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Effective width of interface in a stressed model polymer composite measured by micro-FTi.r.

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The effect of mechanical deformation, produced either by an externally applied strain or by an indentation imprint, on the local spectral response of a polymer was studied by micro-FTi.r. spectroscopy. Two types of specimens were used, a urethane–acrylate polymer film, and a SiC/urethane-acrylate model composite, respectively. The width R of the interfacial zone beyond which the fiber has no influence on the matrix, a parameter that plays a key role in micromechanical models of stress transfer in composites, was measured by micro-FTi.r. for the first time. © 1997 Elsevier Science Ltd.

(Keywords: composites; micro-FTi.r.; interface width)

Introduction

Mechanical stress profiles in the fibrous phase of a composite material may sometimes be quantitatively evaluated by means of modern tools such as micro-Raman spectroscopy[1,2]. Fibers such as graphite and poly(*p*-phenylene-terephthalamide)—or kevlar—are indeed Raman-sensitive, in the sense that, under varying degrees of mechanical loading, frequency shifts are observed in specific peaks. Fiber–matrix interface characteristics, such as the efficiency of stress transfer, may then be accurately determined from such measurements. However, it is difficult to deduce from these measurements the extent of strain or stress effects induced within the matrix. There are indications[3–5] that these effects may be of importance, as the local physical (and possibly chemical) properties of the matrix close to the fiber undergo definite changes. Most polymeric matrices (with the possible exception of polydiacetylene, R.J. Young, private communication) do not appear to exhibit shifts in their Raman peaks, and therefore Raman spectroscopy is usually not appropriate to map the stress field in the matrix surrounding a fiber.

A number of studies have been carried out in the past to assess changes in the i.r. spectra of polymers induced by deformation[6–8]. Typically, a polymer film was subjected to a tensile stress or strain and the changes in position, intensity, and band shape of certain 'stress-sensitive' bands were investigated[9,10]. This idea may possibly be further extended, and microscope FTi.r. studies of the spectral changes in a polymer matrix close to the surface of a fiber could be useful in the assessment of induced stress effects in that region. There are strong indications that there is an "effective" width R to the interface, beyond which the fiber's influence on the matrix becomes negligible. This parameter (which is termed r_e in Li and Grubb's paper[4]) is the radius of the matrix at which the strain in the matrix becomes equal to the average matrix strain. It is a key parameter in the assessment of the adhesion energy and the interface properties[11]. Some theoretical arguments[12], as well as rough estimations[4], have been proposed for the numerical value of R, which in fact has never been measured accurately.

We present here an approach based on microscope FTi.r. spectroscopy, to measure the value of R close to a SiC fiber, within a UV-curable urethane-acrylate based polymer matrix. This matrix was used extensively in our (recent work with single-fiber microcomposites[11]. To the best of our knowledge, micro-FTi.r. has so far not been applied to study the fiber–matrix stress transfer issue.

Experimental

The i.r. absorption spectra were obtained using a Bomem MB-100 FTi.r. spectrometer, combined with a Spectra-Tech i.r. microscope. The measurements were performed in the transmission mode with a resolution of 4 cm^{-1}, 128 scans, and using a 0.08 mm × 0.08 mm mask window. This window effectively represents the size of the beam spot. Each measurement took about 3 min. Two kinds of samples were used: (i) a 16 mm × 6 mm × 0.13 mm UV-cured polymer film (urethane/diacrylate oligomer EBECRYL 4858, Radcure Products, UBC Chemicals) with 2% b.w. of benzyl ketal photoinitiator (IRGACURE 651, Radcure Products, UBC Chemicals) with a 140 mm thick SiC fiber (SCS-6 Avco Specialty Materials TEXTRON) embedded in its mid-plane; (ii) a similar but fiber-free specimen, in which a 140 mm square pyramidal Vickers indentation (with apical angle of 136°) was imprinted using a Leitz Metallux-3 microindentor, with a 4 N load. Microscope FTi.r. data were collected as the specimen was progressively strained to various degrees of extension by means of a hand-driven tensile testing device. The extension data were recorded by means of a micrometer. The mechanical properties of the polymer films were measured in separate experiments using an Instron 4502 tensile tester. These measurements included stress–strain and stress–relaxation curves.

