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FTIR spectroscopy of polymer films under uniaxial stretching

2. Amorphous and semicrystalline poly(ethyleneterephthalate)

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SUMMARY

The FTIR changes in films of amorphous and semicrystalline poly(ethyleneterephthalate), PET, were registrated during uniaxial stretching at small deformations (1%-25%). The accompaning frequency shifts of vibrational bands of benzene ring and glycol residue are analysed. It was shown that the deformation behaviour of the band shifts strongly depends on phase and morphology of polymer sample. High pressure and temperature effects on IR spectra of PET are also discussed.

INTRODUCTION

Mechanical behaviour of polymers at the molecular scale is intensively studied1). There are several questions concerning the transition from elastic to plastic deformation. They include the role of conformational changes in the formation of plasticity and the nature of mechanically-induced effects in amorphous and semicrystalline polymers. PET is the suitable subject for the mechanical studies. It can be easily obtained in the amorphous and semicrystalline state with different morphology. PET is intensively studied by IR and Raman spectroscopy2). The PET IR bands are assigned to the different parts of polymer: benzene ring and glycol residue. The conformational sensitive bands are also known. The structural changes during crystallization of PET and orientational processes in polymer films are registrated well by IR spectra3). However, the spectroscopic changes in PET on heating4), physical ageing5) and under mechanical load6) are rather small. The FTIR temperature spectra of PET have demonstrated that intensity and frequency changes of different bands were caused by intermolecular and intramolecular effects4). In many cases these effects are difficult to separate. Comparative analysis of the small spectroscopic variations induced by different physical effects (temperature, stretching, high pressure) can be used for the clarification of their origin.

The FTIR changes accompaning uniaxial stretching of amorphous and semicrystalline PET films are presented in this paper. The mechanically-induced frequency shifts of various vibrational modes are analysed. The IR changes registrated in PET films under high pressure are discussed in correlation with the results of the stretching experiments.

EXPERIMENTAL

Home-made tensometer7) was used for the simultaneous registration of spectral changes and mechanical behaviour of polymer films during uniaxial stretching. It was installed in the Bruker IFS-113v FTIR spectrometer. All experiments were conducted at room temperature with stretching speed .01 min^{-1}. Dumbell-shape samples (narrow part has width - 5 mm and length - 20 mm) were cut from commercial PET films ("Plastik", Moscow). Three different types of films were tested. The amorphous film (crystallinity

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*Present address and address for offprint requests: Freiburger Metallforschungszentrum der Universität, Stefan-Meier-Strasse 31, W-7800 Freiburg, FRG less than 10%) was 44 μm thick. The two semicrystalline films with thickness 8 μm, PET(1), and 14 μm, PET(2), have similiar crystallinity: PET(1) - 50%, PET(2) - 55%. The size of crystallites was different: 120 Å in PET(1) and 80 Å in PET(2) (WAXS measurements). All films were mechanically anisotropic, however, the IR dichroism studies have not revealed molecular orientation. During measurements IR beam was restricted by rectangular mask (4 mm x 10mm) in the central part of film. Films of amorphous polymer and PET(2) were covered with thin layer of hydrocarbon or fluorocarbon oil to prevent the interference effects in IR spectra. Interferograms (50 scans, resolution 2 cm^{-1}) were collected during stretching of films. Then they were converted to the absorbance spectra. It was assumed that each FTIR spectrum corresponds to stress-strain values at the half-time of IR data accumulation. IR changes which accompany stress release and thermal recovery of deformed PET films were recorded.

