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Residual stresses and molecular orientation in particulate-filled polypropylene

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Residual stresses have been measured in sepiolite-filled and talc-filled polypropylene compounds having filler levels of 10%, 25% and 40% by weight. The stress distributions depart significantly from parabolic in shape after ageing at 20° C, and have also been determined after annealing and after storage at −80° C. Complex changes occur, especially with the talc-filled materials. Some of the changes occurring during annealing can be attributed to changes in molecular orientation, primarily in the skin. The significance of these results is discussed with reference to distortion of injection mouldings.

1. Introduction

It is well known that injection-moulded articles often distort when exposed to elevated temperature. The driving force for this distortion is usually orientation. The build-up of residual stresses in injection-moulded parts is due to the large temperature gradient that is present during solidification process, caused by the low thermal conductivity (diffusivity) of polymer melts.

The experimental determination of residual stresses in injection-moulded polypropylene bars has been performed in several investigations. Coxon and White [1] studied the effect of ageing in injection-moulded bars, Qayyum and White [2] analysed the effect of weathering and Hindle *et al.* [3] reported residual stresses in injection-moulded glass-filled polypropylene. Using a different method of analysis, Kubát and Rigdahl studied the reduction of residual stresses in injection-moulded parts by incorporating metallic fillers [4]. The objective of the present study was to characterize and investigate the effect of ageing on the residual stresses in particulate-filled polypropylene compounds containing sepiolite and talc as fillers, using the layer-removal technique of Treuting and Read [5]. In this analysis, thin layers of uniform thickness are removed from one side of the bar, thus upsetting the residual stress equilibrium existing in the piece. To re-establish equilibrium, the specimen bends into the shape of a circular arc. The gapwise residual stresses in the specimen prior to the layer removal can be calculated by measuring the resultant curvature as a function of depth of material removed.

The second factor that has a significant influence on the behaviour of injection-moulded polypropylene is the degree of molecular orientation and its influence of the microstructure. Injection-moulded polypropylene reveals a two-phase structure of skin and core when observed under the polarized light microscope. The thickness of the skin layer depends on the type of resin and the moulding conditions. Kantz *et al.* [6] performed X-ray diffraction on the skin layer of injection-moulded polypropylene from many angles, and found that the crystallites are oriented biaxially during the injection process. The two-phase skin–core morphology is always easy to see even when the specimen sectioning technique is not perfect, but with careful specimen preparation and analysis more than two layers can often be identified. Mencik and Fitchmun [7], using polarized light microscopy and X-ray diffraction, distinguished three or four different morphologies in their injection-moulded polypropylene, depending on the moulding conditions. The first layer usually consisted of poorly oriented material, with a thickness of 30 μm; the second layer in which the *a*-axis of the polypropylene unit cell showed preferred orientation close to the moulding direction, had a thickness varying between 100 and 700 μm depending on the moulding conditions and on the distance from the gate; the third layer, present only in specimens moulded with short mould-fill times, exhibited both *a*-axis and *c*-axis orientation; and the deepest layer showed uniform rings in the X-ray photographs, interpreted as being produced by isotropic spherulites.

Techniques that have been developed to characterize molecular orientation in polymers involve wide-angle X-ray diffraction, birefringence, infrared dichroism and sonic modulus. Transmission infrared (IR) spectroscopy is widely applied in investigations on thin samples (films, fibres) [8]. In multiphase systems (semicrystalline polymers, conformational isomers, block copolymers and composites) the orientation can be characterized separately in the individual phases, if corresponding absorption bands can be identified in the spectra. This is possible because the absorption of polarized IR radiation in the sample depends on the relative orientation of the polarization plane of the

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radiation and the transition moment of vibration of the molecular group concerned. Orientation of the molecular group corresponding to the respective spectral band is characterized by the dichroic ratio, D, which is the ratio of intensities of the band measured with the plane of polarization, respectively parallel and perpendicular to the orientation direction. The value of D depends on the angle α between the transition moment of vibration of this group and the axis of the polymer chain, and also on the angular distribution of the individual chain axes with respect to the orientation axis. In the case of a uniaxial orientation the orientation distribution function f, has the form

$$f = (3\,\overline{\cos^2\theta} - 1)/2 \qquad (1)$$

where θ is the angle between the local polymer chain axis and the reference direction, here chosen to be the flow direction, and $\overline{\cos^2\theta}$ is the average value for $\cos^2\theta$ over the whole sample. This function f has a value of unity for a sample in which the polymer chains are oriented parallel to the moulding direction. For perfect transverse orientation, $f = -0.5$ and for random orientation $f = 0$. With other orientation distributions, the values for f will lie between these extremes (i.e. $-0.5 < f < 1.0$).

The orientation function, f, is related to the dichroic ratio by the expression [9]

$$f = \left(\frac{D-1}{D+2}\right)\left(\frac{D_0+2}{D_0-1}\right) \qquad (2)$$

where the constant D_0 is the value of the dichroic ratio corresponding to a perfectly oriented sample, and is given by

$$D_0 = 2\cot^2\alpha \qquad (3)$$

Hence, the dichroic ratio of an absorption band can be utilized for the estimation of the average chain orientation when the geometry of the transition moment of the corresponding vibration is known.

In the work described here the morphology of sepiolite- and talc-filled polypropylene compounds in injection-moulded form has been investigated using polarized light microscopy, IR dichroism and wide-angle X-ray diffraction. The residual stress distributions have been measured and the effect of various ageing processes examined.

