Surface and guided polaritons in films of polytetrafluoroethylene

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Multiple-internal-reflection spectra of thick and thin films of polytetrafluoroethylene have been measured. In the region of the C–F stretching vibrations, surface polaritons were observed, and for very thin films guided polaritons were observed. They had been suggested from our earlier work and are now confirmed with this recent investigation. This constitutes the first observation of the phenomena in polymeric materials.

(Keywords: PTFE; MIR; *FTi.r.*; polaritons; surface)

INTRODUCTION

Surface and guided polaritons in ionic crystals have been predicted theoretically[1] and observed experimentally in infra-red[2] and Raman[3] spectroscopy. But such excitations can also exist in non-crystalline films with very strong absorption bands. As was shown previously[4], the reflection spectra of polytetrafluoroethylene (PTFE) films exhibit strong bands corresponding to regions of negative dielectric function as well as a set of bands that exhibit an interference pattern. According to ref. 1 in the non-radiative region we should expect the appearance of surface-wave polaritons and a set of guided-wave polaritons. We studied both kinds of polaritons in various film thicknesses of PTFE with the use of the attenuated total reflection (ATR) technique. The region of strong reflectivity in PTFE and its copolymer with hexafluoropropylene (HFP) appears at 1215, 1155 and 500 cm^{-1}. These bands were observed in every spectrum. Only in spectra of thin films were the guided-wave polaritons observed.

Surface polaritons[5] are excitations whose frequencies are restricted, because of the bounded nature of the 'crystal', to the range between the frequencies of transverse and longitudinal phonons where the permittivity is negative. Whenever the surface polaritons are observed, such as in these PTFE polymers, they are normally propagated over long distances (centimetres) on the surface. They can often be thought of as an open waveguide with low losses in the infra-red region of the spectrum, whereas the losses are very high in the visible region and as such are not observed. Surface polaritons always exist in the frequency regime where the real part of the dielectric function of the 'crystal' is negative and its absolute value exceeds the dielectric constant of the adjacent medium (such as air in our case).

EXPERIMENTAL

Instrumental

In our work we used the Bruker (model IFS-113V) Fourier transform infra-red (FTi.r.) spectrometer that was equipped with a Janos Technology multiple-internal-reflection (MIR) unit. For measurements made at three different angles of incidence, we used a 5 cm long MIR plate made of KRS-5 (refractive index 2.37 at 1100 cm^{-1}). The spectrometer was operated as a single beam over the spectral range from 1300 to 900 cm^{-1}.

Materials

We used three different PTFE films of 7, 17 and 25 μm thickness that were obtained from commercial sources for our thin films. We used thicker films of PTFE and its HFP copolymer for the bulk work. The HFP content of the copolymer was about 10 wt%.

Measurements

The films were pressed to only one side of the MIR plate. The air gap between the plate and the film was adjusted by the pressure used to make the contact between them. Only a very small gap is necessary to excite the surface polaritons. The angles of incidence used with the MIR unit were 30, 45 and 60°. These angles are larger than the critical angle (25°) for total reflection in the KRS-5/air boundary. For these three angles the surface polaritons are coupled with the bulk radiation in the MIR plate. In order to test the decrease in the size of the air boundary, we filled the gap with Nujol. As a result of this experiment, we found that for the Nujol-filled gap sample (see *Figure 3* for the TFE–HFP copolymer) the polariton spectrum was observed only for the two larger angles.

RESULTS AND DISCUSSION

In our previous work[4] we studied the i.r. reflectivity of PTFE and its copolymer films to obtain their optical constants. In the use of these data, we calculated the ATR spectra for the system KRS-5/air/PTFE for both s- and p-polarized light. It appeared that for s (perpendicular) polarization there are reflectivity minima at frequencies lower than the transverse vibrational frequencies. The minima are attributed to frustration of the total reflection in the region of high refractive index of the film (on the low-frequency side of the absorption band where the refractive index is maximal). For p-polarized light there

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are also peaks in the absorption (inside the region of negative dielectric function) that can be attributed to surface polariton excitation.

