Micro-Raman mapping of the transition region in the neck region of stretched poly(vinylidene fluoride)

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A micro-Raman mapping of the transition region corresponding to the non-oriented to oriented transformation zone in the neck was obtained for stretched poly(vinylidene fluoride) (PVF_2). Since Raman spectroscopy is a technique sensitive to the change in the crystalline structure in PVF_2 when this polymer is submitted to a stress, the distribution of the crystalline modification along the neck was obtained from the analysis of the micro-Raman mapping. The results show a gradual increase in the degree of crystalline phase transformation along ~200 μm in the stretching direction.

(Keywords: micro-Raman mapping; neck; poly(vinylidene fluoride); crystalline phase transformation)

Introduction

The stress–strain experiment is a particularly valuable test that gives useful information concerning mechanical properties of polymers. However, the deformation process of polymers during the stress–strain experiment, and more generally in any type of mechanical deformation, is complex. As a result, new methods and studies are continuously proposed and developed to complete our present understanding of the deformation process in polymers[1–9]. In this preliminary work, which is part of a more general investigation of the mechanical properties of polymers carried out in this laboratory[9–13], we present a new approach to analyse the neck which is formed when semicrystalline polymers are submitted to uniaxial cold drawing. The method consists of the micro-Raman mapping of the transition zone between the non-oriented and oriented regions. Raman microspectroscopy permits the vibrational analysis of the transition front with a high spatial resolution (in previous work[11], we demonstrated that the best spatial resolution achieved with our micro-Raman instrument is of the order of 2 μm) without any sample preparation that may affect the microstructure of the transition zone. It is well known[14] that the application of a pressure either by compression or tensile stress in poly(vinylidene fluoride) (PVF_2) produces a crystalline transformation from structure II(α) to I(β) that is well characterized by studying the changes occurring in the Raman spectrum. It was found[13] that the degree of crystalline phase transformation augments gradually as the pressure is increased. The outcome of this previous study was used here to follow the evolution of crystalline modification along the region corresponding to the isotropic to the fibrillar structure transition zone.

Experimental

The PVF_2 sample utilized was the commercial material PVF_2 SOLEF-1012 (provided by Solvay & Cie). For the stretching experiment, a 5 mm thick polymer plate was produced by hot-pressing the PVF_2 pellets at 210°C and then allowing them to cool at room temperature.

Two samples were stretched with an Instron universal machine (model 6025) at two different strain rates (1 and $10\,\mathrm{mm\,min^{-1}}$) up to an elongation of ~40%.

The Raman spectrometer used was a Dilor XY instrument using an argon ion laser for the illumination, and consisted of a substractive dispersion double monochromator coupled to a spectrograph combined with multichannel detection (512 intensified diodes). The Raman instrument was coupled to a standard Olympus microscope and the collection optics system was used in the backscattering configuration. The polarization of the incident beam was perpendicular to the stretching direction of the sample. The analysed zone was directly viewed through a ×100 microscope objective and the Raman mapping of the neck region was obtained moving the sample stage in the *x–y* directions. The laser power at the sample position was of the order of 10 mW and the spectral bandpass was fixed at $5\,\mathrm{cm^{-1}}$. A time acquisition of 2 s was used and the number of scans was 50. The Raman spectra were recorded along the stretching direction at intervals of 20 μm, and along the perpendicular direction at intervals of 40 μm, except near the edge of the sample where the chosen interval of the recorded spectra was 20 μm. Here, it should be noted that only half of the thickness of the sample (in the direction perpendicular to the stretching), i.e. ~2 mm, was analysed since it was assumed that the crystalline distribution is symmetrical in relation to the stretching axis.

The optical micrographs were obtained with Nomarski Interference Contrast (NIC) which allowed sharply defined relief-like images to be obtained.

