MATRIX STRAIN FIELD MAPPING AROUND EMBEDDED FIBRES USING POLARISED RAMAN MICROSCOPY

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SUMMARY: Thermal residual strain distribution in the matrix around embedded fibres in a carbon-polycarbonate single fibre composite has been measured using polarised Raman Microscopy. The method is based on the identification of changes of the molecular orientation distribution due to the presence of the strain field. Molecular orientation distribution is quantified through a series expansion of Legendre functions where the coefficients of the series are determined from the Raman scattering intensities by varying polarisation directions of incident and scattered light. The relation between the elements of the strain tensor and the coefficients of the Legendre series are obtained by straining the polymer uniaxially at different orientations to the polarisation directions. Results indicate that a quantitative measure of shear strain can obtained directly from scattering intensities

KEYWORDS: Polarised Raman spectroscopy, matrix strain measurement, interfacial shear stress distribution.

INTRODUCTION

The mechanical properties of composites depend on the ability of stress transfer at the interface. When external load is applied to a composite stress is transferred from the matrix to the fibre. This interaction between the two phases is reflected by the local deformation pattern in fibre and matrix. Theoretical approaches to describe the load transfer phenomena are based on assumptions regarding the stress distribution in the matrix as well as mechanical behaviour. An experimental characterisation of this local deformation pattern can provide thorough understanding of the load transfer phenomena and lead to improvement or verification of existing models. Using Raman spectroscopy it is possible to measure strain in embedded fibres. Batchelder and co-workers[1] showed that the Raman scattering frequency depends on strain due changes of the interatomic spacing. This phenomena was shown to occur in highly ordered, crystalline fibres such as aramid and carbon. By measuring the strain distribution along embedded fibres the interfacial shear stress can be calculated from force equilibrium at the interface. The Raman technique could then be used to monitor the micro mechanics of composites reinforced by these

fibres. This method has proved very useful to study the interfacial phenomena. However based on the fibre strain distribution the strain field in the surrounding matrix cannot unambiquisly be determined. It is therefore of interest to establish an experimental technique applicable to strain measurement in the matrix phase. This will enable formulation of an improved load transfer model. Measurement of strain in isotropic polymers using the Raman technique is difficult as the frequency shifts of the Raman bands of these materials usually are very small and difficult to detect [2]. Such measurements have not yet been successful unless the strain has been very high. Further difficulties arise in the separation of band shifts related to the different elements of the strain tensor. Another approach to measure strain in isotropic polymers is to study the change of molecular orientation and its interaction with light. This is the basis of the photo-elastic method where the strain state within the material gives rise to a birefringe pattern. The photo-elastic approach has been used by Fiedler and Schulte [3] on glass-epoxy composites. Another approach based on the same phenomena is to use light scattering techniques such as X-ray, infrared and Raman, to characterise the change of molecular orientation. Both infrared and Raman spectroscopy are applicable to amorphous materials. Raman spectroscopy gives more detailed information than infrared spectroscopy and has been widely used to characterise molecular orientation in polymers. Initial studies have shown that the intensity of certain Raman bands of polycabonate are very sensitive to strain, whereas the no significant variation in band position with strain has been detected. This indicates that intensity measurements may provide a measure of strain in amorphous/isotropic polymers.

THEORY

Consider a small representative plane element subjected to a state of strain with the principal strains, ε_1, ε_2 at an angle β to a reference system. The deformation causes a rotation of the structural units of the polymer resulting in a preferred orientation distribution towards the direction of maximum extensional strain, Fig.1.
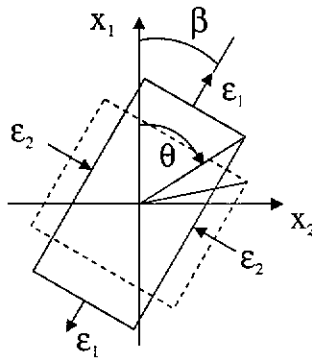

Fig. 1: Rotation of structural unit due to deformation

If a relation between the strain tensor, ε_{ij}, and the molecular orientation distribution can be obtained the strain state may be determined from a quantification of the molecular orientation distribution.

