An Experimental Technique for the Characterization of Molecular Orientation Through the Thickness of Plastic Products

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An experimental technique has been developed for the characterization of the molecular orientation through the thickness of plastic products. The technique consists of milling the specimen to the depth where the molecular orientation is to be measured, polishing the exposed surface, and characterizing the polished surface by external reflection infrared spectroscopy. The technique was first tested on both unoriented and oriented poly(ethylene terephthalate). It was found that the intermediate steps of the process change the apparent surface orientation, but carrying the process to completion (to a finish of 0.05 μm) removes the altered material and leaves a surface whose orientation corresponds to that of the original sample. The technique was also tested on polyetheretherketone (PEEK), high density polyethylene (HDPE), and liquid crystal polymer (LCP). For polymers with a high transition temperature, like PEEK and LCP, the conclusions are the same as for PET. However, for polymers like HDPE, with a low glass transition temperature, the milling and polishing process used to prepare the samples can alter the orientation to a greater extent. This effect can be reduced by cooling the sample with liquid nitrogen during preparation.

INTRODUCTION

Molecular orientation in plastic products can be greatly affected by manufacturing methods. In injection molding, for example, it has been found that polymer molecules at the surface of the molding can be oriented in the flow direction parallel to the mold wall, while in the center the molecules may be completely unoriented (1, 2). Such a variation in the molecular orientation in the thickness direction will generate a difference in both the optical and mechanical properties of different layers through the thickness direction of the injected part and consequently will affect the quality and performance of the final product (3). Therefore, the exact determination of the variation of orientation of the polymer molecules with respect to the specimen's thickness is of great importance, since it can provide a better characterization of plastic products.

For many years, the molecular orientation across plastic products has been characterized by means of both microtoming and optical techniques such as birefringence and infrared spectroscopy (1, 2). Microtoming involves cutting from the molded specimen thin slices, or sections, with a thickness low enough to allow visible or infrared radiation to pass through. The technique is not without problems, however, because the morphological characteristics of the cut sections are affected by the cutting conditions and the quality of the knife. These problems have recently been discussed in detail (4). It was pointed out that

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the local increase in temperature where the knife contacts the specimen and the compression of the section during the cutting are the major factors affecting the dimensions and the morphology of the sections. Recent work involving infrared measurements (5, 6) has also indicated that the microtoming process induces a small but significant change (around 0.05) in the orientation function.

It is the aim of this study to present an alternative method for the characterization of molecular orientation across the thickness of plastic products. It involves the removal of successive layers of polymer from the sample by means of milling and polishing, followed by measurement of the infrared spectrum by means of external specular reflection. The advantages of the latter technique for studying orientation in polymer samples have been demonstrated recently by one of the authors and co-workers (7, 8) as well as by other groups (9–12).

EXPERIMENTAL

The material used in the initial experiments to develop the method was DuPont Selar PT 7086 extrusion grade poly(ethylene terephthalate) without a nucleating agent. This material has a glass transition temperature of 70°C and a crystalline melting temperature of 245°C. A sample of undrawn PET with low crystallinity and orientation was obtained by compression molding of dried granules at 280°C, followed by rapid cooling in a water bath. A sample of oriented PET with a draw ratio (denoted as λ) equal to 5.2 was obtained by drawing semicrystalline material in a roll-drawing process (13). Both the drawn and undrawn specimens were considered to possess a constant molecular orientation through the thickness.

The method was then tested on other materials having different thermal and mechanical properties. These included polymers with high and low glass transition temperatures, as well as a polymer that showed morphological changes under both high temperatures and high shear rates, which may occur during the polishing process. The materials were: extrusion-grade polyetheretherketone (PEEK), Victrex 450G from ICI; extrusion-grade high density polyethylene (HDPE), extruded profile obtained from Fabco Plastics Inc.; and 20% glass-fiber-filled liquid crystal polymer (LCP), Vectra B420. The PEEK and HDPE were first extruded to obtain flat profiles (approximately 1 cm thick and 10 cm wide), then stretched by roll-drawing at high temperatures (13). The PEEK was drawn at 250°C to $\lambda = 3.1$, and the HDPE was drawn at 110°C to $\lambda = 9.6$. The LCP composite was injection-molded on a 70-ton injection-molding machine. The injection parameters were as follows: mold temperature = 50°C; melt temperature = 300°C; injection rate = 5.08 cm/s; holding pressure = 4.14 MPa; holding time = 10 s; and cooling time = 10 s.

The molecular orientation at the surface of the samples was characterized at different stages of the milling and polishing process by means of front-surface external specular reflection infrared spectroscopy (7). The milling process was conducted with water cooling (to maintain the temperature as low as possible) using both a single point cutter and a high cutting speed, in order to minimize the energy dissipated during the fracture and the deformation of the polymer (14). Before the polishing process, samples cut from the milled specimens were placed in a rubber mold, milled surface down, and an epoxy resin was poured into the mold and cured (at room temperature) to provide support for the samples. The next step was to mount the samples in a rotating polishing machine and to polish the milled surface. The step-by-step polishing process is summarized in *Table 1*. The different polishing systems were purchased from Buehler Co., USA. After each step of the polishing process, the quality of the polished surface was checked using an optical microscope and considered acceptable if the scratches generated during a previous polishing step were completely eliminated.

At each stage of the milling-polishing process, infrared reflectance spectra were measured on a Nicolet 170SX FT-IR spectrometer equipped with a Model 134 specular reflectance accessory and a zinc selenide wire grid polarizer from Spectra-Tech Inc. Each spectrum was the result of an accumulation of 128 scans at a resolution of 4 cm^{-1}. The angle of incidence was 11° and a front-surface gold mirror was used as a reference. For oriented specimens, spectra were measured with polarization both parallel and perpendicular to the draw direction. For unoriented specimens, spectra were measured with polarization in two arbitrary but mutually perpendicular directions. The measured reflectance spectra were subjected to Kramers-Kronig transformation in order to obtain the refractive index (n) and absorption index (k) spectra. This was done by means of the commercial software Spectra-Calc™ from Galactic Industries Corp., with the use of their Maclaurin's series algorithm to perform integration. The software was slightly modified in-house to allow calculation of the imaginary molecular polarizability function ϕ from the n and k spectra. The molecular

Table 1. Details on Different Steps of the Polishing Process.