Results and discussion

The mechanical deformation of the UV-cured urethane-acrylate polymer was studied by monitoring the changes in

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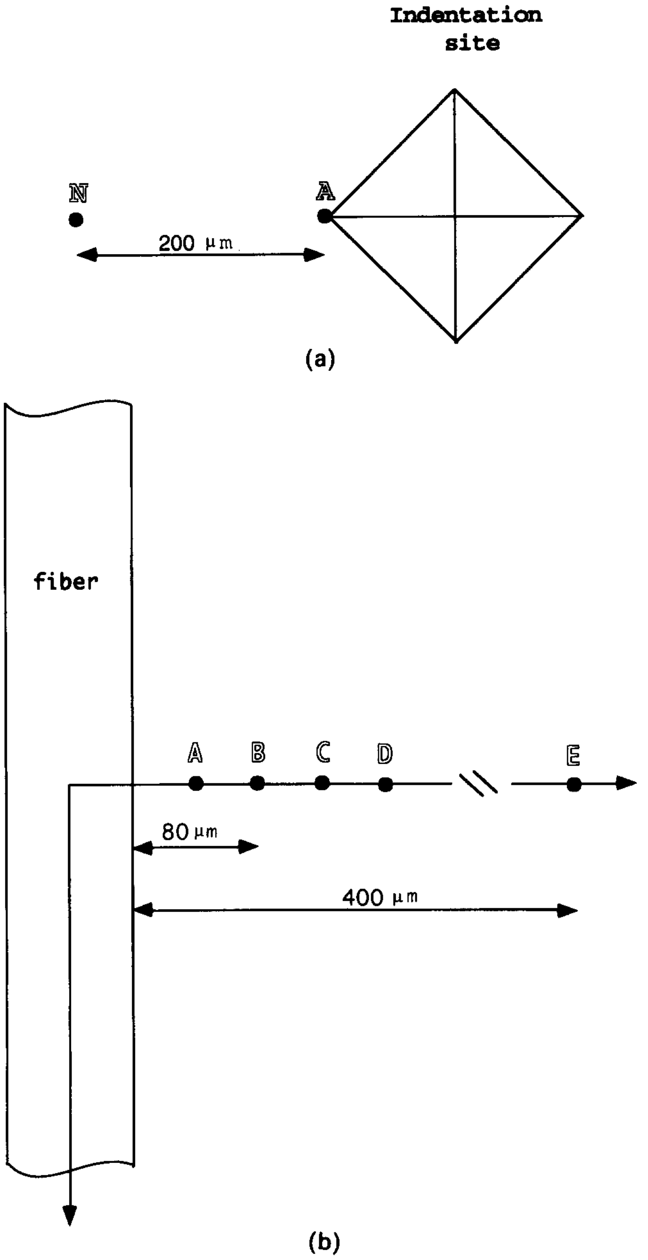

Figure 1 Sites studied by micro-FTi.r.: (a) near an indented region in the pure polymer film; (b) near a fiber in a single-fiber composite

position and intensity of specific i.r. bands in the 1100–750 cm^{-1} region of the i.r. spectrum. The 985 cm^{-1} (characteristic of the –CH wag), 811 cm^{-1} (=CH$_2$ twist), and 774 cm^{-1} (–NH wag) bands were used in the analysis. Micro-FTi.r. measurements were performed at specific sites of the indented polymer film (as shown in *Figure 1a*) and of the single-fiber composite (as shown in *Figure 1b*).

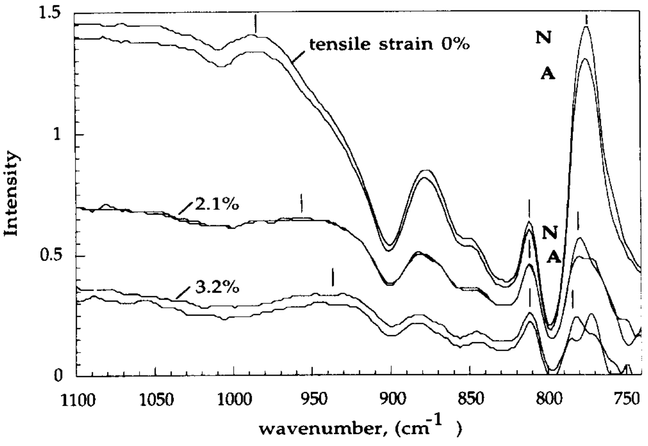

Figure 2 Effect of strain upon FTi.r. spectrum in an indented polymer, at points A and N

