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SHORT COMMUNICATION

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Micro-Raman study of the longitudinal acoustic modes (LAM) evolution along the transition front in uniaxially stretched HDPE

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Abstract Low-frequency Raman spectra were recorded along the transition front of uniaxially cold drawn High Density Polyethylene (HDPE) samples with a Raman microscope instrument. The high spatial resolution capacity of the technique allows to analyze the variation of the Longitudinal Acoustic Mode (LAM) along the transition zone between the isotropic structure and the oriented one. The evolution of the LAM over the transition zone was followed by measuring the LAM intensity, bandwidth and position as a function of the distance along the transition front. The LAMs are affected by the stretching process before the transition zone is reached and the lamellar structure was found to be totally disrupted before the fibrillar structure is formed. Whereas the LAM intensity decreases gradually along the transition region, the bandshape and peak frequency do not change significantly, indicating that the distribution of fully planar zigzag segments in the remaining lamellar structure is not really affected during the deformation process. The concentration of lamella, which still remain dimensionally intact, decreases gradually along the transition zone up to the stage where the structure is getting fibrillar.

Key words Micro-Raman – LAM – deformation – polyethylene – transition front

Introduction

The low-frequency Raman spectrum of semicrystalline polymers has been in the past well explored and the study of the Longitudinal Acoustic Mode (LAM) has been found to bring important information on macromolecular crystals [1–7]. It has been recognized that the LAM frequency is directly related to the crystal thickness of the lamellar structure [8–10]. In most samples the lamella are not uniform in thickness and therefore spectroscopic parameters of the LAM such as intensities, positions and shapes were studied in order to determine the distribution of lengths of planar zigzag segments [11–19]. One effect of the broadening due to this distribution of lengths of straight-chain segments is to displace the observed maximum of the LAM away from the frequency that corresponds to the most likely straight-chain length [12, 13, 17]. Several corrections that take into account instrumental parameters (such as finite resolution of the spectrometer), the temperature and frequency effect on the observed intensity have also been introduced in order to calculate the true shape of the LAM and consequently the exact chain length distribution [12, 13, 16–18].

The study presented here is based on the LAM analysis in order to find out the details of morphological changes that take place in polymeric materials when submitted to a stress. Peterlin et al. [20] proposed a deformation mechanism for cold drawing crystalline polymers consisting of three stages: plastic deformation of the original spherulitic structure, followed by a discontinuous transformation of the lamellae into fiber structure by micronecking and finally the plastic deformation of the formed microfibrils. Cold drawing in crystalline polymers forms a transition region of generally a few hundred microns in the neck where the microstructure passes from an isotropic state to a fibrillar one. We previously showed that micro-Raman spectroscopy is a particularly adequate technique to follow microstructural changes in a localized region [21–25]. The advances that took place in Raman instrumentation over the last decade allows now to analyze with relative ease the low frequency domain of the Raman spectrum, i.e., 10–20 cm^{-1}. We present here the micro-Raman LAMs of HDPE samples demonstrating therefore that the current dispersive systems permit to reject the strong reflected laser line as well as Rayleigh scattering and to record the LAMs with a Raman microscope instrument. This micro-spectroscopic analysis will permit to follow the evolution of the LAM with a high spatial resolution along the transition zone between the isotropic and fibrillar regions and will thus bring new information on the drawing process in semi-crystalline polymers.

Experimental

The Raman spectrometer used here was a Jobin Yvon T64000 instrument using an argon ion laser as a illumination source, and consisted of a subtractive dispersion double monochromator combined with a spectrograph that disperses the light onto a bi-dimensional CCD detector cooled at 140 K. The Raman instrument was coupled to a standard Olympus microscope and the collection optics system was used in the backscattering configuration. The analyzed region was directly visualized through a × 50 objective. The spot size at the sample is of the order of 2 μm. The samples were analyzed without any sample treatment or preparation. The laser frequency used was the 514.5 nm line and the power at the sample was of the order of 4 mW, which allowed recording good quality spectra in relatively short time (i.e., 200 s.) without producing thermal heating effects in the sample. The spectra were recorded with a spectral resolution of 2 cm^{-1}.

Since the exact shape of the broad wing originating from Rayleigh scattering and reflected light was unknown, the baseline was removed using the same mathematical procedure for all spectra (i.e., fifth order polynomial fit). Since the purpose of this work was to follow the evolution of the LAM along the transition region and not to measure the true straight-chain length distribution of the crystalline phase, temperature and frequency factors were not considered.

In order to improve the accuracy in the determination of spectroscopic parameters such as peak position, bandwidth, lineshape (i.e., Gaussian, Lorentzian or a mixture of both) and band intensity, a curve fitting was carried out for each spectrum after background substraction. Several fits were tried leaving all the spectroscopic parameters free to progress and the best result was invariably obtained for all the recorded spectra when the LAM band was fitted with a Gaussian lineshape.