Step	Lap Surface	Abrasive and Size	Cooling Medium	Load (N) (6 specimens)	Speed (rpm)	Time (s)
1	CARBIMET	320 grit SiC	Water	100	150	15
2	CARBIMET	400, 600 grit SiC	Water	100	150	20
	MICROCUT	800 grit SiC	Water	100	150	20
3	TEXMET	3μ Diamond (poly)	—	120	150	180
4	MASTERTEX	MASTERPREP	—	120	150	240

polarizability correlates more closely with the molecular properties, especially for the more intense absorption bands (15). From the ϕ spectra, dichroic ratios and orientation functions were calculated according to the usual procedures (7). In calculating the orientation functions, the orientation was assumed to be uniaxial (fiber symmetry). For the roll-drawn samples, the degree of biaxial orientation is known to be small (13).

RESULTS AND DISCUSSION

Poly(ethylene terephthalate) (PET)

The reflectance spectra obtained for the undrawn highly amorphous PET sample at the different stages of the milling and polishing process are shown in *Fig. 1.* They are all shown at the same reflectance scale in order to illustrate the effect of surface quality on the overall reflectance. The molecular polarizability spectra obtained from the reflectance spectra are shown in *Fig. 2.* In this case, the y-axis scale is adjusted for each case in order to better show the details of the spectra.

Figures 1a and *2a* show the spectra obtained from the surface of the undrawn specimen before any milling or polishing. Contrary to what might be expected, the two polarization directions do not give exactly the same result, although they are very similar. The small difference indicates the presence of slight molecular orientation at the surface of the specimen. The main difference is noted for the CH_2 wagging peak of the trans glycol conformers at 1340 cm^{-1}, which has a dichroic ratio D equal to 1.9. This peak is highly sensitive to orientation. The slight orientation is believed to be due to the excessive compression of the polymer melt in the mold during the molding process, which can orient polymer chains at the surface of the specimen in one arbitrary direction.

Figures 1b and *2b* show the spectra obtained after the milling process. The surface exposed by the milling was 0.1 mm below the original surface of the specimen. It can be seen that the overall intensity of these spectra is considerably lower than that of the preceding ones. This is due to increased surface roughness. As a result, much of the incident radiation is diffusely reflected and therefore not detected by the specular reflection accessory; this gives rise to a low apparent reflectance and poor signal-to-noise ratio. In fact, the weaker peaks are barely visible.

In order to overcome this problem, the quality of the milled surface was improved by progressive polishing. The first step of the polishing process was sanding with 320 grit paper to reduce both the number and the size of defects generated during the milling. The spectra obtained are shown in *Figs. 1c* and *2c.* Because the surface is still fairly rough, they are no better than those of the milled surface. The only improvement, if any, is a somewhat straighter baseline.

After further sanding, to 800 grit, the spectra shown in *Figs. 1d* and *2d* are obtained. Because of the reduced roughness, the reflectance spectra become much more intense and well defined, and all the main characteristic peaks of PET are observed. However the peaks in the ϕ spectra are slightly deformed, indicating that the Kramers-Kronig transformation does not cleanly separate the n and k contributions. Furthermore, comparison of the parallel and perpendicular spectra shows the presence of dichroism, particularly evident for the 1340 cm^{-1} peak. This suggests that the sanding has induced some orientation at the surface of the specimen.

The next stage of the specimen preparation was polishing with 3 μm diamond paste. The resulting spectra are shown in *Figs. 1e* and *2e.* In comparison with the preceding spectra, it can be seen that the overall reflectance level has improved slightly, and, more important, the dichroism has practically disappeared. The oriented material produced by the 800 grit sanding appears to have been removed.

The final stage of the process was polishing with 0.05 μm diamond paste. The spectra, shown in *Figs. 1f* and *2f,* are of excellent quality and are virtually identical in shape. There is no indication of any orientation, as expected for a hot-pressed undrawn sample. The slight orientation observed at the original surface is not seen at lower depths.

Figures 3 and *4* show a similar set of spectra obtained for the highly oriented PET sample. In this case, as expected, the spectra recorded for the initial surface show strong dichroism. The carbonyl band at 1729 cm^{-1} and the benzene ring out-of-plane C-H band at 730 cm^{-1} show perpendicular dichroism because their transition moments are more or less perpendicular to the polymer chain axis. Parallel dichroism, on the other hand, is observed for the CH_2 wagging peak at 1340 cm^{-1}, the in-plane benzene ring C-H peak at 1018 cm^{-1}, and the strong ester peaks around 1330–1240 and 1160–1080 cm^{-1}.

For the oriented sample, the milling process seems to have little effect on the measured reflectance spectra *(Figs. 3b, 4b).* This result is rather surprising, since it was found that in the case of the unoriented sample the milling process drastically reduced the overall intensity of the spectra *(Figs. 1b, 2b).* One possible explanation is a difference in the quality of the milling tool used. Jansen has shown (11) that for a liquid crystal polymer, ultra-milling has a negligible effect on the orientation, but it is critical that the knife be of excellent quality (16). A second possible explanation is a different response of the unoriented and the oriented PET to the milling. The oriented sample was semicrystalline to begin with, and the combination of orientation and higher crystallinity will produce higher mechanical properties. It is of interest to note that the strong complex bands around 1330–1240 and 1160–1080 cm^{-1} show a slightly different shape after milling *(Fig. 3b)* compared with before *(Fig. 3a).* The shape of these bands is sensitive to the PET crystallinity, so this may indicate that the milling has changed the structure somewhat. It can be concluded that while the milling process may work well in certain circumstances, it cannot be considered as a foolproof technique for the characterization of molecular orientation