The deformation difference spectra (DDS) are used for the presentation of the mechano-spectroscopic data. They were obtained by the subtraction of spectra of stressed film from the spectrum of original polymer film. The coefficient of subtraction was determined under the condition of conservation of integral absorbance of the examined bands. This procedure minimizes the influence of intensity changes in the measurements of frequency shifts. For the isolated symmetrical band the DDS obtained in this way should have negative and positive peaks of the identical height. Such shifts were calculated8) in the approximation of Lorentz-type bandshape. However, the mechanically-induced changes of width and shape of bands may influence the accuracy of this approach. The subtraction coefficient for one of the bands was used when the DDS in the spectral regions with several bands were presented for the illustration. The DDS of amorphous film in the regions 1625 cm^{-1} - 1480 cm^{-1} and 950 cm^{-1} - 775 cm^{-1} were obtained with the coefficients of the 1580 cm^{-1} and 795 cm^{-1} bands, correspondingly. The DDS semicrystalline films in the regions 1600 cm^{-1} - 1325 cm^{-1} and 1060 cm^{-1} - 750cm^{-1} were calculated with the coefficients of the 1410 cm^{-1} and 795 cm^{-1} bands. The bands with absorbance less than 0.9 were used for the subtraction procedure.

High pressure effect on IR spectrum of PET films at room temperature was studied with commercial high pressure cell (High Pressure Inc., USA). It was used in combination with the Bruker IR microscope. Initial pressing of polymer film between small diamond anvils leads to the decrease of thickness because some material was pulled out of anvils area. This process was stopped at some critical thickness. The subsequent press-release cycles did not change thickness and the spectral changes became reversible. The area of diamond anvils is much bigger than the thickness of the examined films. Thus, the hydrostatic character of applied pressure is evident in these experiments. The spectroscopic measurements of high pressure effects were conducted during several pressure-release cycles. The spectra of films (resolution 2 cm^{-1}, 200 scans) were measured at the pressure of 20 kbar and in the released state. The high pressure cell was calibrated with polystyrene9).

RESULTS AND DISCUSSION

Amorphous films. The stress-strain curve of amorphous PET film (Fig.1) indicates the plastic behaviour at strains above 4%. Neck appears locally at the yielding point and spreads over the whole sample at higher deformations. It is characterized by the sharp decrease of thickness and width. Crystalinity in the neck becomes higher10). Consequently, deformed film is macroscopically heterogeneous. The situation in IR beam area can be controlled by the integral absorbance of the 795 cm^{-1} band, which is usually used as an internal standard. Necking had been initiated near clamps and entered the IR beam area at the 6% strain (Fig.1). It had occupied the whole beam area at the strain of

23%. At the deformation of 27% stress was released. The relaxed film had the necked part and the residual strain (24%).

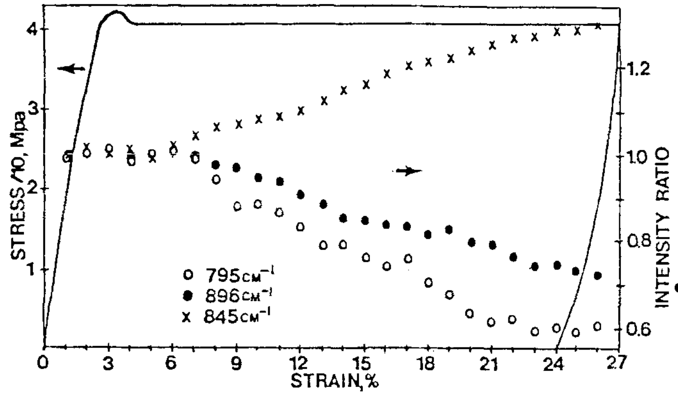


Fig.1 Stress-strain curve for amorphous PET film and the ratios of intensities of the bands during stretching. ○ A_{795}/A_{795} ; • A_{896}/A_{795} ; × A_{845}/A_{795} . A-absorbance in the stressed film, A-absorbance in the original film.