It should be noticed that as the oriented region is approached, the LAM signal is getting very weak and spectroscopic parameters such as band width, intensity and position are determined with a much higher error. Near the oriented region, when the LAMs are getting very weak although still discernible, their spectroscopic parameters could not be determined precisely with the analytical method used here.

The material used for this study is a high density polyethylene (HDPE). Three samples were produced by uniaxial stretching at room temperature at three different drawing rates, i.e., 1, 100 and 500 mm/min. The transition front in the neck was measured for each of these three samples with the optical microscope and was found to be of the order of 260, 200 and 140 μm, respectively.

Results and discussion

The low-frequency Raman spectra recorded along the transition front of the sample stretched at 500 mm/min are plotted in Fig. 1. The 0 μm position was here taken as the limit between the isotropic and the transition zone observed with the optical microscope. Since the transition front in this specimen was measured to be about 140 μm, the oriented region would then begin at the position +140 μm. At low frequency, i.e., below 40 cm^{-1}, the Rayleigh scattering contribution can be noted. Although the experiment was carried out with the backscattering configuration which allows to enter in the instrument some reflected-transmitted light (mainly due to the beam splitter of the microscope), the stray light rejection of the micro-Raman system is good enough to clearly discriminate the LAM at about 14 cm^{-1} from the Rayleigh scattering wing. It was found that below −50 μm, i.e., inside the isotropic region, the LAM band stays approximately constant, whereas above this value the LAM begins to be affected. This effect, which corresponds to the disruption of the lamellar structure, is found to increase as the transition front is reached. It can also be observed in Fig. 1 that above +70 μm, i.e., before the fibrillar structure is reached, the LAM signal has nearly totally disappeared. In the past, it has been argued that the fact that the LAM was not detected or poorly distinguished in the stretched region of

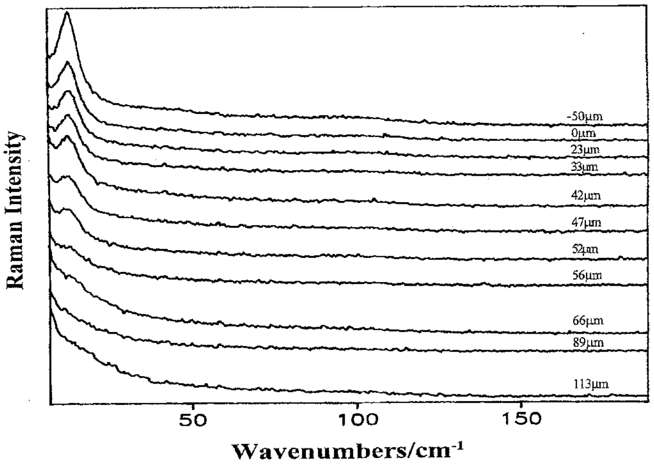

Fig. 1 Low-frequency Raman spectra recorded along the transition region on HDPE samples uniaxially cold drawn (500 mm/min)

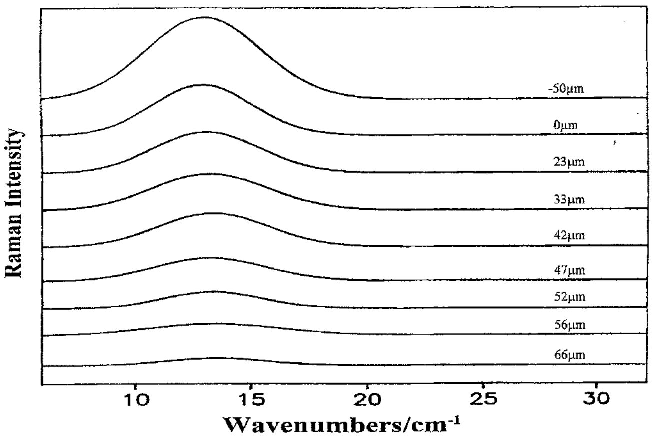

Fig. 2 Substraction of the Rayleigh contribution and curve fitting of the LAM bands represented in Fig. 1

some drawn polymers was perhaps due to optical effects such as instrumentation rejection ratio as a result of a change in the sample morphology or transparency rather than structural variation. This point was carefully checked in this study:

- the "Rayleigh" wing intensity does not vary remarkably as the spectra are recorded at different positions along the transition front.
- Raman spectra of both the isotropic region and fully stretched zone were obtained by conventional macro-Raman spectroscopy and show similar results as those obtained by micro-Raman spectroscopy, the only difference being the better signal-to-noise ratio obtained with the macro-Raman system.
- several isotropic polyethylenes samples of different morphology and nature were studied by micro-Raman spectroscopy showing LAMs of different intensity, bandwidth and position. For example, LAMs frequencies were detected from 11 cm^{-1} up to 27 cm^{-1}.