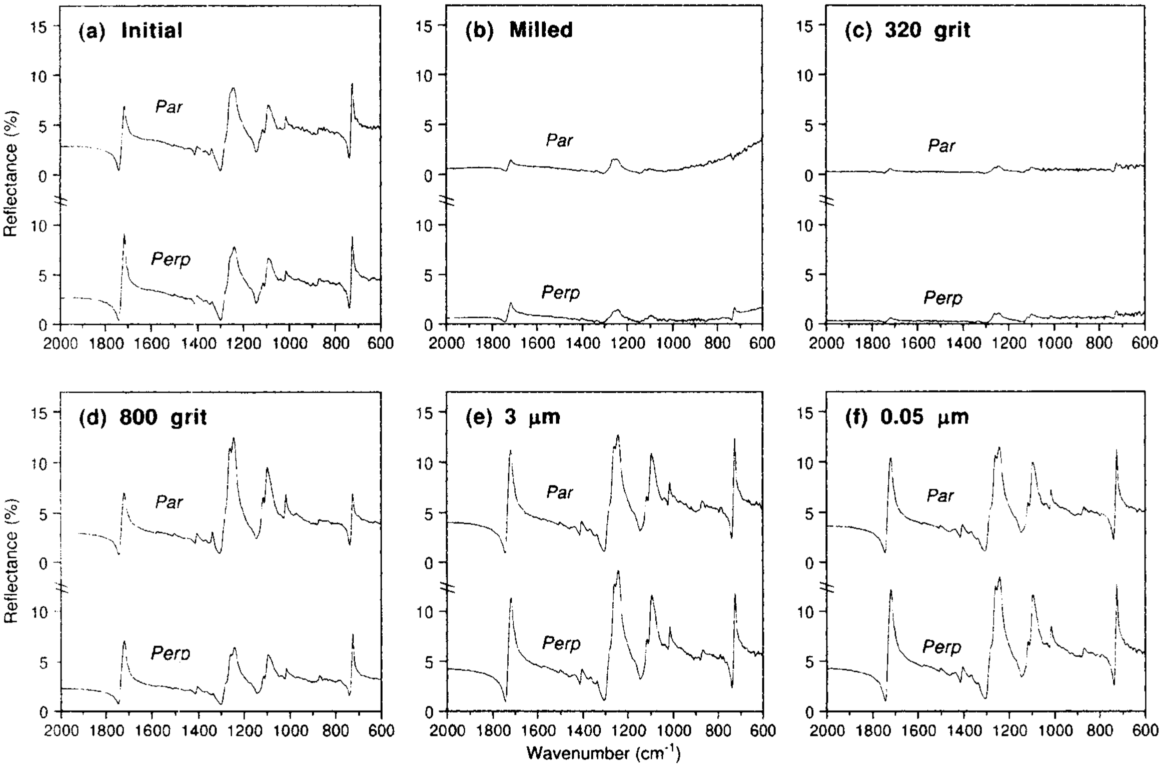

Fig. 1. External reflection spectra measured at the surface of the unoriented PET sample at different stages of the milling and polishing process.

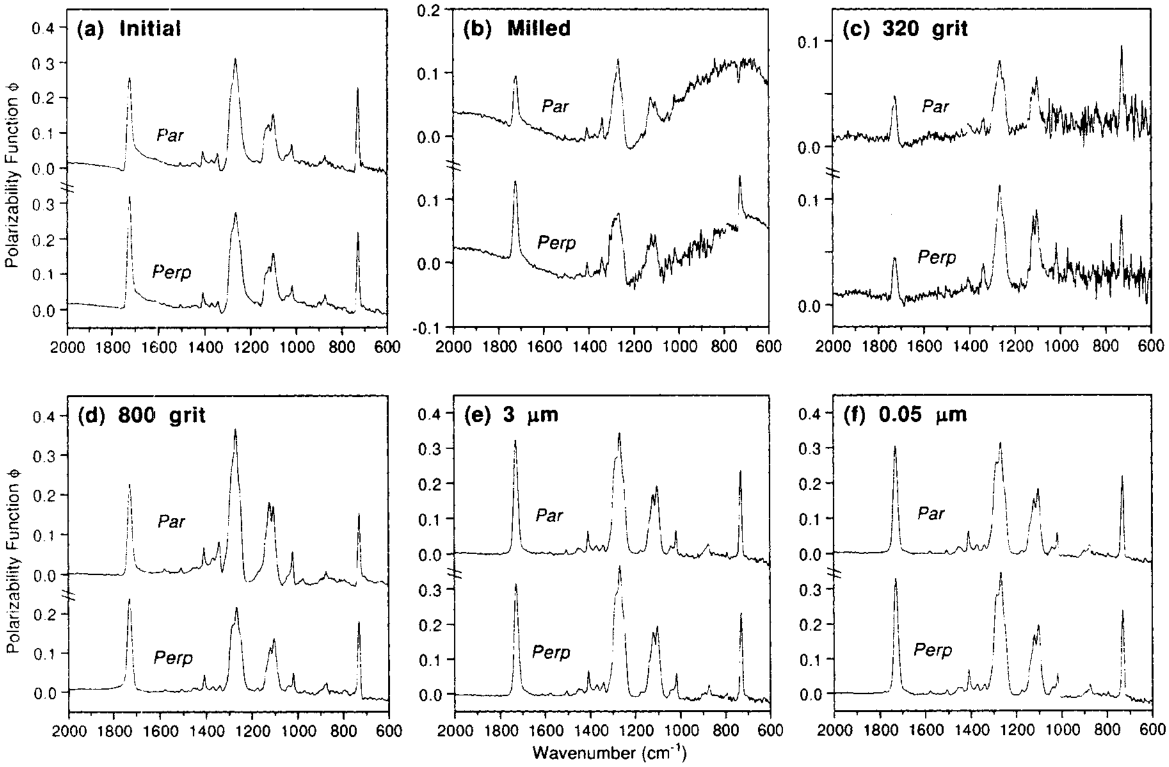

Fig. 2. The spectra of Fig. 1 after conversion into the imaginary molecular polarizability function by means of the Kramers-Kronig transformation.