When a birefringent, isotropic polymer is deformed the polarisation properties are changed which alters the interaction between the electromagnetic field of light and the molecular entities of the polymer. The present approach to strain measurement is based on this phenomena and requires a quantification of the molecular orientation distribution from the Raman scattering.

Characterisation of molecular orientation using polarised Raman spectroscopy

Consider a structural unit of the polymer. This may be a polymer chain or a group of atoms. The polarisability of the structural unit is given by the second rank polarisability tensor, α_{ij}, which determines the amplitude of scattered radiation through the equation

$$E_i(\omega) = const \sum_{j=1}^{3} \alpha_{ij} E_j^0(\omega_0) \cos(\omega t + \delta) \tag{1}$$

The Raman scattering intensity, I_s, of the structural unit is determined from the relation $I_s = I_0 \sum (\sum_{ij} \alpha_{ij} l'_i l_j)^2$, where l'_i, l_j are direction cosines of the polarisation of incident and scattered light. The scattering intensity depends on the orientation of the scattering units with respect to the polarisation directions. Assuming the distribution of orientations to be uniaxially symmetric with respect to the x_1 axis the orientation of the structural unit in the deformed state can be expressed in terms of a single Euler angle θ, Fig.1. For such a distribution of orientations, $N(\theta)$, where $N(\theta) \sin \theta d\theta$ is the fraction of units having orientation within the solid angle $\sin \theta d\theta$ and $2\pi \int_0^\pi N(\theta) \sin \theta d\theta = 1$, the Raman scattering intensity can then be expressed as[4]

$$I_{ij} = I_0 4\pi^2 \int_{-1}^{+1} N(\theta)(l'_i l_j \alpha_{ij})^2 d\xi \tag{2}$$

where $\xi = \cos(\theta)$. From measured values of I_{ij} it is possible to obtain some quantitative information of the form of the orientation distribution function. Following Bower[4] the orientation distribution function is expressed in terms of a series expansion of Legendre functions

$$N(\theta) = \frac{1}{2\pi} \sum_l \left(\frac{2l+1}{2} \right) a_l P_l(\cos(\theta)) \tag{3}$$

Due to the orthogonality of the Legendre functions it follows that the coefficients a_l are the averages $\langle P_l(\cos\theta) \rangle$ of the corresponding polynomials $P_l(\cos(\theta))$ taken over the distribution of orientations[2]. $\langle P_l(\cos(\theta)) \rangle$ will in the sequel be written as P_l. For isotropic polymers $P_0 = 1$, $P_l = 0$, $l \neq 0$. If the assumption is made that the two opposite directions along the chain axis are equivalent, then $N(\theta) = N(\pi - \theta)$ and only even values of l give non-zero coefficients. From the series expansion of the orientation distribution function the scattering intensity can be written as

$$I_{ij} = I_0 4\pi^2 \sum_l P_l A_{ij}^{(l)} \tag{4}$$

where

$$A_{ij}^{(l)} = \frac{1}{2\pi}\left(\frac{2l+1}{2}\right)\int_{-1}^{+1} P_l(\cos\theta)(l_i'l_j\alpha_{ij})^2 d\xi \tag{5}$$

$A_{ij}^{(l)}$ are known quadratic functions of the elements of the polarisability tensor, α_{ij} and have been tabulated by Bower [4]. For a backscattering configuration two independent intensity ratios can be determined

$$R_1 = \frac{I_{12}}{I_{11}} = \frac{\sum_l P_l A_{12}^{(l)}}{\sum_l P_l A_{11}^{(l)}}, \quad R_2 = \frac{I_{12}}{I_{22}} = \frac{\sum_l P_l A_{12}^{(l)}}{\sum_l P_l A_{22}^{(l)}} \tag{6}$$

which provides two equations from which the first two coefficients, P_2 and P_4 ($P_0 = 1$), of the Legendre series can be determined provided the values of the functions $A_{ij}^{(l)}$ are known. For a cylindrical Raman tensor, where $\alpha_{11} = \alpha_{22}, \alpha_{ij} = 0, i \neq j$ the functions $A_{ij}^{(l)}$ can be expressed in terms of the ratio α_{11}/α_{33} which can be determined from measurements on isotropic samples where $P_l = 0, l \neq 0$. According to Bower[5] P_2 and P_4 are adequate to characterise uniaxially symmetric distributions.