These three above issues confirm that the decrease observed in the LAM intensity along the transition region is really due to a change in the structure.

The LAMs of the Raman spectra presented in Fig. 1 after baseline subtraction and curve fitting are plotted in Fig. 2. The intensity, bandwidth and position of the LAM band for the three samples were then measured and plotted in Fig. 3 as a function of the distance along the transition front. These results show that for these three samples the LAM intensity decreases progressively along the neck and disappears before the oriented region is reached, indicating that the lamellar structure is totally disrupted before the fibrillar structure is formed.

Further, the distance over which the intensity of the LAMs diminishes and disappears is found to decrease as the drawing rate augments. This result can be correlated to the increase of temperature detected in a previous work [25] in the transition region as the strain rate is increased, producing then higher chain mobility, and consequently allows for a better and faster structural reorganization [26,27]. These data confirm former micro-Raman studies carried out on other semicrystalline polymers, where the evolution of other structural parameters, such as polymer chain orientation on PP and crystalline phase modification on PVDF, were analyzed along the transition region [23,25].

Both the peak position and the bandwidth of the LAM are approximately constant over the transition zone, whereas the LAM intensity is found to decrease rapidly in this section of the specimen. The fact that no clear progressive change in bandwidth and peak position occurs along the transition region indicates that there is not a noticeable variation in the distribution of lengths of straight chain segments, whereas the LAM intensity is clearly affected. A discontinuous transformation from the spherulitic into fiber structure is produced by micronecking [26] and during this process, unfolding of the molecules in the lamella allows to interconnect them forming the microfibrils. In such deformation process, the density of the micronecks is low at the beginning of the transition region and increases as the fibrillar structure is reached, therefore making the transformation from the isotropic zone to the fibrillar structure to be a gradual process when analyzed by a microscopic method such as micro-Raman spectroscopy. Conversely, the concentration of lamella not transformed yet to microfibrils, and which remain dimensionally intact, decreases gradually along the transition zone up to the stage where the lamellar structure is totally transformed to the fibrillar one.