2. Experimental details

2.1. Materials and specimen production

The test materials utilized were polypropylene (ICI HWM 25), talc-filled polypropylene based on the same polymer (ICI 22T4OH), and sepiolite, supplied by Steetley Minerals Ltd in micronized form. Compounds containing 10, 25 and 40% by weight of filler were produced and tensile bars with the profile given in ASTM D638 were injection moulded. The material preparation procedures and the injection-moulding conditions have been reported in a previous paper [10].

The specimens produced for each composition were divided into four batches as follows:

(i) tested approximately 22 h after moulding;

(ii) stored at ~ 20° C for 1 month before testing;

(iii) stored in a deep freeze cabinet at ~ −80° C for 1 month before testing. These specimens were allowed to cool down for ~ 30 min after moulding and were allowed a further 30 min to warm to room temperature on removing from the cabinet for testing;

(iv) stored at ~ 20° C for 1 month then annealed at 120° C for 6 h before testing.

2.2. Residual stress assessment

The residual stress distribution was determined using the layer removal procedure [5, 11–13]. Thin uniform layers were removed from one surface of the bar by high-speed milling using a single-point cutter with fly cutting action. After each layer removal the radius of curvature of the bar was measured and a plot generated of curvature against depth of removal. From this, the residual stress distribution was determined using the method introduced by Treuting and Read [5].

The form of the Treuting and Read formula used here is given below as Equation 4, and is modified for the case where the curvature perpendicular to the bar axis is negligible. The curvature is difficult to measure in this direction but visual inspection confirmed that it was small. Thus, the error resulting from the use of Equation 4 instead of the more accurate biaxial form will be small, and the analysis presented is perfectly adequate to make the kind of comparisons and deductions made here.

If, after removing material until the machined surface is located at a height z_1 from the central plane of the bar prior to the layer removals, the curvature parallel to the bar axis is $\varrho(z_1)$ and that perpendicular to the bar axis is zero, then the residual stress in the bar axis ($x-$) direction at the position z_1 is given by

$$\sigma_{i,x} = \frac{E}{6(1-\nu^2)}\left[(z_0+z_1)\frac{\mathrm{d}\varrho(z_1)}{\mathrm{d}z_1} + 4(z_0+z_1)^2\varrho(z_1) - 2\int_{z_1}^{z_0}\varrho(z)\,\mathrm{d}z\right] \qquad (4)$$

Values of ϱ, $\mathrm{d}\varrho/\mathrm{d}z$ and $\int_{z_1}^{z_0}\varrho\,\mathrm{d}z$ were read from the curvature against depth plot and inserted into Equation 4 to generate the stress distribution, which represents that present before the first layer removal. The values of Young's modulus, E, used were those measured on bars taken from the same moulding batches, and are shown in Table I. The value taken for Poisson's ratio, ν, was 0.3 for all materials.

TABLE I Young's modulus as a function of ageing

Sample	Young's modulus (GN m^{-2})			
	As-moulded	Aged −80° C	Aged 20° C	Aged 20° C, 6 h 120° C
PP	1.0	1.0	1.0	1.0
PP-Sep 10	1.3	1.2	1.3	1.4
PP-Sep 25	1.5	2.1	2.5	2.1
PP-Sep 40	2.3	2.5	3.4	2.8
PP-Talc 10	1.4	1.7	1.9	1.6
PP-Talc 25	2.1	2.1	3.0	1.9
PP-Talc 40	3.2	2.6	5.2	2.1

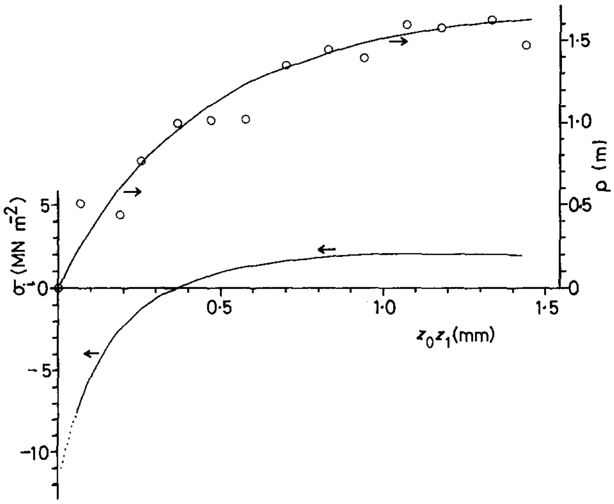

Figure 1 Residual stress analysis for polypropylene aged for 22 h at 20° C. The plot of curvature against depth removed is shown and the corresponding residual stress distribution in one half of the bar (total thickness 3.2 mm).

2.3. Polarized light microscopy

Thin slices were cut from the central part of the specimen both in the moulding direction and transverse to it, using a Leitz microtome set for a 8 μm incremental advance. The specimens were observed in transmission under polarized light.

2.4. Wide-angle X-ray diffraction

Bars milled down from one side only to leave specimens containing skin material only, and others were milled down from both sides to leave specimens containing core material only. X-ray diffractograms were obtained in reflection on a Philips PW1390 with Cu$K\alpha_1$ radiation (λ = 0.1542 nm), using a nickel filter. The goniometer speed was 2θ = 0.5° min^{-1}.

2.5. IR dichroism

Films of the skin and the core, approximately 70 μm thick, were prepared in the same way as for X-ray diffraction. Spectra were recorded on a Nicolet 20-SXB FTIR with the polarization direction of the radiation parallel and perpendicular to the moulding direction.