Results and discussion

The optical micrographs of the transition zone of the two samples analysed are given in *Figure 1. Figures 1a* and *b*, obtained with a microscope objective of ×10, clearly indicate the three different zones, i.e. the isotropic region, the transition region and the oriented zone. It can be observed that for both samples the width of the intermediate region is of the order of 350 μm. Thus, it appears that varying the rate of testing does not affect the interval of the transition zone in the range of the

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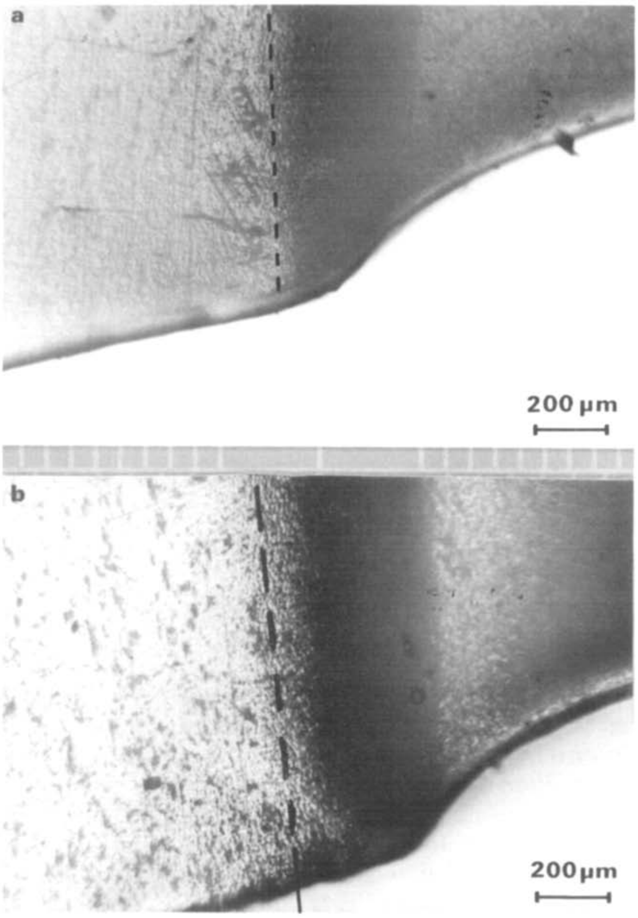

Figure 1 Optical micrographs (×10) of the neck for the two PVF$_2$ samples stretched at (a) 1 mm min^{-1} and (b) 10 mm min^{-1}, showing the isotropic, transition and oriented zones. The broken line indicates the onset of the transition region

testing rates analysed here. It was also observed that the shape and the dimensions of the neck of both samples are very similar.

The crystal transformation in PVF$_2$ from form II(α) to form I(β) can be followed by measuring the intensity of the two Raman bands at 799 and 840 cm^{-1} which are assigned to the non-planar (*TGTG'*) conformation [form II(α)] and to the planar zigzag (*TTTT*) conformation [form I(β)], respectively[15–17].

Figure 2 shows four micro-Raman spectra recorded along the transition zone. In this figure, the crystalline phase transformation from structure II(α) to I(β) is clearly seen as the recorded position is scanned along the transition zone from the isotropic region to the oriented zone.

The relative evolution of the crystalline modification along the neck can be followed by determining the coefficient $R = 100\, I_{840\mathrm{cm}^{-1}}/(I_{840\mathrm{cm}^{-1}} + I_{799\mathrm{cm}^{-1}})$. Here, it must be noted that the orientation of the polymer chains may produce an evolution in the scattering cross-section that may be of different degree depending on the vibrational mode considered and the polarization of the exciting field in relation to the orientation of the sample. The effect of orientation may thus contribute to the evolution of the coefficient *R* along the neck. However, an estimation of the maximum contribution introduced by intensity changes due to the orientation process in the measurement of the crystalline transformation coefficient was determined by measuring *R* in the fibrillar zone with