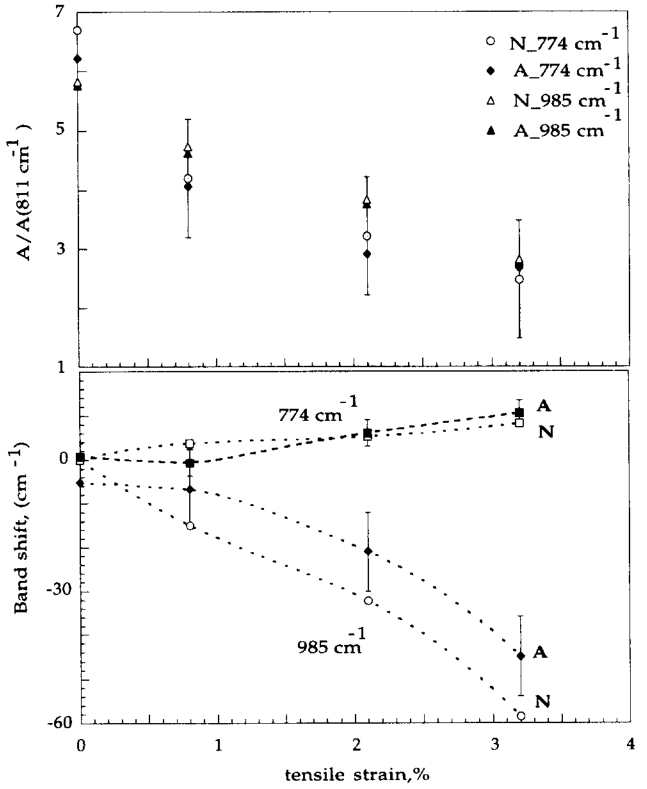

Figure 3 Area ratios for the 774 cm^{-1} and 985 cm^{-1} bands, relative to the 811 cm^{-1} band, and frequency shift, as a function of tensile strain. For clarity, error bars are shown for selected data sets only (the missing error bars are of the same order of magnitude as those shown)

Indented polymer. Changes in the intensity of specific peaks in the i.r. spectrum were studied as a function of applied strain in the indented film. A typical result away from the indentation (site N in *Figure 1a*) is shown in *Figure 2*. As seen, both intensity variations (in the 774 cm^{-1} peak for example) and bands shifts (in the 985 cm^{-1} for example) can be observed, due to tensile strain. The 985 cm^{-1} band is broad, but although the maximum of the peak is at times difficult to pinpoint, there is no doubt that there are some strong changes in the peak location. It is possible that the 985 cm^{-1} band is a composite band but, even if it were so, the shift exists and the only change would be in the *amount* of shift (assuming that only one of the presumed hidden peaks is shifting). The broadness and flatness of the band is due to spectral saturation caused by the thickness of the polymer film. The changes in the band intensities were normalized with respect to the change in intensity of the 811 cm^{-1} band (thus only relative intensity changes were considered), so as to eliminate as much as possible the effects of a changing baseline.

Comparing the spectra at points N (far from the indentation) and A (near the sharp edge of the pyramidal indent), a decrease in intensity of the 774 cm^{-1} band at both points is observed (*Figure 2*), as a result of an increase in applied tensile strain. This effect was observed in the past