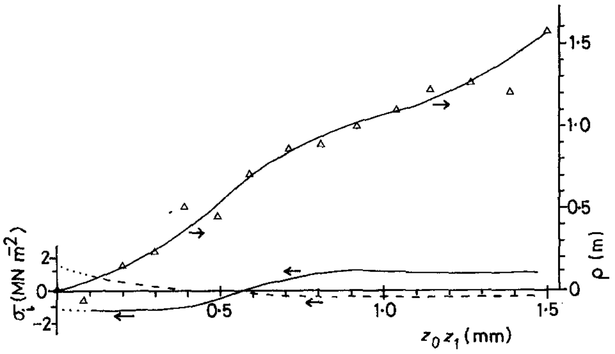

Figure 2 Residual stress analysis for polypropylene aged for 1 month at 20° C. The plot of curvature against depth removed and the correponding residual stress distribution are shown as solid lines. The broken lines shows the results of a similar analysis on polypropylene annealed for 6 h at 120° C.

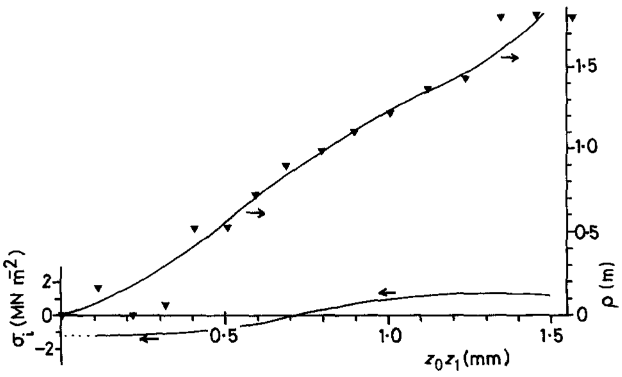

Figure 3 Residual stress analysis for polypropylene aged for 1 month at −80° C. The curvature plot and the corresponding residual stress distribution are both shown.

3. Results

3.1. Residual stress analysis

3.1.1. Unfilled polypropylene

The residual stress distribution in unfilled polypropylene stored for 22 h at room temperature before conducting the layer removal analysis was in the shape of a flattened parabola, with a maximum tensile stress of approximately 2 MN m^{-2} and with the compressive stress rising to ~ 12 MN m^{-2} near the surface (Fig. 1). After 1 month ageing at room temperature the stresses fell to very low values, < 1 MN m^{-2} (Fig. 2). Ageing at −80° C produced similar changes (Fig. 3). With specimens annealed at 120° C a lot of scatter was found in the curvature readings and these are not shown for that reason. This is commonly found in specimens in which the stress levels are very low, and analysis of smooth curves constructed through the curvature data points did indeed indicate very low stress levels, significantly below 1 MN m^{-2}, and therefore too small to be of any practical importance. This analysis indicated tensile stress had developed near to the surface (Fig. 2). This result is based on very scattered data and, if standing alone, would not merit mentioning, but it emerges later that it is not a unique result.

3.1.2. Sepiolite-filled polypropylene

Bars containing 10% sepiolite filler had very modest stresses when tested 22 h after moulding, with the tensile maximum ~ 1 MN m^{-2} and a compressive maximum of < 5 MN m^{-2} near the surface (Fig. 4). Ageing at −80° C caused a reduction in the magnitude

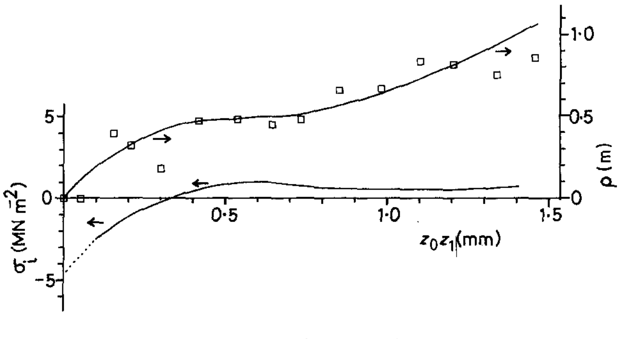

Figure 4 Residual stress analysis for polypropylene with 10% sepiolite filler, aged for 22 h at 20° C. The curvature plot and the corresponding residual stress distribution are both shown.

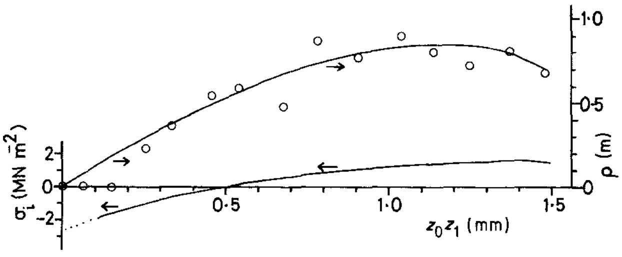

Figure 5 Residual stress analysis for polypropylene with 10% sepiolite filler, aged for 1 month at −80° C, showing both the curvature plot and the corresponding residual stress distribution.

of the compressive stresses (Fig. 5) and ageing at room temperature for a month produced even lower stress everywhere (Fig. 6). Although the data obtained with bars annealed at 120° C showed considerable scatter (as was also the case with unfilled material treated in the same way, see above), the data and results are shown in full here (Fig. 6) because of the interesting discovery that the stress distribution has reversed its sense. This was shown when, on removing layers, the bar developed a curvature in the opposite sense to that obtained with bars having the more conventional distribution with tensile stresses in the interior and compressive stresses near to the surface. Thus, although in the presence of the scatter no precise measurement of stress is possible, there is firm indication that the stresses in the interior are very small and compressive, whereas tensile stresses have developed near to the surface. This encourages us to consider that the similar result obtained with unfilled polypropylene may not necessarily be spurious.