Experimental MIR spectra of bulk PTFE (*Figure 1*) show the same features as described above. The surface polariton line at $1155\,\mathrm{cm}^{-1}$ is well defined, while the other two surface polariton lines appearing at 1215 and $500\,\mathrm{cm}^{-1}$ are broader. Bulk PTFE samples do not show any anisotropy in the plane of the sample. The experimental spectra are practically the same for the two different orientations of the sample (one perpendicular to the other). For films with a defined direction of stretching there is some anisotropy. Even for films that are not very thin, such as the $25\,\mu$m thick copolymer film, the anisotropy is not very large but can be seen easily in *Figure 2*. The filling of the air gap with Nujol leads to a low frequency shift of the surface polariton lines (*Figure 3*). The copolymer spectra shown in *Figure 2* exhibit a weak band near $980\,\mathrm{cm}^{-1}$ that is attributed to a group vibration from the comonomer of HFP. The independence of its position on polarization indicates that it cannot be attributed to a surface polariton. This band is weak because of the low concentration of HFP (10 wt%) in the sample.

For very thin films we performed calculations to detail the main features of the elementary excitations of the film. These showed the maxima of absorption corresponding to the excitation of guided modes in the films for both s- and p-polarized light. The maxima are on the low-frequency side of the strong absorption band. Inside the band observed with p-polarized light, the surface polariton line appears. In *Figure 4*, we show the excitation frequency dependences (a) on the reduced wavevector (or effective refractive index) $H_x = n \sin\theta$ for $7\,\mu$m thick film and (b) on the film thickness d for $\theta = 30°$. The dielectric function of the PTFE was chosen as being two Lorentzian oscillators with effective frequencies of transverse vibrations at 1155 and $1215\,\mathrm{cm}^{-1}$, and longitudinal vibrations at 1165 and $1253\,\mathrm{cm}^{-1}$, respectively. The

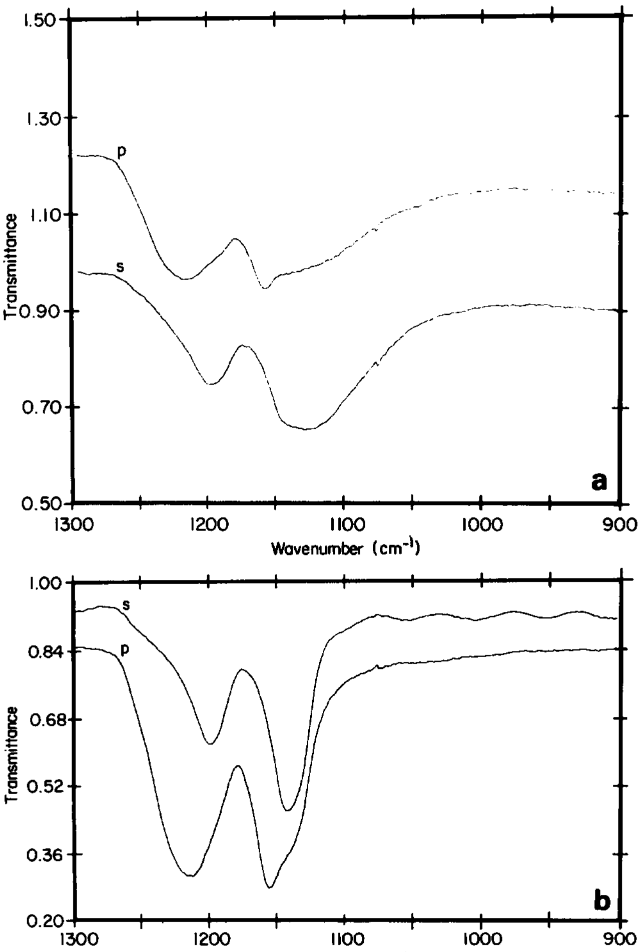


Figure 1 MIR transmittance spectra of bulk PTFE at angles (a) 30° and (b) 45°. Spectra of both s- and p-polarized light are shown