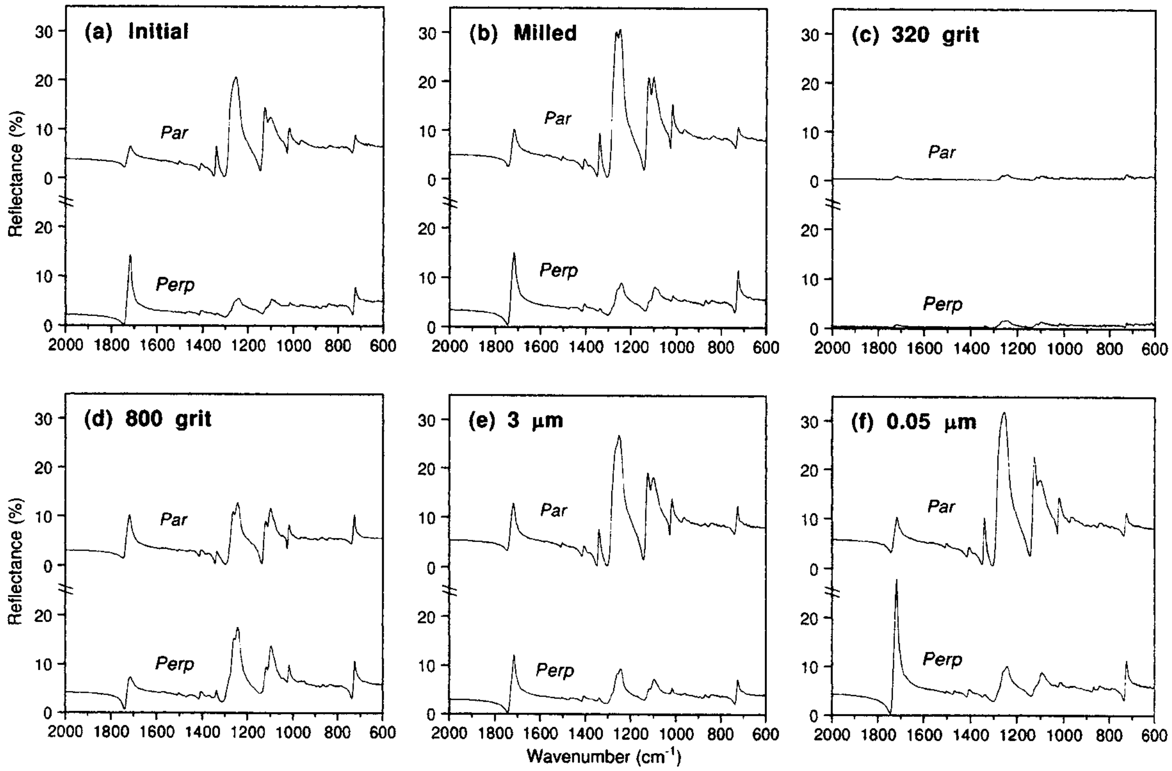

Fig. 3. External reflection spectra measured at the surface of the oriented PET sample at different stages of the milling and polishing process.

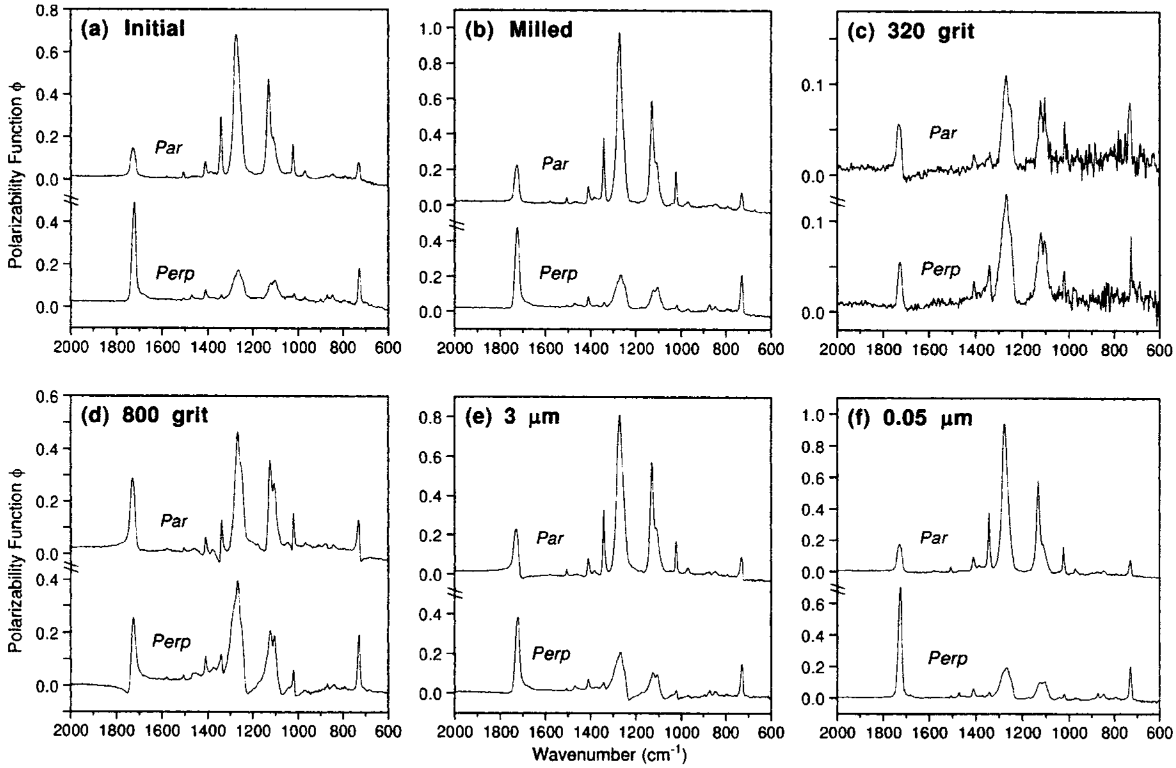

Fig. 4. The spectra of Fig. 3 after conversion into the imaginary molecular polarizability function by means of the Kramers-Kronig transformation.

through the thickness of plastic products. It appears that the characteristics of the milled surface can depend on the sharpness of the cutting tool, the milling direction, and the material's properties.

As was the case for the undrawn sample, the spectra recorded after 320 grit sanding were very poor (*Figs. 3c, 4c*). After sanding to 800 grit (*Figs. 3d, 4d*), the overall intensity increases significantly but the ϕ spectra show somewhat deformed peaks and much lower dichroism than the initial surface. The surface layer at this stage has lost much of its orientation. The next stage (3 μm diamond polishing) removes most of this disturbed material and restores much of the dichroism (*Figs. 3e, 4e*), but the peaks in the ϕ spectra are still somewhat deformed. It is the final polishing step (0.05 μm diamond) that gives the highest reflectance level and the greatest difference between parallel and perpendicular polarization (*Figs. 3f, 4f*). Furthermore, and this is the most important observation, the spectra obtained after the final polishing step are virtually identical to those obtained from the original surface (*Figs. 3a, 4a*), except that they are more intense overall. We conclude therefore that the complete milling and polishing process results in a surface whose properties correspond to those of the original sample. This is true even though the intermediate stages may produce surfaces that are rough and may contain material that has been altered by the treatment. The final polishing step removes the altered material and leaves a surface that is smooth enough to eliminate any effects of polarization scrambling.

There may be some question as to whether the drawn sample indeed possessed the same degree of orientation at the surface as at the depth exposed by our procedure. This is difficult to verify, but we believe it to be the case. It is known that for drawn samples, orientation gradients are much smaller than those observed in injection molded samples (2). If a gradient did exist in our sample, in order for the two sets of spectra (*Figs. 3a and 3f*) to match so well, our procedure would have to alter the orientation of the newly exposed surface by an amount just sufficient to exactly compensate for the gradient difference. This is highly unlikely.

In an attempt to quantify the effects just discussed, dichroic ratios were calculated from the ϕ spectra for various peaks in the PET spectrum. Unfortunately, the overall intensity of a front-surface reflection spectrum is affected by a number of factors, such as surface roughness and sample positioning in the accessory. Even when the surface is highly polished and parallel and perpendicular spectra are measured consecutively without moving the sample, variations are observed. Thus for the polished unoriented PET sample (*Fig. 1f*), where the two spectra should be identical, there is a slight difference in overall intensity, even though the shape of the spectra is the same. This variation in intensity must be taken into account in calculating dichroic ratios. Fortunately, in the case of PET, it is possible to normalize the spectra with respect to a reference peak at 1410 cm^{-1}, which is known to be insensitive to both orientation and crystallinity (17). After the spectra are multiplied by the factors required to bring the area of this peak to a fixed chosen value, dichroic ratios can be calculated for other peaks by taking the ratio of the peak areas in the parallel and perpendicular spectra.