Polypropylene compounds with 25% and 40% sepiolite gave similar results to one another. The stresses were very low in the bars tested 22 h after moulding, and lower still after ageing at room temperature (Figs 7, 8). In a departure from the behaviour observed with the 10% filled and unfilled materials, the specimens aged at −80° C were found to contain significant stresses, with tensile stresses of the order of 2 to 3 MN m^{-2} in the interior and compressive stresses rising steeply to over 10 MN m^{-2} near to the surface (Figs 9, 10). After annealing at 120° C stresses were very small everywhere (Figs 9, 10).

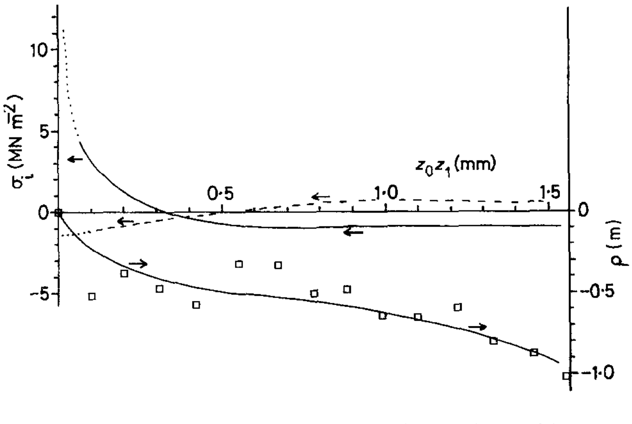

Figure 6 Residual stress analysis for polypropylene with 10% sepiolite filler annealed for 6 h at 120° C. The curvature plot and the corresponding residual stress distribution are shown (solid lines). The broken line shows the stress distribution for bars aged for 1 month at 20° C.

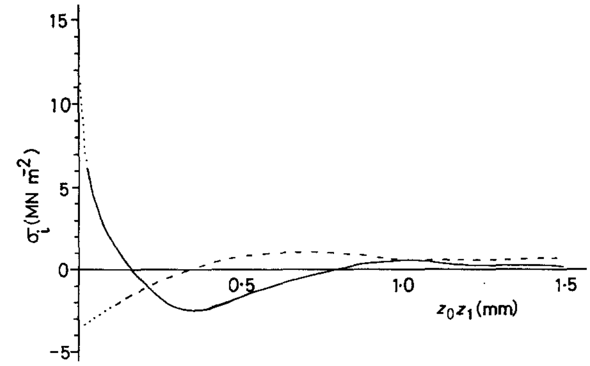

Figure 7 Residual stress distributions for polypropylene with 25% sepiolite filler, aged at 20° C: (——) 22 h; (– – –) 1 month.

3.1.3. *Talc-filled polypropylene*

Bars made from polypropylene with talc as filler and tested 22 h after moulding had fairly low residual stresses at all compositions. The residual stress profiles departed significantly from the parabolic form (Figs 11 to 14) though precise location was not possible in the presence of considerable scatter in the curvature data. Smaller stresses were measured after ageing for a month at room temperature with both the 10% and 40% compounds, but the 25% compound apparently developed higher stresses (Figs 11, 13, 14). The overall level of stress was also very small after annealing at 120° C (Figs 12 to 14). The stress distributions for samples aged at −80° C do not fit any particular pattern. At 10% loading the profile resembles that obtained from the specimen aged for 1 month at room temperature, and at 40% loading the profile is similar to that obtained with the annealed sample. The profile obtained for the specimen with 25% talc is very complex (Fig. 13) but was derived from curvature data with a large amount of scatter.

3.2. Polarized light microscopy

Fig. 15a shows a polarized light micrograph of an injection-moulded specimen sectioned parallel to the flow direction, showing clearly the skin–core morphology. At higher magnification, three zones are visible: the first one, nearest the surface, has a thickness of ~ 18 μm showing transcrystallinity; the second zone has a thickness of ~ 80 μm, and the third, innermost zone, shows spherulites (Fig. 15b).

The introduction of the fillers makes the skin–core boundary less sharp and the skin thickness is more difficult to measure accurately (Fig. 16). However, this thickness seems to increase in the filled compounds at low filler levels. At high filler levels the contrast disappears altogether and it is uncertain whether or not there is a skin–core morphology

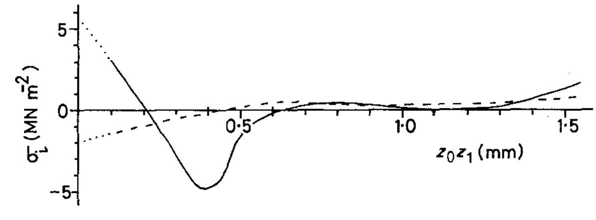

Figure 8 Residual stress distributions for polypropylene with 40% sepiolite filler, aged at 20° C: (——) 22 h; (– – –) 1 month.