The mechano-spectroscopic data of the amorphous film are presented in Fig.2A-2D. The intensity changes and frequency shifts of several bands of benzene ring in the spectral region 1625 cm^{-1} - 1490 cm^{-1} are seen from the DDS in Fig.2A and 2C. These effects have appeared at the beginning of stretching and developed at the higher deformations. The 1580 cm^{-1} band demonstrates the interesting behaviour in the prenecked material. This band exists only in the IR spectrum of amorphous PET. Its low frequency shift (Fig.2C) had appeared in the inelastic region, reached the maximum value at the yielding point and then decreased. This dependence is similiar to the stress behaviour. The symmetric derivative-like shape of the DDS shows that the low frequency shift of the 1580 cm^{-1} band occurs without evident bandshape variation up to the 8% strain. The spectral difference effect at the higher deformations shows the influence of the bandshape changes. The similiar effect was revealed in the DDS of the necked material under stress and in the released state. (Corresponding points of the stress-strain curve, Fig.1, - 27% and 24% strain). Unfortunatelly, the magnitutudes of the low frequency shift of the 1508 cm^{-1} were not well reproducible because of the high intensity of this band.

The behaviour of the conformational bands, 898 cm^{-1} - gauche and 845 cm^{-1} - trans (CH_2 rocking modes of glycol residue) during stretching is shown in Fig.2. It is evident that the increase of trans/gauche ratio follows the neck appearence and propagation. Conformational changes were not observed in the prenecked material. The intensity of the 898 cm^{-1} band increases slightly at small deformations. This effect and the decrease of the 873 cm^{-1} band are caused, perhaps, by the intermolecular changes.

The most popular PET band at 973 cm^{-1} is assigned to the C-O stretching vibration of glycol residue in trans conformation. This band is sensitive to molecular order. It is the low intensity, broad band in amorphous material. However, it becomes the intensive and sharp one in crystalline phase. The 973 cm^{-1} band shifts to lower frequencies in the oriented PET films under stress⁶⁾. The behaviour of this band during stretching of unoriented amorphous film is shown in Fig.2C and 2D. The small differential effects were detected in the DDS at the strains up to 7%. They can be assigned to the low frequency shift of the broad 973 cm^{-1} band. The DDS become more complex at higher deformations, perhaps due to the heterogeneity appeared in the film. However, the DDS of the 973 cm^{-1} band show rather symmetrical shape in the necked material under the load and in the released state.