Relation between strain tensor and orientation parameters

In order to measure strain it remains to establish a relation between the strain tensor and the orientation parameters. This relation may generally be written as

$$P_l = k_{ij}^{(l)} \varepsilon_{ij} \tag{7}$$

for $i, j = 1, 2$. Writing ε_{ij} in terms of principal strains, ε_1 and ε_2 where $\varepsilon_1 = e$ and $\varepsilon_2 = -\nu e$, Eq.7 becomes $P_l = K^{(l)}(\beta)e$ where β is the direction of applied strain, e (Fig.1). The function $K^{(l)}(\beta)$ are given by

$$\begin{aligned}
K^{(l)}(\beta) &= \frac{1}{2}(\cos(2\beta)(k_{11}^{(l)} - k_{22}^{(l)}) + (k_{11}^{(l)} + k_{22}^{(l)}) + \sin(2\beta)) \\
&\quad -\nu(\cos(2\beta)(k_{22}^{(l)} - k_{11}^{(l)}) + (k_{11}^{(l)} + k_{22}^{(l)}) - \sin(2\beta))
\end{aligned} \tag{8}$$

By straining a sample at different angles with known strain e, $K^{(l)}(\beta)$ can be determined from measured values of $P_l(\beta)$ using the relation $P_l = K^{(l)}(\beta)e$. From Eq.7 the parameters $k_{ij}^{(l)}$ can then be determined. At least three measurements are required to determine $k_{ij}^{(l)}$. When $k_{ij}^{(l)}$ are determined strain can be determined from the relation $P_l = k_{ij}^{(l)} \varepsilon_{ij}$. As only two coefficients, $P^{(l)}$, can be determined the strain tensor can in general not be uniquely determined.

EXPERIMENTAL

The polymer matrix used was amorphous polycarbonate and the Raman band at 885 cm^{-1} was used to monitor molecular orientation. Earlier investigations have shown that

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this line is strongly affected by molecular orientation[6]. This line have been assigned to C-(C=O)-C stretching in the backbone direction[7]. The Raman band is highly polarised with an intensity ratio in isotropic state of 0.1. An A_{1g} vibrational mode where $\alpha_{11} = \alpha_{22} \neq \alpha_{33}$, $\alpha_{ij} = 0$ for $i \neq j$ was assumed. Raman spectra were excited using a 633 nm line of a HeNe laser. The laser was focused onto the sample through a × 50 objective to give a laser spot of approximately $2\mu m$ in diameter. Scattered light was collected using a diffraction grating and CCD camera. Both incident and scattered light were polarised to give three independent intensity measurements I_{11}, I_{22}, I_{12}.

In order to determine the relation between strain and spectral changes dogbone samples of the bulk polymer were strained uniaxially while recording the Raman spectra. The samples were strained at $\beta=0$, 45 and 90° to the reference frame with uniaxial strain e, Fig.2. In each experiment depolarisation ratios were measured. From the experimen-
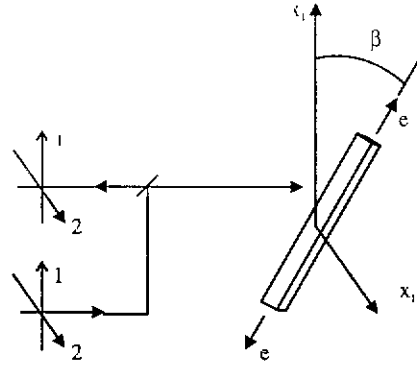

Fig. 2: Geometric arrangement used to determine relation between principal strain and orientation parameter.

tal data $P_l(\beta)$ and thus $K^{(l)}(\beta)$ were determined from which $k_{ij}^{(l)}$ were calculated. Having established a quantitative relation between strain and spectral changes through Eq.7 and Eq.8 a deformation analysis of the composite can be accomplished.