Apparent dichroic ratios were thus calculated for different peaks in the ϕ spectra of *Figs. 2* and *4* by taking ratios of integrated peak areas and applying a correction based on the 1410 cm^{-1} reference peak. The results obtained for the undrawn and drawn samples of PET are summarized in *Tables 2* and *3*, respectively. In the case of the amorphous undrawn PET (*Table 2*), the dichroic ratios for all the characteristic peaks after the final step of the polishing process are close to 1, indicating that there is no molecular orientation in this specimen. As mentioned previously, the initial surface of this sample shows evidence of slight orientation. At intermediate steps of the process, however, such as after milling and 800 grit sanding, the calculated apparent orientation is not negligible and the measured dichroic ratios differ significantly from 1. This may be attributed to the imperfect quality of the surface and the possible presence of a deformed polymer on it. However, after the final step this material is removed and these effects disappear. Thus the overall process of the milling and polishing operations does not disturb or generate molecular orientation in PET. In the case of the semicrystalline oriented PET (*Table 3*), it was also found that the measured dichroic ratio depends on the quality of the polished surface. The final dichroic ratios are virtually identical to the ones recorded at the surface of the specimen, given the experimental errors involved.

Table 2. Evolution of the Apparent Dichroic Ratio for the Unoriented PET Sample After Each Step of the Milling and Polishing Process. (Where the transition moment angle is known, calculated orientation functions are shown in parentheses.)

Peak → (cm^{-1})	1340	1020	727	1725	1263	1100
Surface	1.90 (0.29)	1.02 (0.00)	1.09 (−0.04)	0.92	1.12	1.06
Milling	1.02 (0.01)	0.89 (−0.05)	—	0.53	1.05	0.97
Step 1	0.90 (−0.04)	—	1.60 (−0.33)	1.26	1.10	0.91
Step 2	4.46 (0.66)	2.21 (0.34)	0.79 (0.15)	0.79	1.43	1.21
Step 3	0.92 (−0.03)	0.89 (−0.05)	1.14 (−0.09)	1.07	0.97	1.01
Step 4	0.93 (−0.03)	0.98 (−0.01)	1.07 (−0.04)	0.97	0.99	1.01

Table 3. Evolution of the Apparent Dichroic Ratio for the Oriented PET Sample After Each Step of the Milling and Polishing Process. (Where the transition moment angle is known, calculated orientation functions are shown in parentheses.)

Peak → (cm^{-1})	1340	1020	727	1725	1263	1100
Surface	9.46 (0.90)	3.59 (0.55)	0.30 (0.60)	0.22	2.08	1.83
Milling	8.67 (0.89)	4.18 (0.61)	0.24 (0.68)	0.28	1.98	1.75
Step 1	0.47 (−0.26)	0.89 (−0.03)	2.87 (−0.76)	1.31	0.71	0.89
Step 2	1.80 (0.26)	1.40 (0.13)	0.59 (0.32)	0.94	0.71	1.20
Step 3	5.40 (0.73)	2.44 (0.38)	0.35 (0.54)	0.35	1.30	1.45
Step 4	8.14 (0.86)	4.30 (0.63)	0.34 (0.56)	0.22	2.03	1.90

However, as for the case of the undrawn sample, the apparent dichroic ratios at intermediate stages of the process, especially after the sanding steps, are substantially different from the true values.

Polyetheretherketone (PEEK)

Polyetheretherketone was included in the study because of its high glass transition temperature, $T_g \sim 150$°C. Spectra recorded at the surface of the oriented PEEK sample in directions parallel and perpendicular to the draw direction are shown in *Fig. 5a*. Almost all the absorption bands show significant dichroism, suggesting the presence of high molecular orientation at the surface of this specimen. It can be seen that the two spectra of *Fig. 5a* do not have the same "baseline" reflectance values in regions where there are no absorption peaks (for example, at 2000 cm^{-1}). Some of the reasons for this variation in overall reflectance intensity were discussed above in connection with PET, where the problem can be overcome by using the 1410 cm^{-1} peak as an internal reference. Unfortunately no such peak has been identified for PEEK, so it was necessary to use a different procedure to correct the spectra. The theoretical value of the reflectance R at normal incidence when there is no absorption is given by $R = [(n-1)/(n+1)]^2$, where n is the refractive index. For unoriented PEEK, n = 1.68 so the calculated baseline reflectance is 0.064 or 6.4%. Hence the reflectance spectra were scaled to give R = 6.4% at 2000 cm^{-1}, before performing the Kramers-Kronig transformation to give the ϕ spectra required to calculate the dichroic ratios. In fact, oriented PEEK will have different refractive indices in the draw and transverse directions (i.e., birefringence) and so will be expected to give somewhat different values of R for the parallel and perpendicular polarization. Hence the approach just described must be considered an approximation and the values of the dichroic ratios obtained will be slightly different from the true values. However, for the present work this is not a serious problem because the error is systematic and the object is not to determine absolute values of the orientation but rather to compare on a relative basis the values obtained at different stages.

In the present investigation, the specific bands considered occur at 1648, 1599, 1492, and 1190 cm^{-1}. The band at 1648 cm^{-1} is associated with the stretching of the carbonyl group and has a transition moment angle α equal to 90° (18). The bands at 1599 and 1492 cm^{-1} are associated with phenyl ring vibrations and the one at 1190 cm^{-1} is characteristic of the diphenyl ether group. From a correlation of their dichroic behavior with that of the carbonyl band, the transition moment angles for the peaks at 1599, 1492, and 1190 cm^{-1} have been estimated to be 37°, 28°, and 31° respectively (19). Based on these values, the orientation function *f* for each of these bands has been computed and the results obtained are summarized in *Table 4*. The orientation is found to be rather high, with an average value of *f* around 0.55.