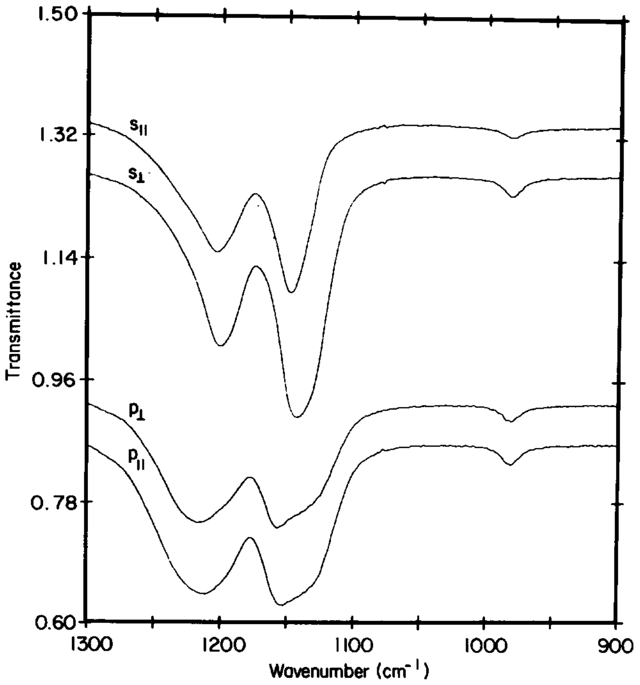


Figure 2 MIR transmittance spectra of a $25\,\mu$m thick film of poly(TFE–HFP). Spectra of both s- and p-polarized light for perpendicular and parallel orientations of the film are shown

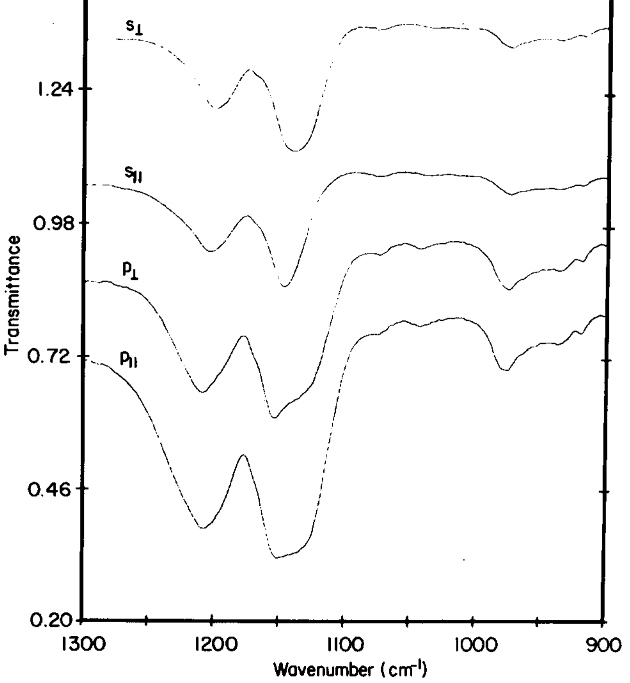


Figure 3 Same sample and the same designations seen in *Figure 2* except that the gap between sample and the MIR plate is filled with Nujol

surface polariton frequency increases only slightly with wavevector (*Figure 4*). The dispersion is small because of the small oscillator strength (or small effective transverse–longitudinal splitting). Guided s- and p-polarized polaritons have larger dispersion especially at low index (lower frequencies), but closer to the transverse frequency (chain line). All lines closest to this line were eliminated from the dispersion curves of guided polaritons shown. For thickness dependence (*Figure 4b*) the surface polariton frequency is constant because the thicknesses shown are much larger than the penetration depth of the surface polariton electromagnetic field in PTFE. Surface polaritons on both sides of the film are not mixed. In this situation not all guided polaritons are shown. Only those branches closest to the upper limit are omitted.