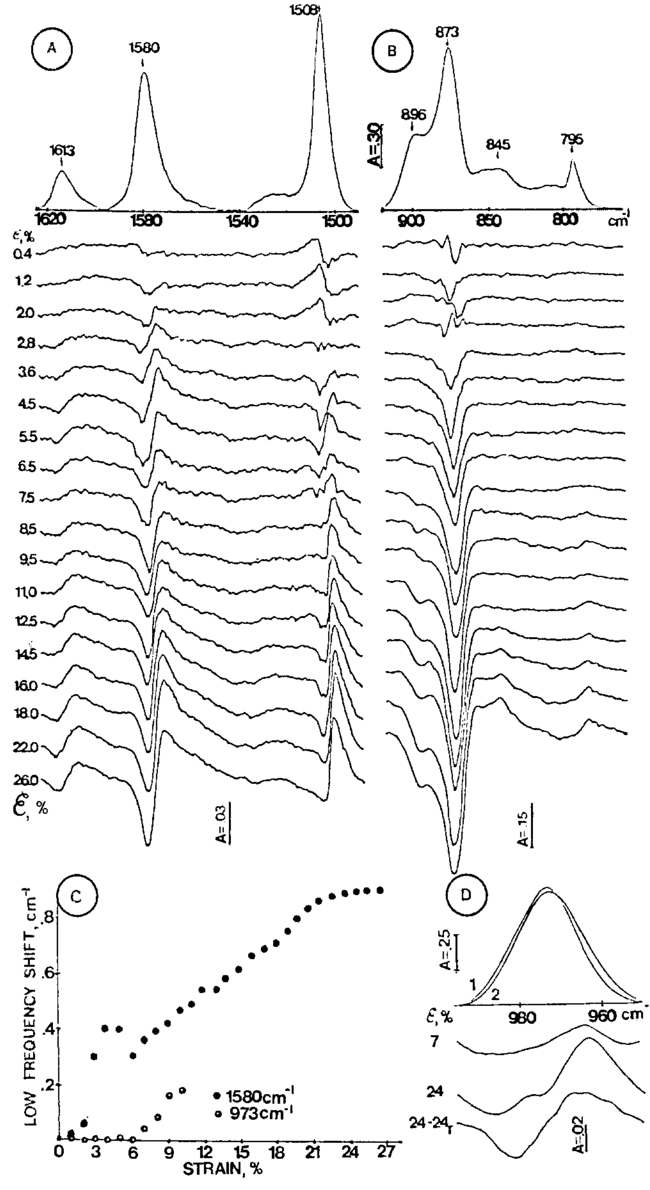


Fig.2 A,B - The FTIR spectra (upper) and the DDS (lower) of amorphous PET film; C - The strain dependencies of the low frequency shifts of the 1580cm^{-1} and 973cm^{-1} bands; D - The 973cm^{-1} band in the original(1), and the deformed film(2). Strain-24%. In the lower part DDS at 7% and 24% strains. 24-24$_r$ - difference spectrum of stressed and released film at the 24% strain.

The influence of pressure on the IR spectra of amorphous PET film is seen from Fig.3. The initial pressing has led to decrease of the film thickness, and crystallinity had increased. This is seen from the increased ratios of intensities of the 973 cm^{-1}/795 cm^{-1} and 845 cm^{-1}/898 cm^{-1} bands. The pressure effect is evident without difference spectra. The bands of benzene ring (1580 cm^{-1}, 1508 cm^{-1}, 1410 cm^{-1}, 1018 cm^{-1} and 873 cm^{-1}) shift to high frequencies, and their intensities decrease. Under high pressure the glycole residue bands (845 cm^{-1}, 898 cm^{-1}, 973 cm^{-1} and 1042 cm^{-1}) become broader and less intensive. The 973 cm^{-1} and 795 cm^{-1} bands shift to low frequencies, and the intensity of the latter increases. The pressure-induced spectral changes were reversible.