Figure 6 shows spectra recorded from the surface of the PEEK sample after the final step of the same milling and polishing procedure used for the PET samples. This surface was 0.1 mm below the original

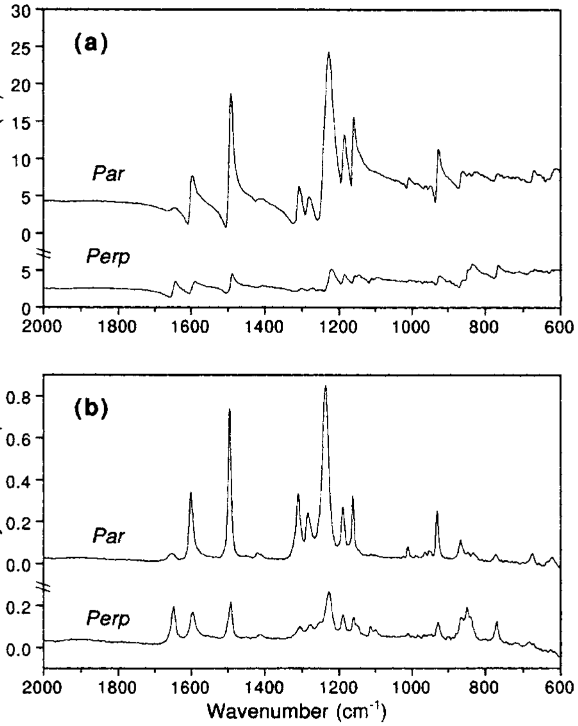

Fig. 5. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the original surface of the oriented PEEK sample.

Table 4. Dichroic Ratios and Orientation Functions (in Parentheses) Obtained for the Oriented PEEK Sample.

Peak (cm^{-1}) →	1648	1599	1492	1190
Original Surface	0.27 (0.64)	1.98 (0.52)	3.22 (0.62)	2.26 (0.48)
Sub-skin layer	0.29 (0.60)	1.92 (0.50)	2.78 (0.55)	2.09 (0.43)

surface of the specimen. The spectra have exactly the same appearance as those obtained for the original surface, but their overall intensity is considerably higher because of the better quality of the polished surface. Moreover, *Table 4* shows that the orientation functions computed for the bands considered above are almost identical to those obtained for the original surface, suggesting that the milling and polishing process has not significantly changed the molecular orientation in the drawn PEEK. These results, together with those already obtained for PET, show that the milling and polishing process is a reliable technique for the characterization of molecular orientation in polymers with high glass transition temperatures.

High Density Polyethylene (HDPE)

High density polyethylene was chosen because of its low glass transition temperature of -120°C. Spectra recorded before and after the milling and polishing process are shown in *Figs. 7* and *8* respectively. In comparison with PET and PEEK, the vibrational bands of HDPE are fewer and weaker because of the very different chemical structure. In *Fig. 7*, only the C-H stretching bands at 2918 and 2857 cm^{-1} are well defined, and the spectra are complicated by a small degree of reflection from the back surface of the sample. The spectra of *Fig. 8* are of much better quality. Mounting the sample in epoxy resin eliminates the back surface reflection, and polishing leads to higher overall reflectance and a straighter baseline. Before they were used to calculate the polarizability spectra, the reflectance spectra were corrected in a manner similar to that used for PEEK, except that they were normalized to $R = 4\%$ ($n = 1.5$) at 4000 cm^{-1}. All the major peaks in polyethylene show perpendicular dichroism. From a look at dichroism of the 2918–2850 peaks in *Figs. 7b* and *8b*, it is clear that the polished surface exhibits a lower apparent degree of molecular orientation. Dichroic ratios and orientation functions were calculated for the vibrations at 2918–2850 cm^{-1}, 1473–1460 cm^{-1}, and 730–720 cm^{-1} based on the reported transition moment angles of 70°, 79°, and 90° respectively (20). The results, summarized in *Table 5*, confirm the lower orientation for the polished surface. The effect is most pronounced for the 2918–2850 cm^{-1} band, which is also the most intense and therefore subject to less experimental error. A probable reason for the lower apparent orientation is that the milling and polishing were done with water as a cooling medium, at a temperature higher

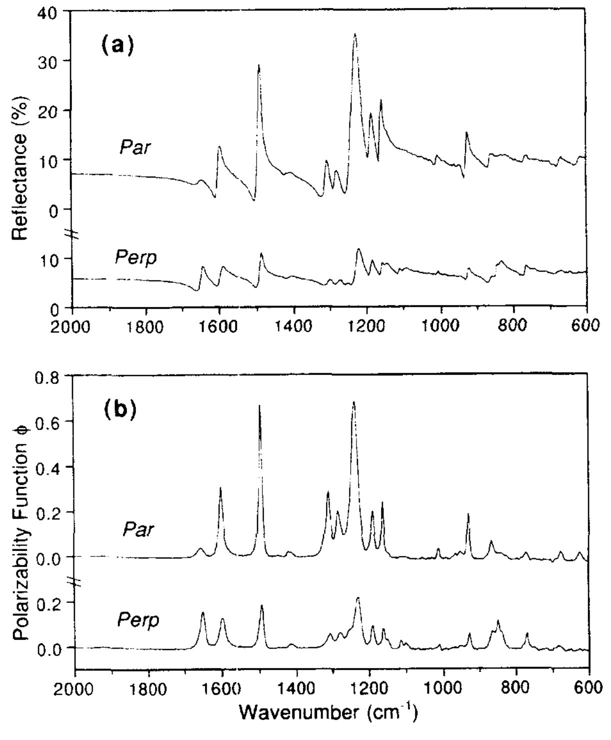

Fig. 6. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the surface of the oriented PEEK sample after the complete milling and polishing process.

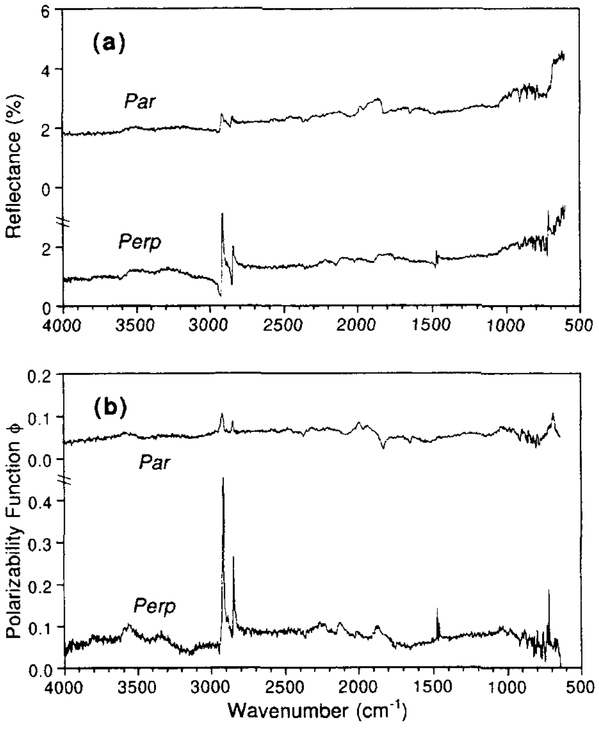

Fig. 7. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the original surface of the oriented HDPE sample.

than the glass transition of the polymer, so the polymer orientation may have been altered by the process. To check this, a second specimen was prepared using liquid nitrogen at a temperature of −196°C as a cooling medium. The spectra obtained from this surface are shown in *Fig. 9*. The dichroism and the calculated orientation functions (*Table 5*) are higher than for the water-cooled specimen, suggesting that the low values obtained for the water-cooled specimen are indeed at least partly due to changes induced by the polishing process. However, the values obtained with liquid nitrogen polishing are still lower than those for the original surface. Hence, while the use of liquid nitrogen during the different polishing steps appears to reduce the extent of relaxation of the polymer chains in HDPE, it does not prevent it completely. Perhaps further optimization of the polishing conditions to ensure more thorough cooling of the HDPE would improve the results.