Single fibres (unsized, PAN based high modulus carbon) were embedded in amorphous polycarbonate, Fig.3A. The sample geometry shown on Fig.3A was chosen in order to prevent depolarisation effects.

The single fibre composites were heated to 250°C for 5 min and subsequently cooled at 30°C/min. During cooling residual strains develop as indicated from the birefringes, Fig.3B. The sample was placed on a motorised stage enabling Raman spectra to be recorded at discrete points around the fibre. The sampling area is shown on Fig.3B. $x_1, x_2=(0,0)$ corresponds to the right upper corner of the fibre.
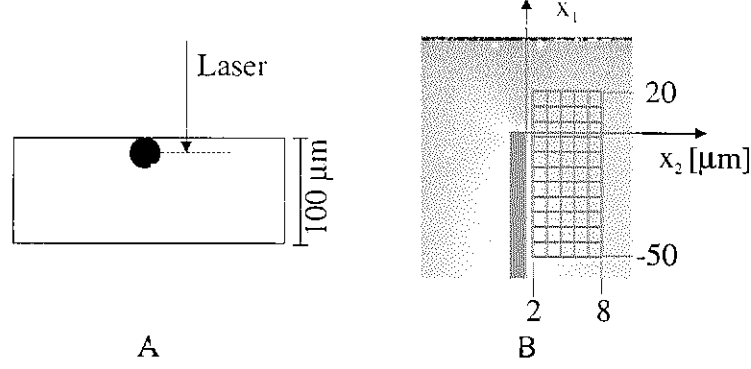
Fig. 3: Raman sampling on micro composite, A) Sample geometry. B) Area mapping around embedded fibre

RESULTS AND ANALYSIS

Strain sensitivity of orientation parameters

Figure 4A shows variation of intensity ratios, $R_n(\beta)(= R_n^\beta, n = 1, 2)$ (Eq.6) as function applied strain e. Data has been fitted to a linear function using least squares method. Error bars indicate the span between maximum and minimum values. Orientation pa-
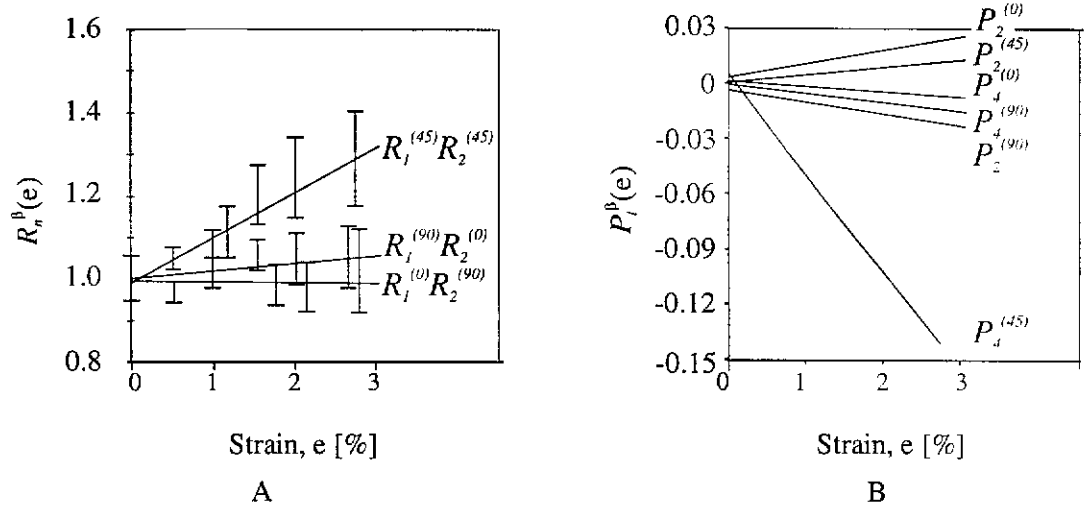