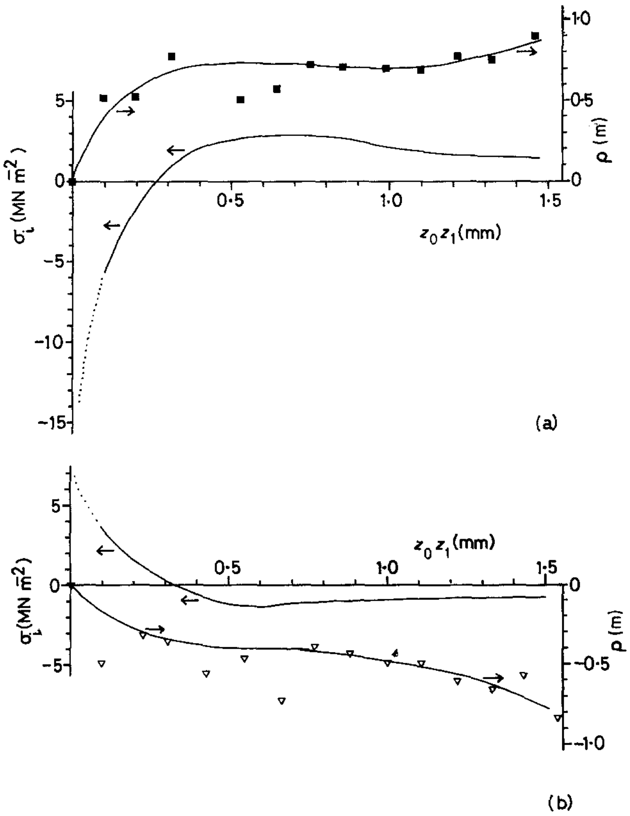

Figure 9 Residual stress analysis for polypropylene with 25% sepiolite filler: (a) aged at −80° C for 1 month; (b) annealed at 120° C for 6 h.

present, though X-ray diffraction and infrared dichroic ratio measurements from samples taken near to the surface and from the interior, respectively, show significant structural differences (see below).

3.3. Wide-angle X-ray diffraction

3.3.1. Polypropylene

Fig. 17 shows the wide-angle X-ray diffractograms of skin and core layers. These indicate that the crystalline structure of the core consists entirely of α-crystals (monoclinic system) whereas the skin layer contains mainly α-crystals but with a small fraction of β-crystals (hexagonal system) as well; the latter is shown by the presence of a weak reflection appearing at $2\theta = 16.1°$ corresponding to the (1 0 0) reflection of the β-form.

Annealed samples show the same crystalline structure. The diffractograms obtained from core samples showed almost no change after annealing but differences in the relative intensities of the peaks were observed for the skin samples.

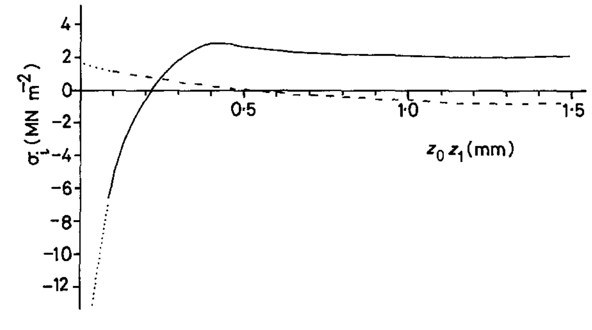

Figure 10 Residual stress distributions for polypropylene with 40% sepiolite filler: (———) aged at −80° C for 1 month; (– – –) annealed at 120° C for 6 h.

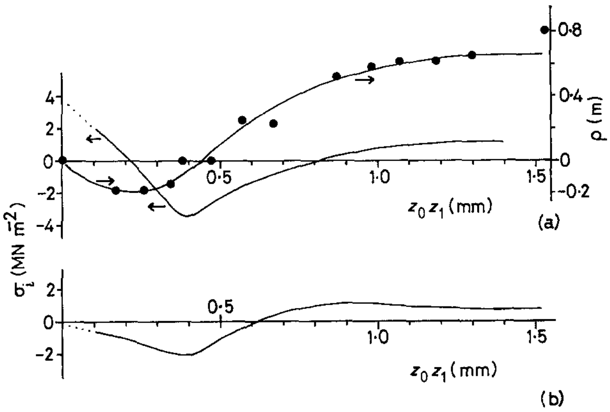

Figure 11 Residual stress analysis for polypropylene with 10% talc filler aged at 20° C. (a) Curvature plot and corresponding stress distribution for 22 h ageing; (b) stress distribution for 1 month ageing.

3.3.2. Sepiolite-filled polypropylene

Diffractograms (not shown) contain the peaks of the polypropylene together with the reflections attributed to the sepiolite. β-crystals are again shown to be present in the skin layer. Practically no change was observed after annealing at 120° C or ageing at −80° C, in the case of the core samples. Changes were observed in the case of the skin samples, but the magnitude was smaller than was observed with the unfilled polypropylene.