Experimental spectra of the surface and guided polaritons of the 7 μm thick PTFE film are shown in *Figure 5* for all three angles of incidence. For each angle s- and p-polarized spectra are given for two different orientations of the film stretching direction relative to the plane of incidence (parallel and perpendicular). The difference is due to the anisotropy of the film because of stretching. For the angle of incidence of 30°, in accordance with previous calculations (*Figure 4*), the minima caused by guided-wave excitation are well resolved, for 45° the distance between them decreases and at 60° they are almost unresolved.

For the 17 μm thick PTFE film, well defined peaks could be seen only at 30° (*Figure 6a*). For higher angles guided polaritons are also unresolved (*Figure 6b*) because

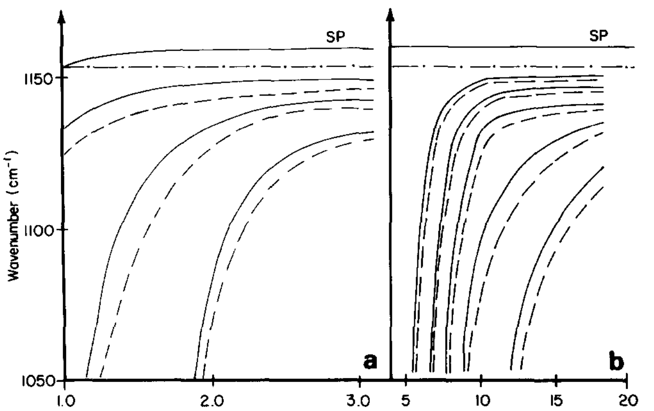
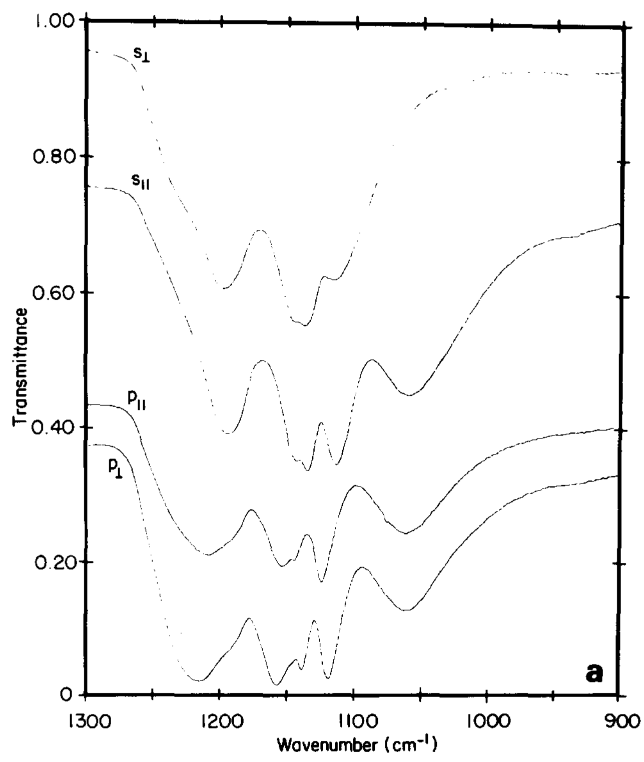


Figure 4 Calculated dependences of the film excitation frequencies (a) on the reduced wavevector (7 μm thick film) and (b) on the film thickness ($\theta = 30°$). SP means surface polariton branch; the lower curves are p-polarized (———) and s-polarized (– – –) guided modes. The chain line is a limiting frequency for the guided polaritons



