TOF-SIMS spectra. However, we knew that the TOF-SIMS technique is very surface-specific, with a typical sampling depth of only 10 Å. Thus, it was conceivable that the 1,5-naphthalenedisulphonate anions were actually present in the *bulk* of the overlayers but, for some unknown reason, were depleted from the *surface* of these composites. Indeed, Kuhn *et al.* have shown that the u.v. spectra of aqueous basic solutions utilized to dedope their conducting polymer–fibre composite samples contained absorption peaks characteristic of *both* dopant anions[29]. Furthermore, we noted that the Milliken group have reported significant and reproducible improvements in both the conductivity and the thermal stability of polypyrrole–textile composites prepared from experiments which utilize the 1,5-naphthalenedisulphonate salt relative to similar experiments in which this species is deliberately excluded[29]. Therefore we carried out a similar, albeit qualitative, u.v. spectroscopic analysis of a 1.25 M NaOH solution which was used to dedope our own polypyrrole–polyester textile sample. We observed an absorption envelope with fine structure at 287, 298 and 320 nm (not shown) which is characteristic of the 1,5-naphthalenedisulphonate anion. Thus we conclude that both aromatic sulphonate dopant anions are *present* in the polypyrrole–polyester fibre composite, although for some unknown reason only the 5-sulphosalicylate anion is present at a significant concentration at the *surface* of the sample.

Our *FT* Raman spectra of the 5-sulphosalicylic acid and the 1,5-naphthalenedisulphonic acid (disodium salt) control samples are shown in *Figure 3*. The former species has a strong Raman peak at 789 cm^{-1}, whereas the latter control sample has an intense peak at 1356 cm^{-1}. Prior to our examination of the composite samples we anticipated that if the polypyrrole overlayers contained either (or both) of these dopant anions then the above-mentioned bands were the ones most likely to be observed in addition to spectral features due to the polypyrrole component and the polyester/quartz underlying substrates. The *FT* Raman spectra of the polypyrrole–polyester composite and the original untreated polyester substrate are shown in *Figure 4*. The

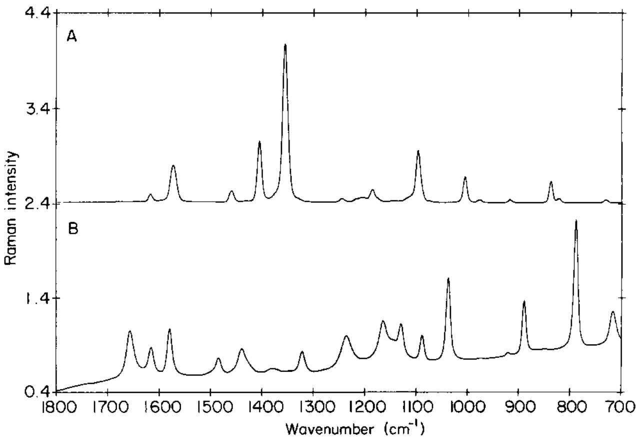

Figure 3 *FT* Raman spectra of the control samples (A) 1,5-naphthalenedisulphonic acid (disodium salt) and (B) 5-sulphosalicyclic acid

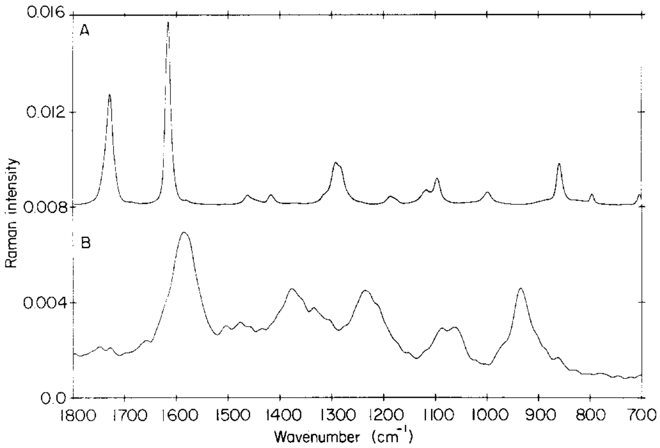

Figure 4 *FT* Raman spectra of (A) the untreated polyester textile and (B) the polypyrrole–polyester textile composite

most prominent Raman peaks observed in the spectrum of the composite sample are due to the polypyrrole component (and are in good agreement with the literature spectra of electrochemically synthesized polypyrrole films[33,34]) although this composite sample consists of at least 95% polyester substrate by mass! An essentially identical spectrum (not shown) was obtained for the polypyrrole–quartz composite. Furthermore, neither spectrum contains any features attributable to either of the two aromatic sulphonate dopant anions. In the case of the 1,5-naphthalenedisulphonate dopant anion, whose presence has already been confirmed by our u.v. experiments, its 1356 cm^{-1} peak (and other lesser peaks) is probably 'lost' under the spectral features due to the cationic polypyrrole chains. However, the absence of the 789 cm^{-1} peak due to the 5-sulphosalicylate species (whose presence has been confirmed by our TOF-SIMS experiments) is not so easily explained. In principle this peak should be easily observable since the Raman spectrum of polypyrrole is relatively featureless from 750 to 800 cm^{-1}. We note that other workers have recently discussed the difficulties of assigning bands due to dopant anions in the vibrational spectra of polypyrrole films[35].