3.3.3. Talc-filled polypropylene

The diffractograms of the skin and core samples are quite different. The (0 4 0) polypropylene reflection at $2\theta = 16.8°$ is much more intense in the case of the skin samples. Practically no differences were observed when aged or annealed in the case of the core samples. In the case of the skin samples high intensities of the (0 4 0) reflection of the polypropylene and the (0 0 4) and (0 0 6) reflections from the (oriented) talc dominate the diffractometer trace, making detailed deductions about the organization of the polypropylene

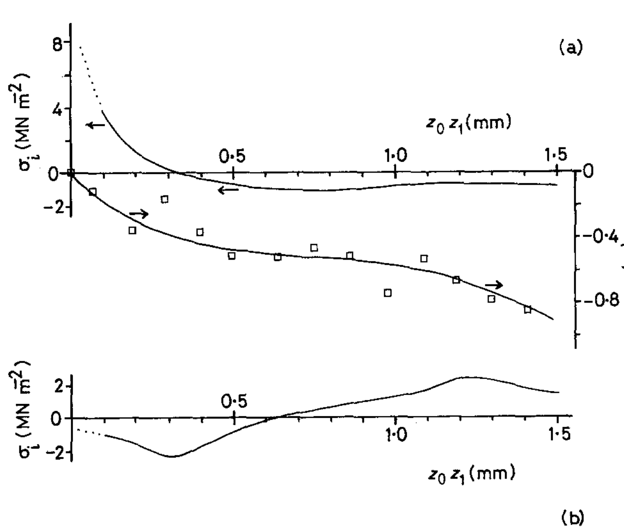

Figure 12 Residual stress analysis for polypropylene with 10% talc filler. (a) Curvature plot and corresponding stress distribution for bars annealed at 120° C for 6 h; (b) stress distribution for bars aged at −80° C for 1 month.

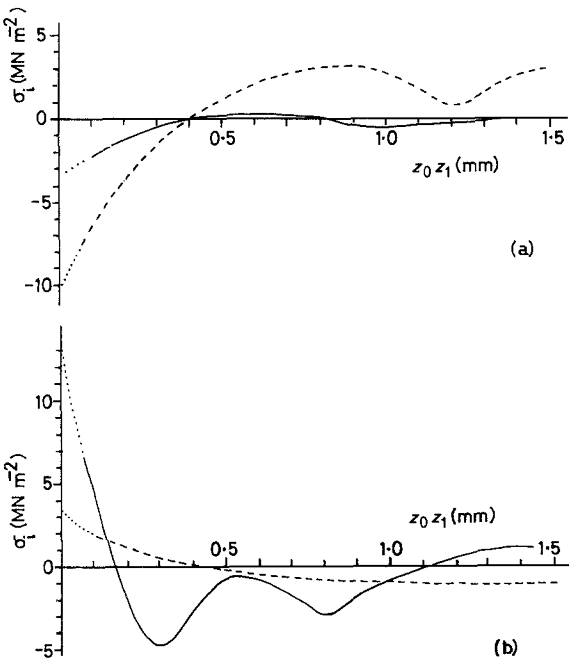

Figure 13 Residual stress distributions for polypropylene with 25% talc filler. (a) aged at 20° C, (——) 22 h, (– – –) 1 month; (b) (——) aged at −80° C for 1 month, (– – –) annealed at 120° C for 6 h.

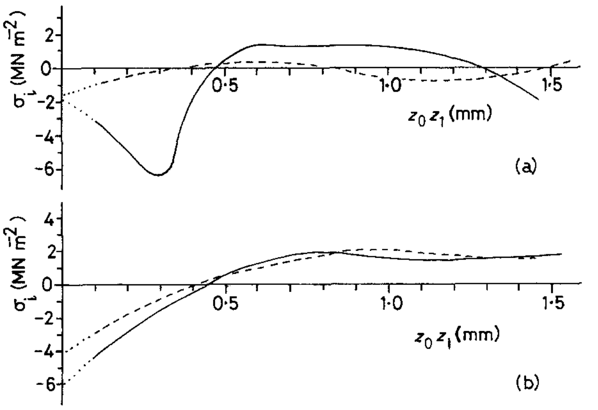

Figure 14 Residual stress distributions for polypropylene with 40% talc filler (a) aged at 20° C, (——) 22 h, (– – –) 1 month; (b) (——) aged at −80° C for 1 month, (– – –) annealed at 120° C for 6 h.

difficult to achieve with certainty. No peak was visible at $2\theta \simeq 16°$, but this cannot be taken to indicate complete absence of the β-form because of the low sensitivity setting, dictated by the strong peaks mentioned above.

3.4. IR dichroism

Fig. 18 shows the FTIR spectra of skin samples for compounds containing 10% by weight of sepiolite and talc, respectively, for both the parallel and perpendicular polarization directions, and Fig. 19 shows the spectrum of a core sample from the 10% talc-filled compound. For the quantitative characterization of chain alignment resulting from the injection-moulding process, the 841 and 1256 cm^{-1} absorption bands have been selected.

In the IR spectrum of polypropylene the absorption bands can be assigned to axial or equatorial mode vibrations, whose transition moment directions are oriented parallel and perpendicular to the 3_1 helix axis, respectively. The absorption band at 841 cm^{-1} has been attributed to the crystalline phase, being assigned to the CH$_2$ rocking deformation mode [14], having a strong absorption when the polarization direction is parallel to the transition moment. For this band an angle $\alpha = 14.3°$ has been determined [15]. There are some infrared absorption bands that are characterized by absorption in both the crystalline and the amorphous phases, one example being the 1256 cm^{-1} band. This band has parallel polarization and has been assigned to a twisting of the CH$_2$ groups coupled with the axial and equatorial bending CH modes [16]. Because this band results from absorption in both the crystalline and amorphous regions, its infrared dichroism is taken to correlate with some average orientation function. In this paper we use a value of $\alpha = 32.9°$ for the calculation of the average orientation function, obtained by replotting data given by Samuels [17].