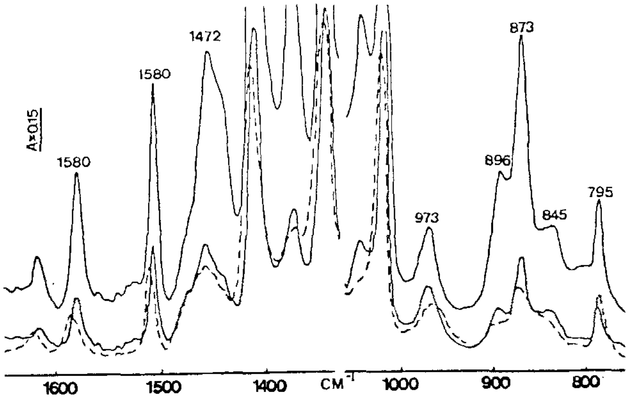
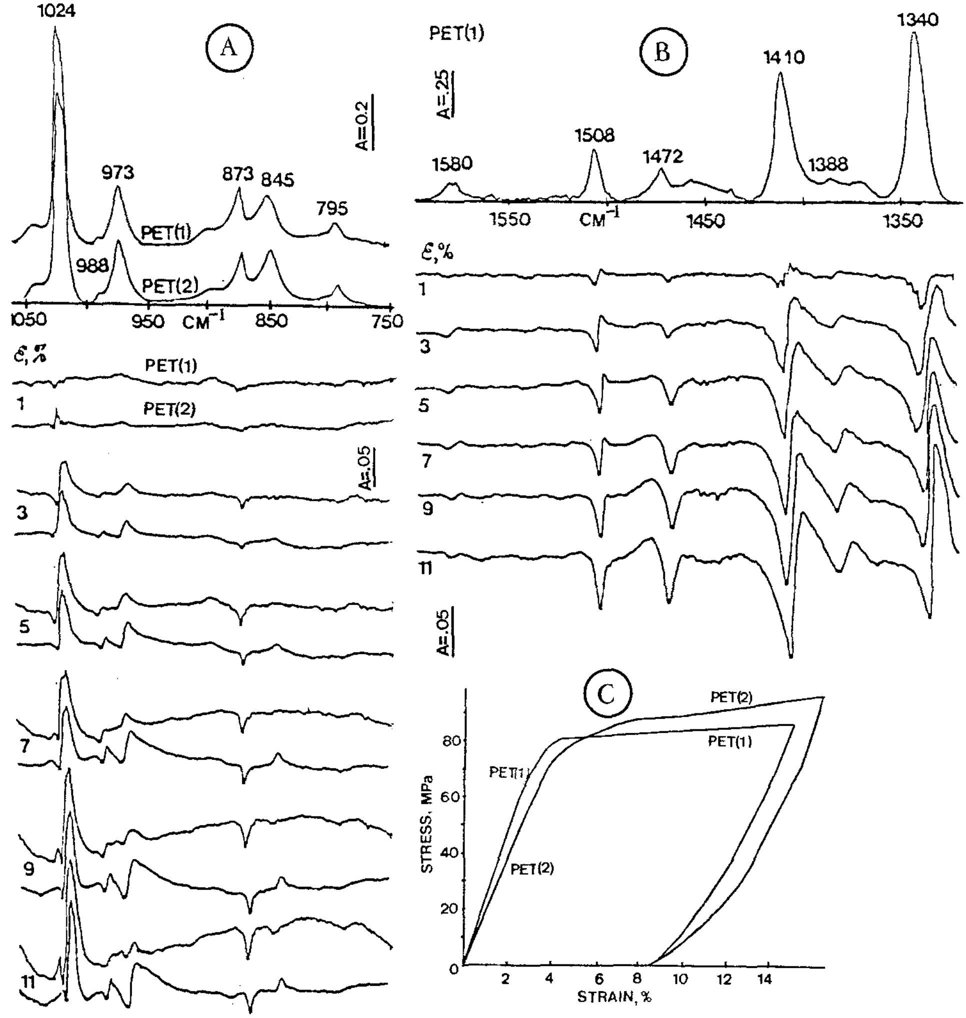


Figure 3. The FTIR spectra of amorphous PET film: 1 - original, 2 - after initial pressing, (both in solid line), dotted line - under high pressure (20 kbar).

Semicrystalline films. Films of semicrystalline PET showed no evident necking during uniaxial stretching. Thus, the mechano-spectroscopic studies of these macroscopically homogeneous films can be carried out in a broader deformation range than in amorphous films. The stress-strain curves of PET(1) and PET(2) films and the corresponding DDS spectra are presented in Fig.4A-4C. They show differences in the plasticity region, where the stress level of PET(2) film is higher. Sensitivity of all IR bands of semicrystalline PET to stretching is evident. The mechanically-induced spectral changes include low frequency shifts, intensity and bandshape variations. They are similiar to the IR changes registrated on heating4). Only the 873 cm^{-1} band behaves differently. It shifts to lower frequencies at the elevated temperatures. During stretching, however, only intensity variations were detected. The first changes in the spectrum of the deformed film have appeared when stress was applied. They are pronounced for the benzene ring bands (1508 cm^{-1}, 1410 cm^{-1} 1388 cm^{-1} and 1340 cm^{-1}). The effects in the DDS (Fig.5), which correspond to the low frequency shifts of these bands (exception is the 1508 cm^{-1} band, see below), increased during stretching. The behaviour of bands in the region 1050 cm^{-1} - 750 cm^{-1} was different. The small intensity changes have been registrated at the strains higher than 5% for amorphous band at 1042 cm^{-1} and the conformational sensitive 898 cm^{-1} and 845 cm^{-1} bands. These bands are correlated with the molecular behaviour of polymer during plastic deformation.