Why do the underlying polyester and quartz substrates contribute so little to the Raman spectra of the composite samples? We believe that the Raman radiation scattered by both these substrates is rather efficiently reabsorbed in each case by the polypyrrole overlayer (i.e. total internal absorption). Actually, a close inspection of *Figure 4* reveals several weak Raman bands due to the underlying polyester substrate at 1728, 1615 (shoulder) and 859 cm^{-1} in the spectrum of the polypyrrole–polyester composite. The observed low intensity of these latter features is entirely consistent with extensive coverage of the fibre substrates by the conducting polymer (if a significant fraction of substrate had remained uncoated then these substrate bands would be more intense).

A typical scanning electron micrograph of the polypyrrole–polyester textile composite is shown in *Figure 5*. This high quality image was obtained *without* sputter-coating the sample. In earlier work we described the characterization of polypyrrole–quartz composites by scanning tunnelling microscopy[28]. Each of these two techniques require electrically conductive samples, thus our results are indirect evidence for essentially *continuous* overlayers of polypyrrole over both types of fibre substrate.

Our *FT*i.r. microscopy studies of the polypyrrole–fibre composites were rather disappointing. The i.r. spectra of these composites were dominated by features due to the underlying polyester and quartz substrates, respectively, with little spectroscopic evidence for the polypyrrole overlayer in either sample. This is illustrated for the polypyrrole–polyester composite and the corresponding polyester substrate in *Figure 6*. The i.r. spectrum of both this composite and that of the polypyrrole–quartz composite contains only a single, weak band at

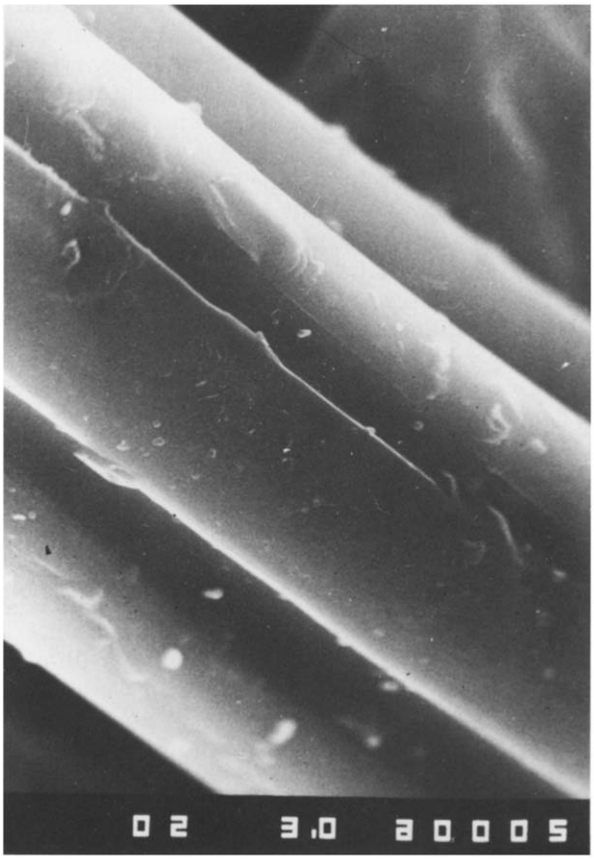

Figure 5 Typical scanning electron micrograph of the polypyrrole–polyester textile composite. This image was obtained *directly* without sputter-coating the sample

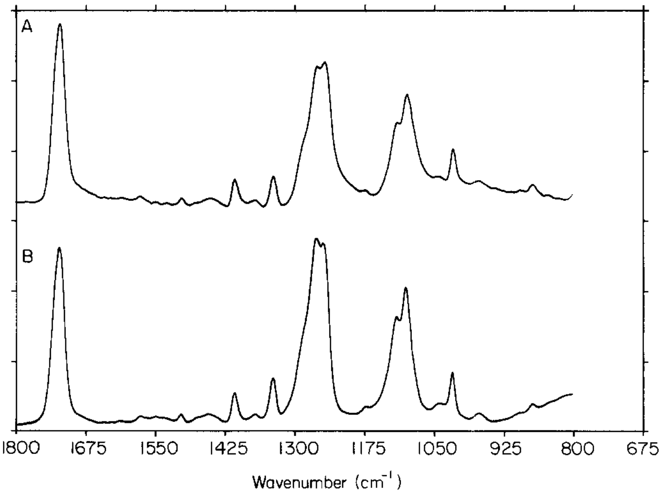

Figure 6 *FT*i.r. microscopy spectra of (A) the untreated polyester textile and (B) the polypyrrole–polyester textile composite

1549 cm^{-1} attributable to the polypyrrole component. These observations reflect the fact that such i.r. measurements probe the bulk (rather than just the surface) of the composites which, as previously stated, comprise at least 95% fibre substrate by mass. Thus our *FT* Raman and i.r. measurements provide *complementary* information about the conducting polymer composites.

CONCLUSIONS

Using a combination of TOF-SIMS and u.v. spectroscopy we have confirmed that the Milliken polypyrrole–fibre composites contain both the 5-sulphosalicylate and the 1,5-naphthalenedisulphonate species as dopant anions. Furthermore, the TOF-SIMS technique confirms that only one of these dopants (the 5-sulphosalicylate anion) is present at a significant concentration in the *surface* (top 10 Å) of these composites. At present we have no satisfactory explanation for the surface depletion of the 1,5-naphthalenedisulphonate species.

FT Raman spectroscopy is suitable for the characterization of the cationic polypyrrole chains in the conducting polymer overlayer but yields surprisingly little information on either the dopant anions or the underlying substrate. In contrast, our *FT*i.r. microscopy spectra were dominated by the substrate component of the composites, particularly for the polypyrrole–polyester sample. Thus our *FT* Raman and i.r. measurements provide *complementary* information about the conducting polymer composites.

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