The values obtained for the dichroic ratio, and both the crystalline (f_c) and average (f_{av}) orientation functions are presented in Table II for skin and core samples from bars aged approximately 5 months at room temperature before testing.

The crystalline orientation function for the skin decreases when increasing the filler content in the case of the sepiolite-filled compounds. The talc filled ones display a maximum at 25% level. The orientation function is similar in compounds containing 40% filler with both sepiolite and talc. The average orientation

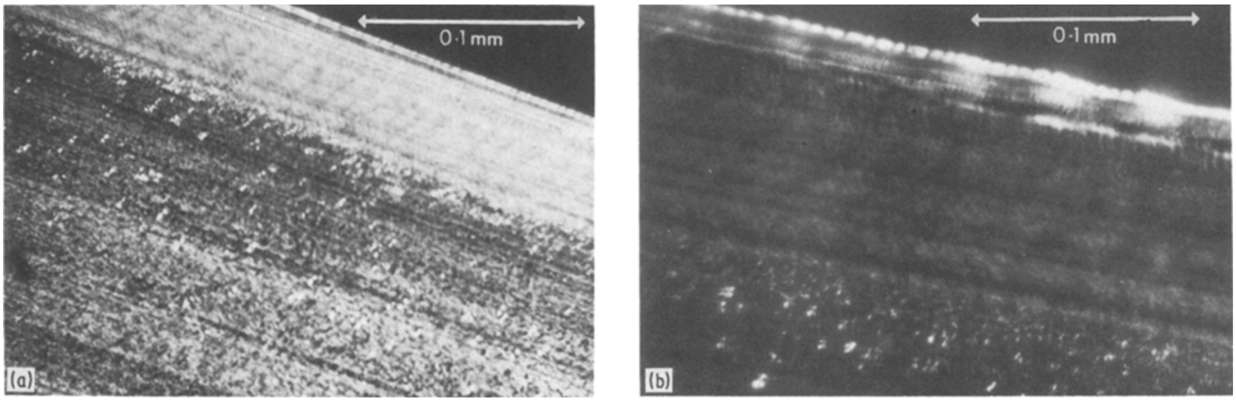

Figure 15 (a) Polarized light micrograph of a microtomed section from a polypropylene bar. The section contains the moulding direction, i.e. it represents the xz-plane (see Section 2.2). (b) Higher magnification image taken close to the moulded surface.

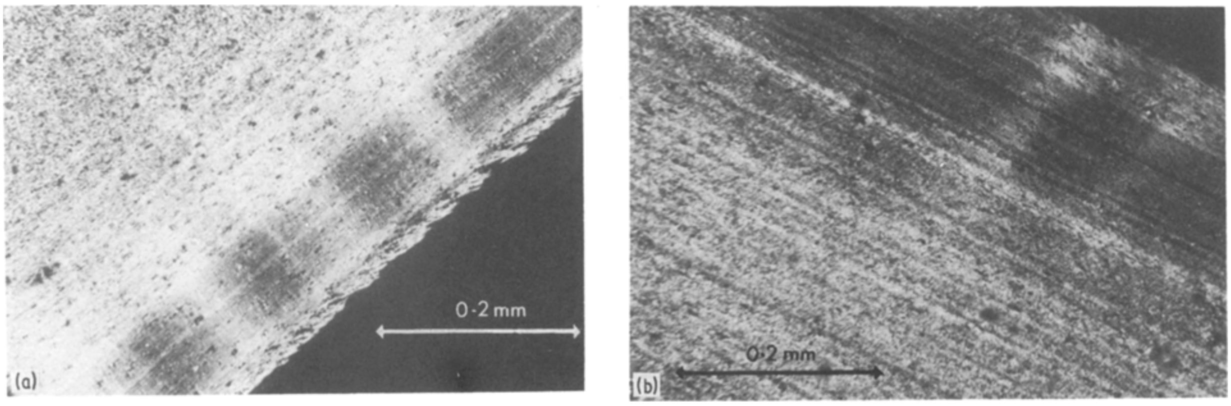

Figure 16 Polarized light micrographs of microtomed sections from bars made from polypropylene with 10% filler. The sections are cut normal to the flow direction, i.e. they represent the *yz*-plane. (a) sepiolite as filler; (b) talc as filler.

function shows the same behaviour. The orientation function obtained with core samples is very small in most cases and negative for all samples except those with 25% talc as filler. These data indicate that as a result of injection moulding the molecular chains tend to be aligned parallel to the moulding direction in the skin and in a direction perpendicular to it in the core. In most cases preferred orientation is more pronounced in the skin than in the core.

Dichroic ratio measurements were also carried out on selected samples aged at ~ 20° C for 1 month, then annealed at 120° C for 6 h and left for 4 months at room temperature before testing. The crystal orientation function, f_c, decreased significantly compared to that obtained with the corresponding non-annealed samples from the skin, whereas the effect on the core material was much lower.

4. Discussion

4.1. Residual stresses

In previous studies it was shown that in unfilled polypropylene the residual stresses decayed considerably at room temperature [1, 18]. Storage at −40° C slowed down the process and at −196° C (liquid nitrogen temperature) the decay process was apparently stopped completely. Subsequent studies involving storage at −85° C indicate some changes can occur at this temperature, but that they are less rapid or less complete than those at −40° C. It should be noted that stress relaxation experiments conducted on injection-moulded polypropylene bars under applied loads in uniaxial tension have shown that the stress decays to a non-zero limit, sometimes called the internal stress, σ_i [1, 15]. σ_i may be a significant fraction of the initial stress, σ_0, and the ratio σ_i/σ_0 for many polymers tested at room temperature or above was found to lie in the range 0.3 to 0.7. The behaviour has been explained with reference to the two-site theory for rate processes [19, 20]. There is no reason to expect the response to residual stresses to be any different to that obtained under an applied load, and it is reasonable to expect that residual stresses should decay towards a limiting value that may differ significantly from zero. Thus, it is within this framework that the results presented above should be considered.