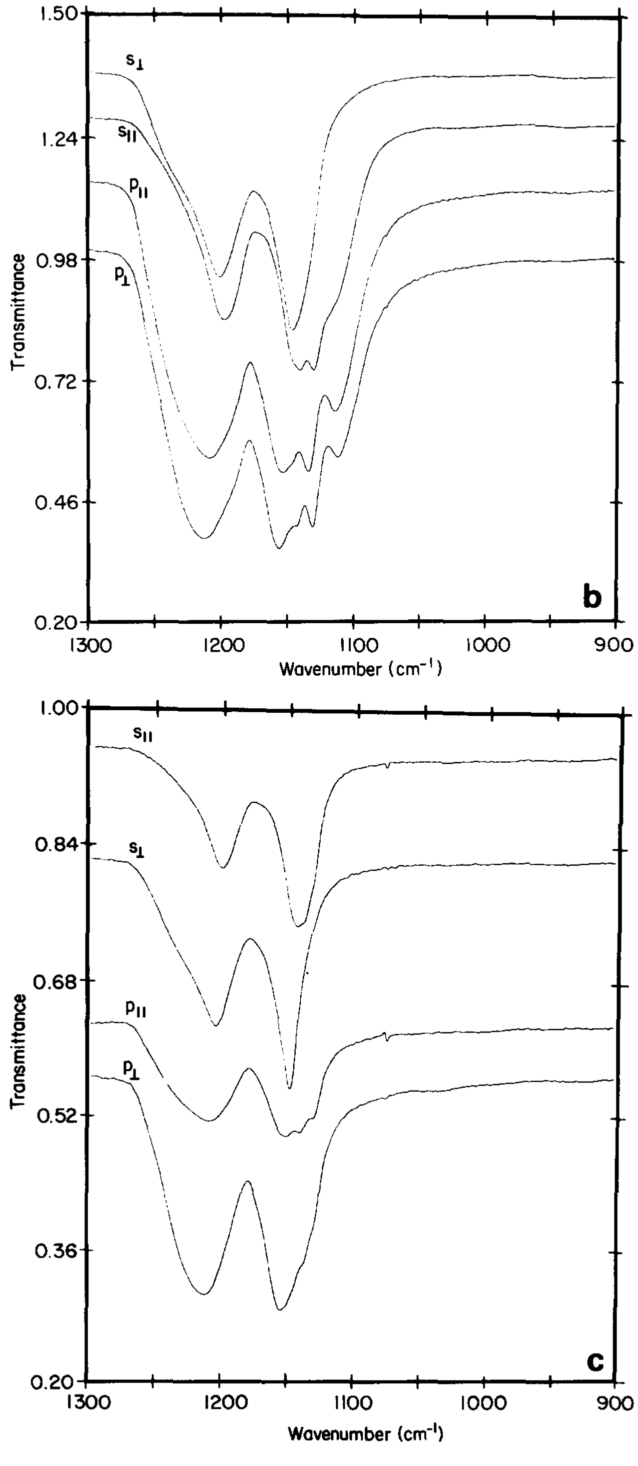


Figure 5 MIR transmittance spectra of 7 μm thick PTFE film at angles of incidence (a) 30°, (b) 45° and (c) 60°. Both s- and p-polarized spectra for perpendicular and parallel orientations to the plane of incidence in the film stretch direction are shown for each angle