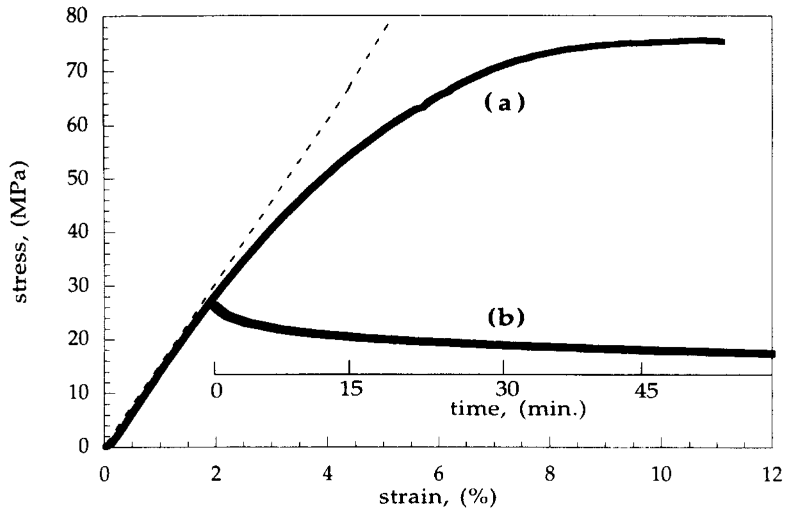

Figure 4 (a) Tensile stress–strain curve, and (b) stress–relaxation curve of the polymer film

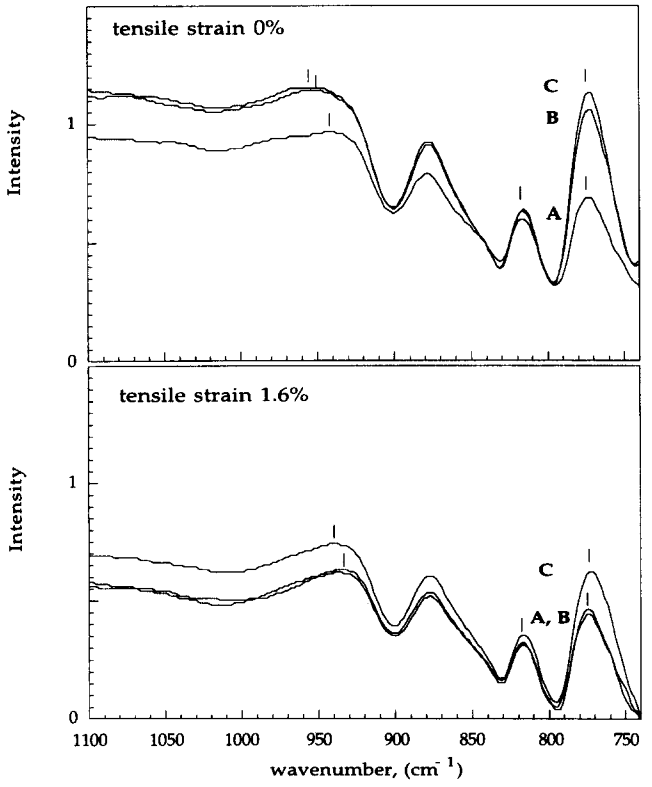

Figure 5 Micro-FTi.r. spectra at points A, B, and C (see *Figure 1b*) of the single fiber reinforced polymer film, in the unstrained and strained states