Fig. 4: A) Variation of intensity ratios, R_1 and R_2 as function of applied strain e, B) Variation of orientation parameters as function of strain.

rameters, $P_l(\beta)(= P_l^\beta, l = 2, 4)$ were determined as function of applied strain, e and for the different values of β from the data regressions of R_1^β, R_2^β using Eq.6, Fig.4B. From the measured values of $P_l^{(\beta)}$, $K_n^{(\beta)}$ could be determined and $k_{ij}^{(l)}$ calculated. Values are given in Table 1.

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	$k_{11}^{(l)}$	$k_{22}^{(l)}$	$k_{12}^{(l)}$
$l=2$	5.70	-4.34	7.07
$l=4$	-5.74	-7.16	-71.60

It can be seen that $k_{12}^{(4)} >> k_{11}^{(4)}, k_{22}^{(4)}$ which means that P_4 is much more sensitive to shear strain. A negative value P_4 contributes to an orientation distribution towards 45° equal to the principal direction for pure shear. We may then to a good approximation write

$$\varepsilon_{12} = \frac{P_4}{k_{12}^{(4)}} \qquad (9)$$

Thus based on Eq.9 the shear strain can be determined directly from the measured orientation parameter, P_4. In the following Eq.9 is applied to determine the residual shear stress distribution around embedded fibres.

Strain field mapping of micro composites

Figure 5 shows measured depolarisation ratios around embedded fibre in the carbon-polycarbonate composite. From the variation of the intensity ratios it can be seen that presence of the fibre significantly affects the molecular orientation distribution. The coordinate values corresponds to the reference system shown on Fig.3.
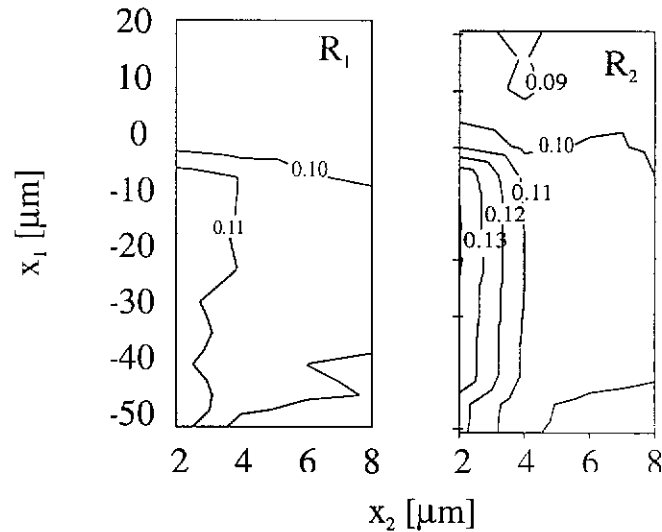

Fig. 5: Variation of intensity ratios around embedded fibre.