The mechano-spectroscopic behaviour of the "amorphous" 1580 cm^{-1} band, the benzene ring mode at 1508 cm^{-1} and the trans glycol residue band at 973 cm^{-1} are more evident from the DDS in Fig.5-6. Semicrystalline films, as well as amorphous one, demonstrate the low frequency shifts of the 1580 cm^{-1} and the 1508 cm^{-1} bands. The behaviour of the 1508 cm^{-1} band in the PET(1) and PET(2) films is similiar. The 1580 cm^{-1} band (benzene ring vibration in amorphous phase), however, behaves differently above the yielding point. The difference spectral effect in PET(1) film at 1580 cm^{-1} corresponds to the low frequency shift at the small strains. The different shape of the DDS at the higher strains can be explained as the influence of the high frequency shift. This effect had not dissapeared after the stress release. Similiar behaviour was found for the 973 cm^{-1} band in the PET(1) sample. The low frequency shift is evident at the small strains and changes at the higher ones. The different ratio of the spectral effects of the 1024 cm^{-1}, 973 cm^{-1} and 845 cm^{-1} bands for the PET(1) and PET(2) films at higher strains is seen from Fig.4A. These results show us that structural alternations in the region of plasticity depend on the morphology of the semicrystalline films. This conclusion correlates well to the results of the X-ray studies11).



Figures 4 A-B - The FTIR absorbance spectra (upper part) and DDS (lower part) at different strains, %, of the semicrystalline films, PET(1) and PET(2), in the different spectral regions. C - The stress-strain curves of the semicrystalline films, PET(1) and PET(2) at the ambient conditions. Stretching was carried out with the rate .01 min^{-1}.

The influence of high pressure on the FTIR spectra of semicrystalline films is shown in Fig.7. Initial pressing induces slight decrease of crystallinity, and the regularity bands at 1388 cm^{-1} and 988 cm^{-1} almost disappeared. Most of the bands shift to high frequencies under high pressure. This behaviour is similiar to the one observed in amorphous PET. The pressure-induced low frequency shift and the intensification of the band at 795 cm^{-1} confirm this conclusion. The spectral differences were reversible in the press-release cycles.

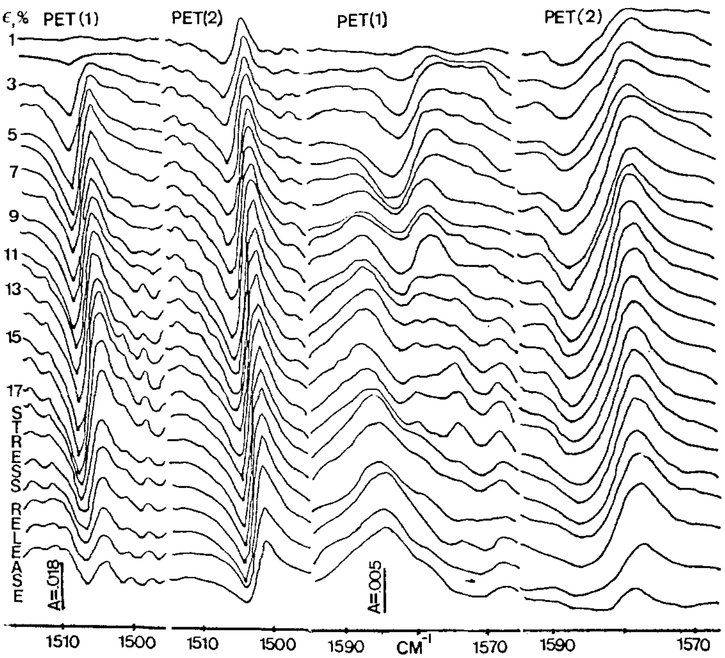


Figure 5. The DDS of PET(1) and PET(2) films in the regions of 1580 cm^{-1} and 1508 cm^{-1} bands at different strains, ε%. The effect of stress release is also shown.