An interesting trend in *Table 5* is worth noting. The higher the frequency of the band used, the greater is the variation of the apparent dichroism as a function of the surface preparation. This may be a wavelength-related effect. At 2900 cm^{-1} the wavelength is 3.4 μm, whereas at 725 cm^{-1} it is 13.8 μm. Since the depth of the sample that is probed is proportional to the wavelength, the shorter-wavelength bands "see" less deeply into the sample and would be expected to be more affected by a thin surface layer of disturbed material.

Table 5. Dichroic Ratios and Orientation Functions (in Parentheses) Obtained for the Oriented HDPE Sample.

Peak (cm^{-1}) →	2918–2850	1473–1460	730–719
Original Surface	0.22 (1.00)	0.20 (0.80)	0.10 (0.84)
Sub-skin layer (water cooling)	0.54 (0.52)	0.33 (0.63)	0.14 (0.80)
Sub-skin layer (liquid nitrogen cooling)	0.38 (0.77)	0.30 (0.67)	0.12 (0.82)

Liquid Crystal Polymer (LCP)

The milling and polishing technique was also applied to a new class of polymer that is finding increasing use, namely thermotropic liquid crystalline polymers (LCP). These materials are recognized for their high strength, high modulus, and high chemical resistance. One of them was chosen for study because they can easily change their morphological characteristics under both high temperatures and high shear rates (21), for example during the polishing process. Unlike the roll-drawn samples of PET, PEEK, and HDPE previously discussed, the LCP sample used in this study was injection-molded and contained glass reinforcement.

It has been reported in the literature that the microstructure of injection-molded LCP specimens in the thickness direction shows the presence of the so-called skin-core structure (22). The skin layer is highly ori-

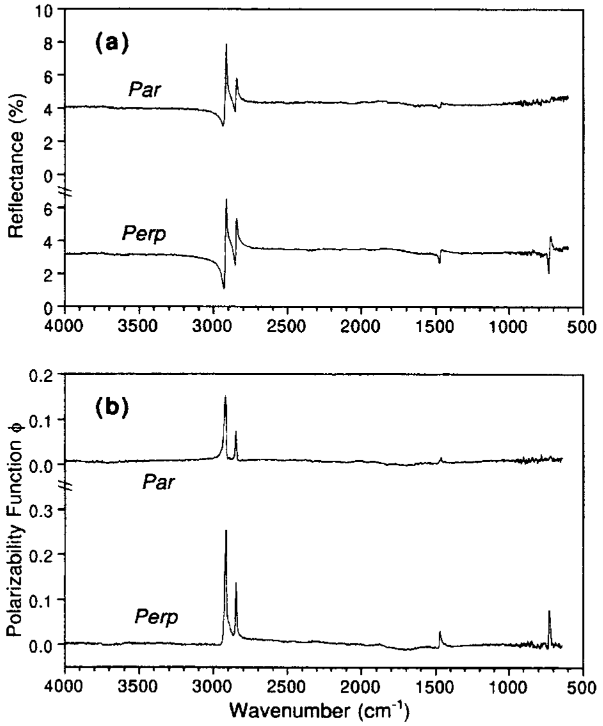

Fig. 8. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the surface of the oriented HDPE sample after milling and polishing with with water as a cooling medium.

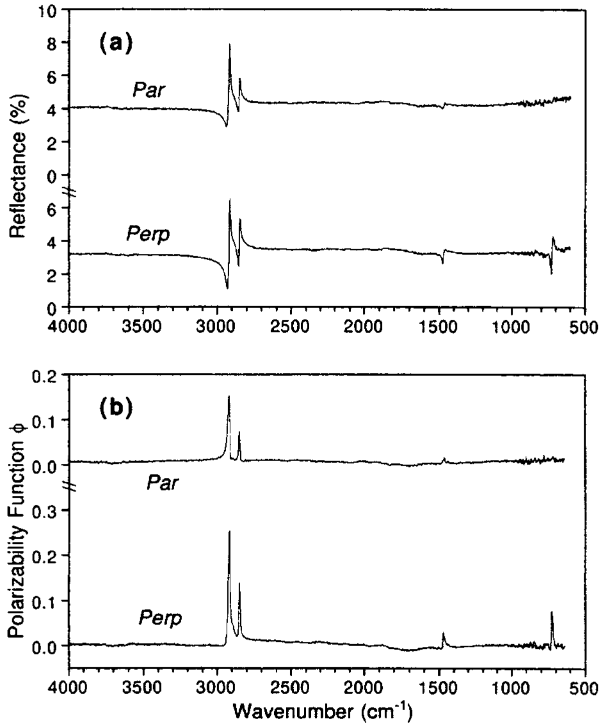

Fig. 9. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the surface of the oriented HDPE sample after milling and polishing with the aid of liquid nitrogen as cooling medium.

Table 6. Dichroic Ratios and Orientation Functions (in Parentheses) Obtained for Injection-Molded LCP Sample.

Peak (cm^{-1}) →	1735	1631	1509	1470
Original Surface	0.54 (0.35)	4.42 (0.53)	2.81 (0.37)	3.33 (0.43)
Sub-skin layer	0.79 (0.15)	1.40 (0.11)	1.31 (0.09)	1.48 (0.13)

ented as a result of the advancing melt front, which orients polymer chains parallel to the mold wall in the flow direction. Between the skin and the core layers exists a sub-skin layer that is less oriented because of the shear flow therein. In the core of the molding, however, the molecular chains were found to be poorly oriented because of the presence of plug flow in this area.