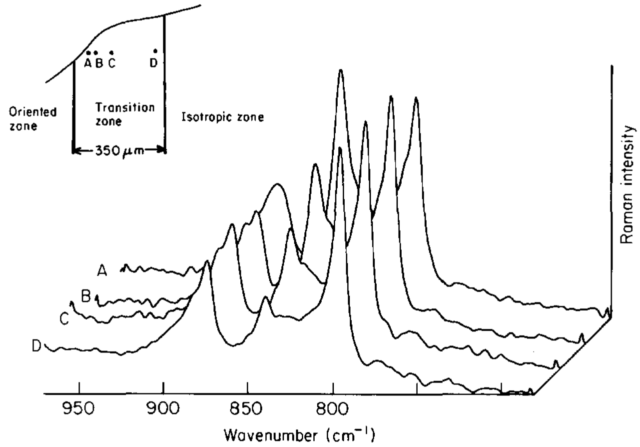

Figure 2 Micro-Raman spectra of PVF$_2$ recorded in the transition zone at positions A, B, C and D

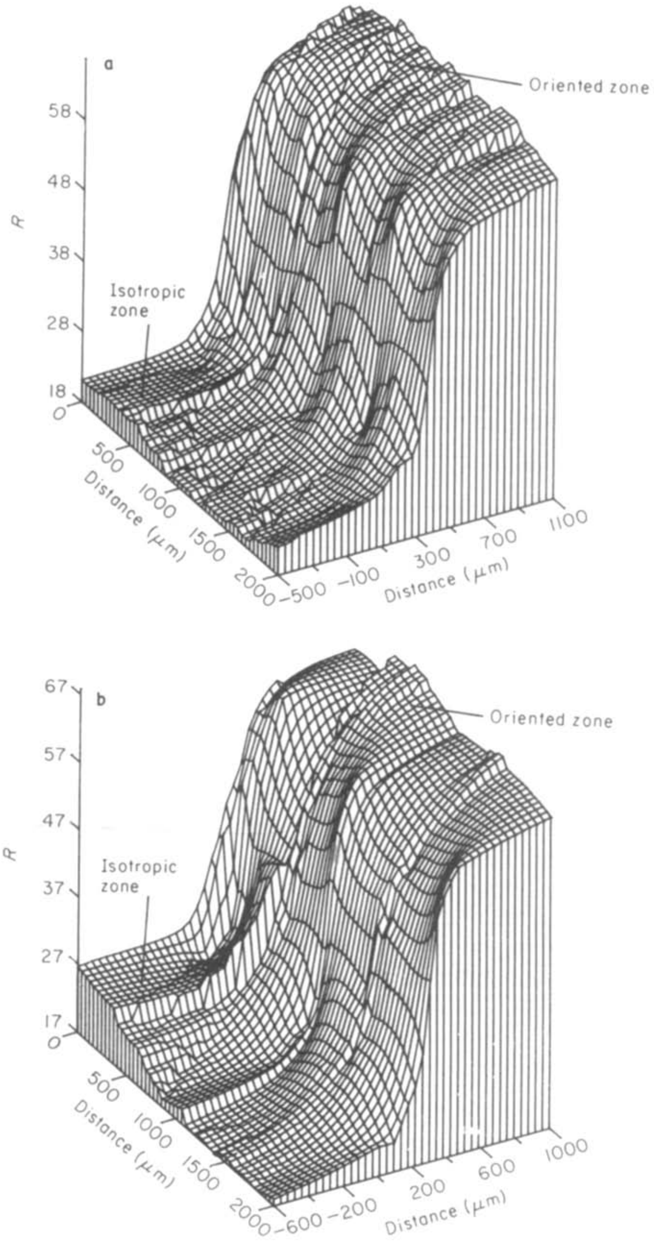

Figure 3 Three-dimensional map representing the coefficient of the crystalline modification *R* along the neck for the two samples stretched at (a) 1 mm min^{-1} and (b) 10 mm min^{-1}

a laser beam polarized parallel and perpendicular to the stretching direction of the sample, respectively. The variation between the two values of R was found to be $\sim 10\%$ whereas in the isotropic region, as predicted by the theory for the backscattering configuration[18], the coefficient R was found to be independent of the polarization of the laser. Such a variation found for the maximum contribution due to orientation ($\sim 10\%$) is much lower than the variation of R along the transition zone, which is $>200\%$. As a result, no attempt was made to correct for the relative intensity change due to orientation.