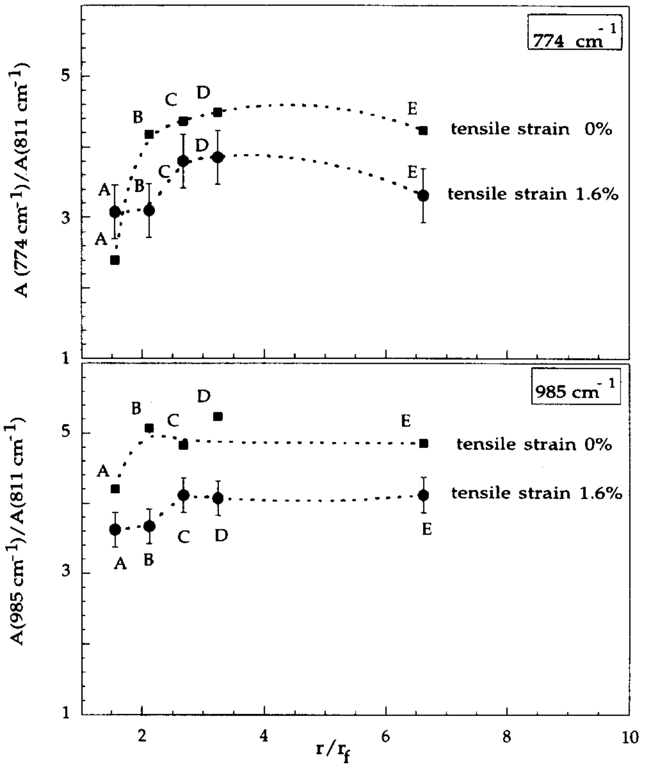

Figure 6 Area ratios for the 774 cm^{-1} and 985 cm^{-1} bands, relative to the 811 cm^{-1} band, as a function of radial position r in the vicinity of the single fiber (r_f = fiber radius). For clarity, error bars are shown for selected data sets only (the missing error bars are of the same order of magnitude as those shown)

for other polymers[9,10,13] and is thought to be due to conformation changes in the molecular network. This is further emphasized in *Figure 3*, where normalized peak areas are plotted for both points A and N with respect to applied strain (as stated earlier, the 811 cm^{-1} band, for which only a very small intensity change could be detected, was taken as reference peak). A change in the rate of peak area decrease is observed at a strain of 1.5%, approximately, corresponding to the yield strain of the polymer (such effects were observed in the past for other polymers as well[13]). *Figure 2* also reveals frequency shifts at specific wavenumbers, namely, the 985 cm^{-1} and 774 cm^{-1} bands, also seen in *Figure 3* for points A and N. Regarding the 985 cm^{-1} band, the peak shift difference between points N and A probably reflects the absence and presence, respectively, of perturbating local residual strain induced by the indentation[14]. The effect of stress relaxation, which may arise during i.r. testing of the polymer film, was found to be mild only (*Figure 4*), and was not considered further.

Single-fiber composite. Two types of micro-FTi.r. data are shown in *Figure 5*, for unstrained and 1.6% strained specimens, respectively. Changes in the FTi.r. spectra along the radial direction are observed. The peak shift, resulting from the specimen preparation alone, is about 10 cm^{-1} (no applied strain), and it is about half that value under a strain of 1.6%. The variations of normalized area ratios A(774 cm^{-1})/A(811 cm^{-1}), A(985 cm^{-1})/A(811 cm^{-1}) as a function of radial position are shown in *Figure 6*.

The major result from these data is that it is possible to determine the width *R* of the interfacial zone beyond which the fiber has no influence on the matrix. The spectral changes observed reflect a strong increase of the strain close to the fiber, and its progressive decrease (within 2–4 fiber radii) from the fiber surface. In other words, the value of *R* is about 2–4 fiber radii for the material system used here. This result is in good agreement with other estimations[4,5] as well as with our own assumption in recent work[11]. Although this was not the purpose here, it is possible to translate the spectral changes observed into a local matrix strain or stress, provided that more accurate measurements are made. Assuming small strains, the peak area and frequency changes may be assumed to be proportional to the local strain (or stress). One might then use point D (*Figure 1b*) as a reference point where the local strain in the matrix is equal to the applied tensile strain, and then calculate the local strains at points A, B, C, and E relative to the reference point, based on peak area variations and on peak shift variations. This work will be performed in the near future.

Conclusions

It is possible to use micro-FTi.r. spectroscopy to detect changes in band characteristics (width, area, shape, etc) within a well-defined matrix region near a fiber, due to the presence of the fiber, and detect additional changes due to the application of a mechanical deformation. It is then possible to translate this information into a local stress or strain, although we only limited ourselves here to the measurement of the width of the zone beyond which the fiber has no effect on its surrounding matrix. The beam width used in this work was about 80 μm and we therefore found it preferable to use a thick SiC fiber in a matrix as a model system (this also dictates a minimum thickness for the matrix, which may create problems of spectrum saturation). As long as the nature of the fiber–matrix interface does not change significantly when moving from a 100 μm fiber to a 10 μm fiber (these dimensions are both much larger than the polymer network scale), the measurements of fiber-induced perturbation should remain valid. For the SiC-based polymer composite studied here, we found that **R**~2–4 fiber diameters. We plan to extend the technique to map the strain field in a polymer matrix with high fiber content, and to other systems.

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