Figure 10 shows spectra recorded at the surface of the LCP molding, measured with the polarization direction parallel and perpendicular to the flow direction. From this *Figure* it can be clearly seen that several bands show significant dichroism, suggesting that polymer chains at the surface of the molding are highly oriented. To compute the orientation function *f*, the following bands were considered: 1735, 1631, 1509, and 1470 cm^{-1}. The band at 1735 cm^{-1} is associated with the carbonyl stretching vibration, whose transition moment should be more-or-less perpendicular to the molecular chain axis. The other major bands are known to be parallel bands associated with skeletal vibrations of the benzene and naphthalene rings in the polymer (23). As was done for the other polymers, the reflectance spectra were normalized to a common reference value (5% at 2200 cm^{-1}) and transformed into molecular polarizability spectra that were then used to calculate dichroic ratios. Approximate orientation functions were calculated by assuming transition moment angles of 0° for the parallel bands and 90° for the carbonyl band. The results, given in *Table 6*, confirm that the polymer chains are oriented in the flow direction, as pointed out by many authors. As already mentioned, this is due to the effect of the advancing melt front which orients the polymer chains in the flow direction.

Spectra recorded at the sub-skin layer of this specimen, after the polishing process, are shown in *Fig. 11*. It is clear that the difference between parallel and perpendicular polarizations is less pronounced than in *Fig. 10*. The calculated dichroic ratios and orientation functions for the bands of interest are given in *Table 6* and they clearly show a lower degree of molecular orientation in the sub-skin layer of the molding. In this case the difference is real and not a result of the polishing process. Similar results have been obtained by Jansen *et al.* (11) and Barres *et al.* (24). Such a decrease of the molecular orientation at the sub-skin layer has been attributed to the shear flow in this area, which according to Ide and Ophir (22, 25) produces significantly less molecular orientation.

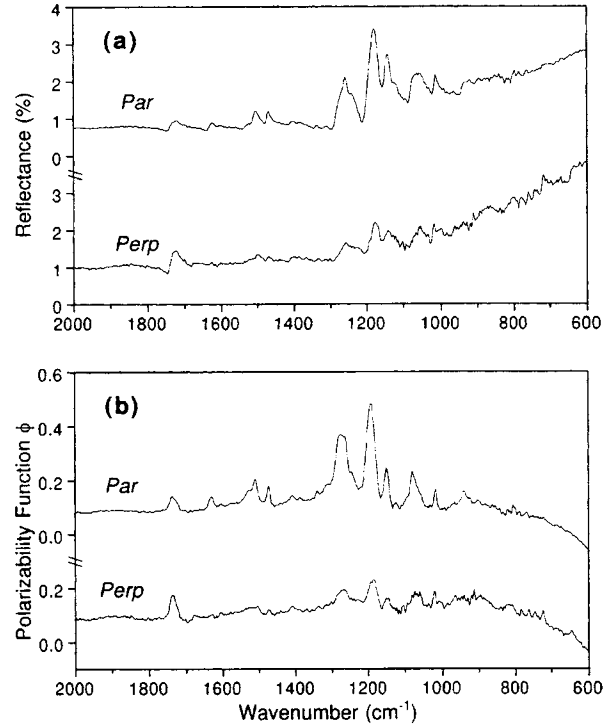

Fig. 10. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the original surface of the injection-molded glass-filled LCP sample.

In comparing *Figs. 10* and *11*, it can be seen that the sub-skin layer gives a very different spectrum from the surface layer at wavenumbers less than 1100 cm^{-1}. This is because the polishing exposes the reinforcing glass fibers, which possess strong IR absorption bands in this region. It is interesting to consider the possibility that reflection infrared spectroscopy might be used to obtain information on the orientation of the fibers themselves within the matrix, a phenomenon that is usually studied by polishing and visible-light microscopy. However, such an analysis might be difficult because of the complex optical effects arising from interaction between the infrared radiation and the two-phase system.

CONCLUSION

The aim of this study was to develop a relatively easy technique for the accurate characterization of molecular orientation across the thickness of plastic products. This technique consists of milling the specimen to the depth where molecular orientation is to be measured, polishing the surface produced by the milling process, and characterizing the polished surface by external reflection infrared spectroscopy. In the case of PET, it has been found that at intermediate steps of the milling and polishing process, the apparent molecular orientation can change depending on the quality of the resulting surface. However, when the polishing is taken to the final finish of 0.05 μm, the material disturbed by the previous polishing steps

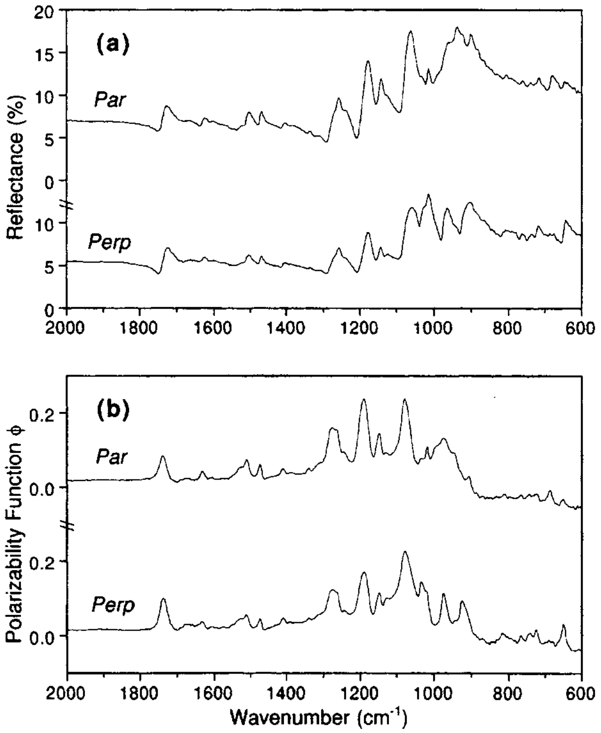

Fig. 11. Reflectance spectra (a) and corresponding polarizability spectra (b) measured at the surface of the injection-molded glass-filled LCP sample after milling and polishing.

is removed, the quality of the reflectance spectra is greatly improved, and if any disturbed material is still present, its thickness is negligible in comparison with the infrared sampling depth. As a result, the reflectance spectra give an accurate measure of the true orientation and the milling and polishing procedure used can be considered a reliable technique for the characterization of molecular orientation in the thickness direction of plastic products.

A similar result was obtained for another polymer with a high glass transition temperature, namely PEEK. However, the technique was found to be less reliable for polymers with a low glass transition temperature, such as HDPE. In this case, it appears that the heat generated by the polishing process affects the sample to a greater extent than for PET or PEEK, so the measured molecular orientation was found to be significantly affected by the milling and polishing process. Cooling with liquid nitrogen instead of water during the polishing operations was found to reduce the extent of the problem but did not eliminate it completely.

The technique was also applied to injection-molded glass-reinforced LCP. In this case, it showed that there is a lower level of orientation at the sub-skin layer of the molding compared with the surface. This is in agreement with results recently reported in the literature for injection-molded LCP materials and further confirms the utility of our technique for the characterization of molecular orientation in the thickness direction of plastic products.

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