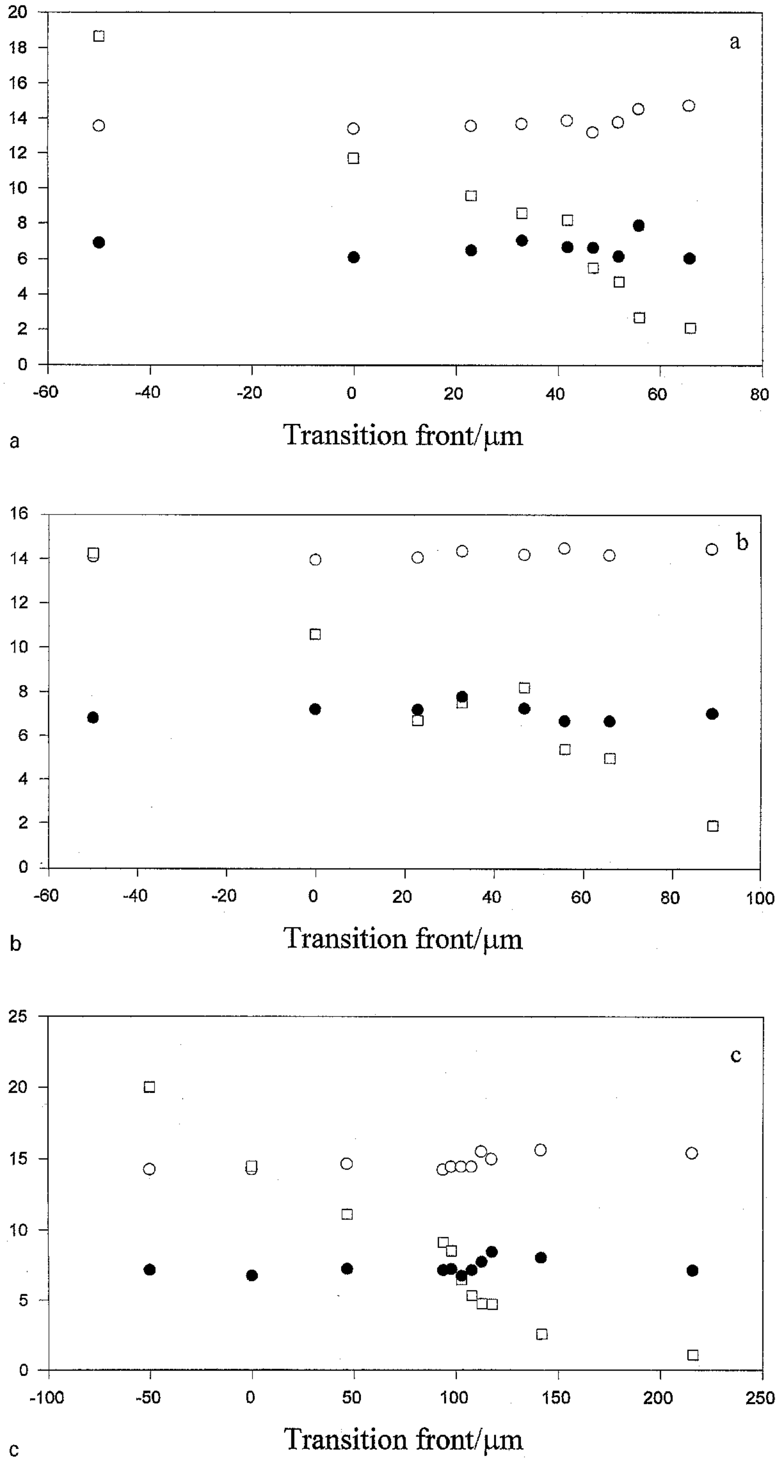

Fig. 3 Evolution of the peak intensity/a.u. (□), peak position/cm^{-1} (○) and bandwidth/cm^{-1} (●) of the LAM recorded for HDPE samples drawn at (a) 500 mm/min, (b) 100 mm/min and (c) 1 mm/min

Conclusions

The analysis of the evolution of the LAMs along the transition region of stretched HDPE shows that Raman spectroscopy is a powerful method to follow structural change along a specific area with a high spatial resolution. The main structural changes occur in the transition zone and the LAM was found to disappear before the oriented morphology is reached, indicating that the lamellar structure is totally disrupted before the fibrillar structure is formed. Further, the distance over which the transformation takes place decreases as the drawing rate is increased due to higher chain mobility at higher strain rate [25].

While both the bandwidth and LAM position stay relatively constant along the transition, the intensity decreases progressively. This feature can be explained by the micronecking formation, in which a transformation from lamellae into fibrillar structure is produced. Along the transition zone, the lamellae that have not yet been transformed through micronecking to fibrils stay dimensionally unchanged.

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References

1. Koenig JL, Tabb DL (1974) J Macromol Sci Phys 9:141
2. Fraser GV, Hendra PJ, Cudby MEA, Willis HA (1974) J Mater Sci 9:1270
3. Hendra PJ, Majid HA (1977) Polymer 18:573
4. Rabolt JF, Fanconi B (1977) Polymer 18:1258
5. Rabolt JF, Fanconi B (1977) J Polym Sci, Polym Lett 15:121
6. Hendra PJ, Majid HA (1977) J Polym Sci, Polym Lett 15:259
7. Cutler DJ, Hendra PJ, Sang RD (1979) Discuss Faraday Soc 68:320
8. Schaufele RF, Shimanouchi T (1967) J Chem Phys 47:3605
9. Hsu SL, Krimm S, Krause S, Yeh SY (1976) J Polym Sci, Polym Lett 14:195
10. Snyder RG, Scherer JR, Peterlin A (1981) Macromolecules 14:77
11. Folkes MJ, Keller A, Stejny J, Goggin PL, Fraser V, Hendra PJ (1975) Colloid & Polym Sci 253:354
12. Snyder RG, Krause SJ, Scherer JR (1978) J Polym Sci, Polym Phys Ed 16:1593
13. Capaccio G, Ward IM, Wilding MA (1979) Discuss Faraday Soc 68:328
14. Snyder RG, Krause SJ, Scherer JR (1980) J Polym Sci, Polym Phys Ed 18:421
15. Snyder RG, Scherer JR (1980) J Polym Sci, Polym Phys Ed 18:421
16. Capaccio G, Wilding MA, Ward IM (1981) J Polym Sci, Polym Phys Ed 19:1489
17. Snyder RG, Scherer JR, Reneker DH, Colson JP (1982) Polymer 23:1286
18. Wang YK, Waldman DA, Stein RS, Hsu SL (1982) J Appl Phys 53:6591
19. Glotin M, Mandelkern L (1983) J Polym Sci, Polym Lett 21:29
20. Peterlin A, Corneliussen R (1968) J Polym Sci A-2 6:1273
21. Jawhari T, Merino JC, Pastor JM (1992) J Mater Sci 27:2231
22. Jawhari T, Merino JC, Pastor JM (1992) J Mater Sci 27:2237
23. Jawhari T, Merino JC, Rodríguez-Cabello JC, Pastor JM (1992) Polym Commun 33:4199
24. Jawhari T, Merino JC, Rodríguez-Cabello JC, Pastor JM (1993) Polymer 34:1613
25. Pastor JM, Jawhari T, Merino JC, Fraile J (1993) Makromol Chem Macromol Symp 72:131
26. Peterlin A (1971) J Mater Sci 6:490
27. Peterlin A (1987) Colloid Polym Sci 265:357