The coefficient R was determined for each analysed position of the neck and plotted in a three-dimensional map with the help of a graphic program that gives the best interpolation between each recorded point. The outcome for both samples is given in *Figure 3*.

From these results, it can be observed that the variation of the degree of crystalline modification is similar for both testing rates. The crystalline transformation occurs between 200 μm and 600 μm (here the origin along the stretching direction is taken at the beginning of the transition zone as indicated in *Figure 1* by the broken line). Further, most of the crystalline modification varies gradually with the distance along the stretching direction over a transition region of $\sim 200\,\mu$m. In the direction perpendicular to the stretching, the degree of crystalline transformation is found to be nearly constant, thus, the two samples analysed do not present any significant alteration in the crystalline transformation due to the edges. However, near the edges of the neck, the profile of the crystalline phase transformation distribution appears to be different. This is due to the discontinuity and the geometry of the limits of the neck.

Conclusions

It has been illustrated how the micro-Raman technique can be used to provide the distribution of crystalline phase transformation along the neck of stretched PVF$_2$ samples with a high spatial resolution. Also, these preliminary results give new information about the plastic deformation process through the analysis of the change of microstructure in the neck. The whole crystalline transformation occurs along an interval of $\sim 400\,\mu$m. Most of the crystalline modification is also found to vary gradually along the stretching direction over a distance of $\sim 200\,\mu$m. The crystalline phase distribution along the neck shows a very similar pattern for the two strain rates analysed here. Further work which combines this micro-vibrational method with other studies on the cold drawing process in semicrystalline polymers, such as the variation of temperature during neck formation, shape of the neck as a function of experimental conditions, etc., is currently being carried out in order to correlate the mechanical properties with the changes in the microstructure of the polymer.

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References

1 Siesler, H. W. *Pure Appl. Chem.* 1985, **57**, 1603

2 Hendra, P. J., Taylor, M. A. and Willis, H. A. *Polymer* 1985, **26**, 1501

3 Shimamura, K. 'Morphology of Polymers' (Ed. B. Sedlácek), Walter de Gruyter, Berlin, 1986, p. 319

4 Furuta, M., Hosoda, S. and Kojima, K. *J. Appl. Polym. Sci.* 1987, **33**, 401

5 Liu, T. and Harrison, I. R. *Polymer* 1987, **28**, 1860

6 Hammond, C. L., Hendra, P. J., Lator, B. G., Maddams, W. F. and Willis, H. A. *Polymer* 1988, **29**, 49

7 Xu, X., Zasse, B. and Monnerie, L. *J. Polym. Sci. B* 1989, **27**, 355

8 Nakagawa, M., Horii, F. and Kitamaru, R. *Polymer* 1990, **31**, 323

9 Rodriguez-Cabello, J. C., Merino, J. C., Jawhari, T. and Pastor, J. M. in preparation

10 Merino, J. C., Martin, B. and Pastor, J. M. *Meas. Sci. Technol.* 1991, **2**, 740

11 Jawhari, T., Merino, J. C. and Pastor, J. M. *J. Mater. Sci.* 1992, **27**, 2231

12 Merino, J. C., Martin, B., Jawhari, T., Pastor, J. M. and Nieto, J. *Polym. Test.* 1991, **10**, 379

13 Jawhari, T., Merino, J. C. and Pastor, J. M. *J. Mater. Sci.* 1992, **27**, 2237

14 Tashiro, K. and Kobayashi, M. *Phase Transitions* 1989, **18**, 213

15 Boerio, F. G. and Koenig, J. L. *J. Polym. Sci. A2* 1969, **7**, 1489

16 Boerio, F. G. and Koenig, J. L. *J. Polym. Sci. A2* 1969, **9**, 1317

17 Cessac, J. L. and Curro, J. J. *J. Polym. Sci.* 1974, **12**, 695

18 Gilson, T. R. and Hendra, P. J. 'Laser Raman Spectroscopy', Wiley-Interscience, London, 1970, p. 65