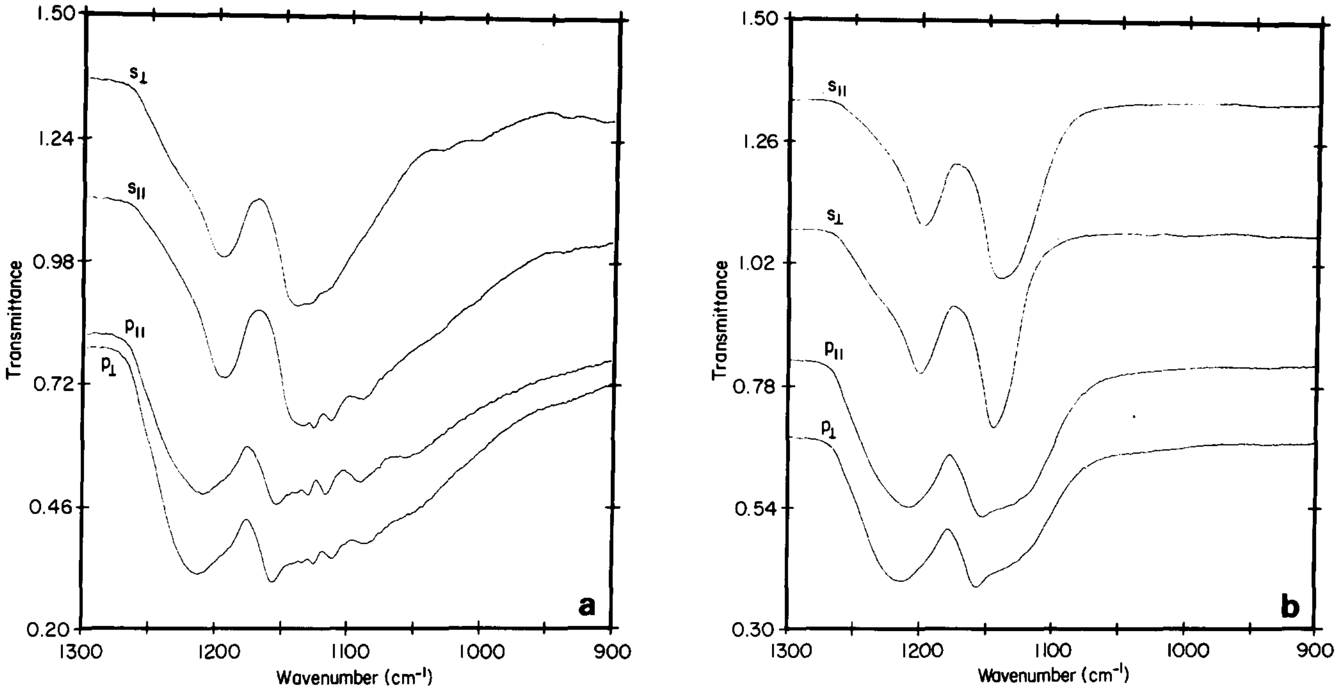


Figure 6 MIR transmittance spectra of 17 μm thick PTFE film at the angles of incidence (a) 30° and (b) 45°. All designations are the same as given in *Figure 5*

of the small distance between minima (compare with *Figure 4b*). The surface polaritons for all films are also sensitive to film anisotropy. For the thin film the difference in the surface polariton minima positions at two orientations is smaller. This means that thin films are more anisotropic, as was seen previously[4] with the use of external reflectivity.

Of the three thin films studied, the thickest was 25 μm thick. Its anisotropy was small, as it showed none in the surface polariton spectra obtained. No guided polaritons were observed either because they are too closely spaced for this film thickness and are strongly overlapped in the infra-red.

CONCLUSIONS

We obtained surface and guided polariton spectra of films of polytetrafluoroethylene and its copolymer with hexafluoropropylene. Results obtained from the thin-film examinations were in good qualitative agreement with the preliminary calculations (see *Figure 4*), even though the quantitative agreement was less good because of the model parameters used in the calculations. They were different from the actual ones. In order to obtain both the actual values of the thickness and the refractive indices for the principal direction from the MIR measurement, we need to use more angles of incidence. By performing this work, we would be able to obtain an even better description of the dispersion curves because we were able currently to use only three angles in our measurements. They did not yield sufficient information to obtain the best quantitative results. Nevertheless, we have found for the first time the existence of surface polaritons on a polymer surface. For bulk films the large linewidths and the narrow frequency regions provided little opportunity to obtain the dispersion. It might have been possible to perform the measurements if angles closer to the critical angle of total reflection could be achieved.

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