From the intensity ratios the orientation parameters P_2, P_4 were determined from which the shear stress was calculated using Eq.9 and the constitutive relation for isotropic polycarbonate, Fig.6A. Results are compared to a Finite Element (FE) analysis, Fig.6B. In the FE analysis temperature dependence of elastic properties of polycarbonate has been taken into account. Results are seen to agree well. However it can be seen that the FE model predicts a more localised shear stress distribution with a maximum towards the fibre end whereas the Raman measurements indicate a broader shear stress distribution along the fibre. This trend has also been observed in photo-elastic analysis and
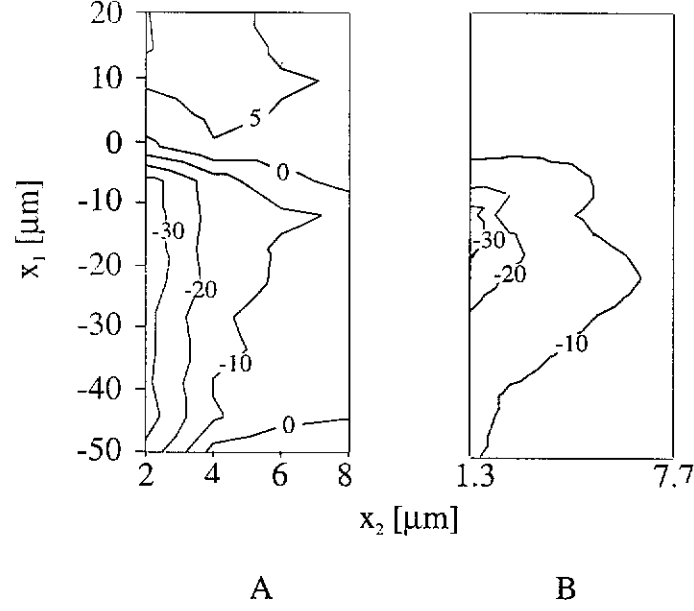
Fig. 6: Shear stress distribution $\sigma_{12}(x_1,x_2)$ [MPa], around embedded fibre, A) Raman spectroscopy, B) Finite Element analysis.

has been suggested to occur due to localised plasticity causing a redistribution of stress. The maximum value of shear stress indeed indicates that plasticity may occur. It is of
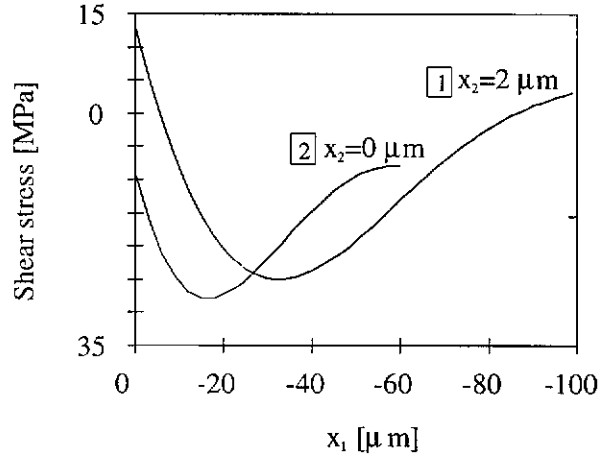

Fig. 7: Interfacial shear stress distribution.

interest to compare to the prediction of interfacial shear stress to Raman measurements based on fibre strain distribution and the balance of force principle. From measurements of residual fibre strain distribution using the 2660 cm^{-1} peak the interfacial shear stress was calculated using the one dimensional equilibrium equation, ($\sigma_{12} = E_{f,1}\frac{d_f}{4}\frac{d\varepsilon_{11}}{dx_1}$), where $d_f = 7\mu$m (fibre diameter) and $E_{f,1}$=350 GPa (longitudinal Youngs modulus of fibre). Figure 7 shows the variation of shear stress close to the fibre using the two Raman approaches (1=matrix measurement x_2=2μm, 2=fibre measurement and balance of force principle x_2=0μm,interface) The curves in Fig. 7 are data regressions using the least

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squares method. It can be seen that results from the two experimental approaches show the same tendency. The shift in the position of maximum interfacial shear stress may partly be explained by the difference in the distance from the fibre (x_2). The results from the matrix measurements were found to agree very well with a photo-elastic analysis reported by Fiedler and Schulte[3].

CONCLUSIONS

A new method to measure strain in the matrix has been developed based on the polarisation theory of Raman scattering. The method has been applied to measure shear stress distribution in the matrix around embedded fibres. Results were found to agree quantitatively with Finite Element and interfacial shear stress distribution determined from Raman measurements of the fibre strain. However the results must be considered preliminary and future work will be directed towards the determination of all the elements of the strain tensor, confocal measurements and extension to biaxial orientation distribution.

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