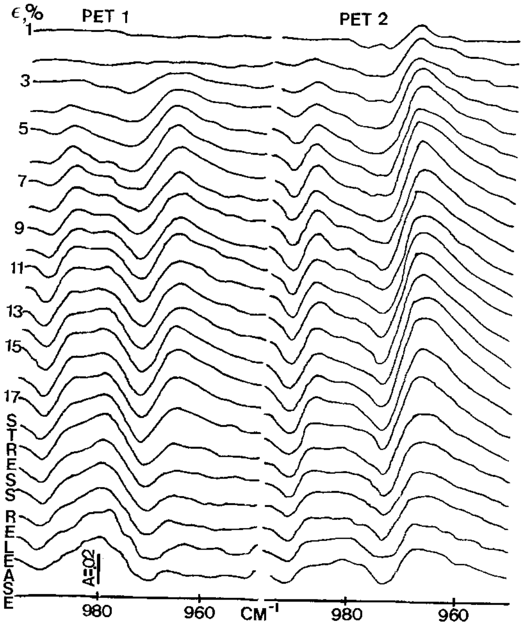
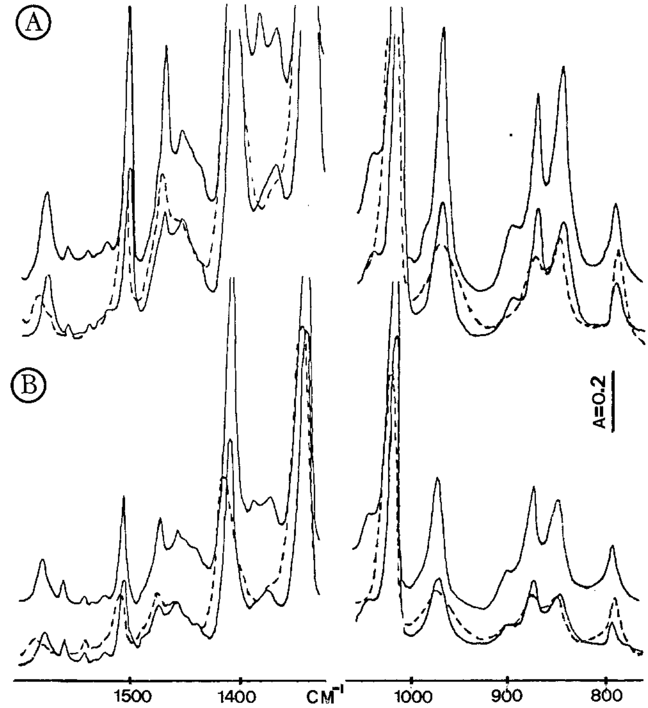


Figure 6. The DDS of PET(1) and PET(2) films in the region of the 973 cm^{-1} band at different strains, ε %. The effect of stress release is shown.



Figures 7A-7B. The FTIR spectra of semicrystalline PET(2), A, and PET(1), B, films. In the upper parts - the absorption spectra of original films (solid lines), in the lower parts - the absorption spectra of films after the initial pressing (solid line) and under high pressure (20 kbar) (dotted lines).

CONCLUSION

FTIR spectroscopy appears to be useful for the detection of small structural changes in polymer films induced by stretching and high pressure. The responses of crystalline and amorphous phases, as well as benzene ring and glycol residue moieties, to external mechanical field are different. They also depend on morphology of polymer. The conformational changes in the amorphous film were registrated in the necked part. They were not found in the semicrystalline samples. The density increase under high pressure leads to the high frequency shifts of IR bands. The low frequency shifts were induced by heating and stretching. These effects may be assigned to the density decrease, associated with the stretching and heating. Thus, the shifts can be used as a measure of local changes in vicinity of various molecular groups caused by external field. The nature of bands determines their sensitivity to the volume changes[12]. Combined studies of the high pressure and stretching effects should be used for the separation of the hydrostatic and the shear contributions to the frequency shifts.

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