The results obtained with unfilled polypropylene are fairly straightforward and can be explained as follows. Immediately after moulding the residual stresses will be at their highest levels and will begin to decay at once. Thus, after 22 h at room temperature significant reduction in stress levels will have taken place. Further decay takes place on prolonged ageing (e.g. for 1 month), and the results presented here seem to indicate that a similar reduction can even take place at −80° C. Annealing at 120° C caused a very marked reduction in stress levels, and at this point we comment only that the much scattered data seem to indicate small tensile stresses at the surface, that is, a reversal

TABLE II Parameters calculated from the IR dichroism for samples aged at room temperature and those aged at room temperature and then annealed at 120° C for 6 h

Sample	Skin				Core			
	D_c	D_{av}	f_c	f_{av}	D_c	D_{av}	f_c	f_{av}
Aged 3 months at room temperature								
PP	1.75	1.74	0.22	0.35	0.93	0.92	−0.02	−0.05
PP-Sep 10	1.67	1.61	0.20	0.31	0.88	0.88	−0.05	−0.07
PP-Sep 25	1.55	1.45	0.17	0.24	0.91	0.95	−0.03	−0.03
PP-Sep 40	1.21	1.30	0.07	0.16	0.90	0.81	−0.04	−0.12
PP-Talc 10	1.54	1.50	0.17	0.26	0.77	0.78	−0.09	−0.14
PP-Talc 25	1.72	1.62	0.21	0.31	1.01	1.00	0.01	0
PP-Talc 40	1.22	1.24	0.08	0.13	0.80	0.75	−0.08	−0.16
Aged at room temperature and annealed for 6 h at 120° C								
PP	1.21	1.22	0.07	0.12	0.65	0.66	−0.14	−0.23
PP-Sep 25	1.07	1.51	0.02	0.03	1.00	0.97	0	−0.02
PP-Talc 25	1.53	1.58	0.16	0.29	0.77	0.83	−0.09	−0.01

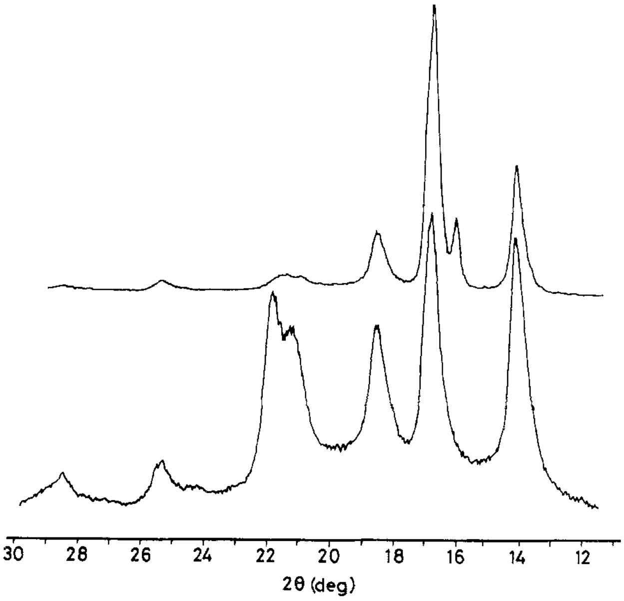

Figure 17 X-ray diffractometer traces from injection-moulded polypropylene: upper trace from skin; lower trace from core.

in sense, but the stresses are so small that, taken alone, this could not be regarded as significant. It gains relevance when considered in connection with other results discussed below.

Other results obtained with polypropylene having 10% by weight sepiolite filler show broadly similar results. The stresses 22 h after moulding were lower than in the unfilled material. Ageing both at room temperature and at $-80°$ C caused the stresses to fall, and weak stresses with reversed sense were again obtained after annealing. At 25% and 40% sepiolite loadings the residual stress profile most resembling the flattened parabola that is the most familiar form in studies of injection mouldings is that obtained after ageing at $-80°$ C. We believe this is closest to the as-moulded distribution and that a combination of the high filler content obstructing molecular motion and the low temperature has preserved the original state most faithfully. This does not explain why tensile stresses were found near the surface in both 25% and 40% sepiolite filled polypropylene after ageing for 22 h at room temperature. This could be caused by relaxations occurring at different rates in the skin and core and implies that this has an important effect at short times. Apparently, after 1 month ageing, sufficient time has elapsed to permit all important relaxations to reach close to their equilibrium state and the profiles revert to pseudo-parabolic with the conventional sense, tensile in the interior and compressive near to the surface.

Annealing again causes development of weak tensile stresses near to the surface. Reversal of the sense of stress has been observed before, on outdoor weathering in a hot climate with several polymers, but not polypropylene [2, 21]. Tensile stresses have been made to develop near the surface of polypropylene bars on applying a temperature gradient [22], but the only previous examples we have discovered in which the sense of residual stress reversed on annealing at a uniform temperature was with poly(4-methyl pentene-1)

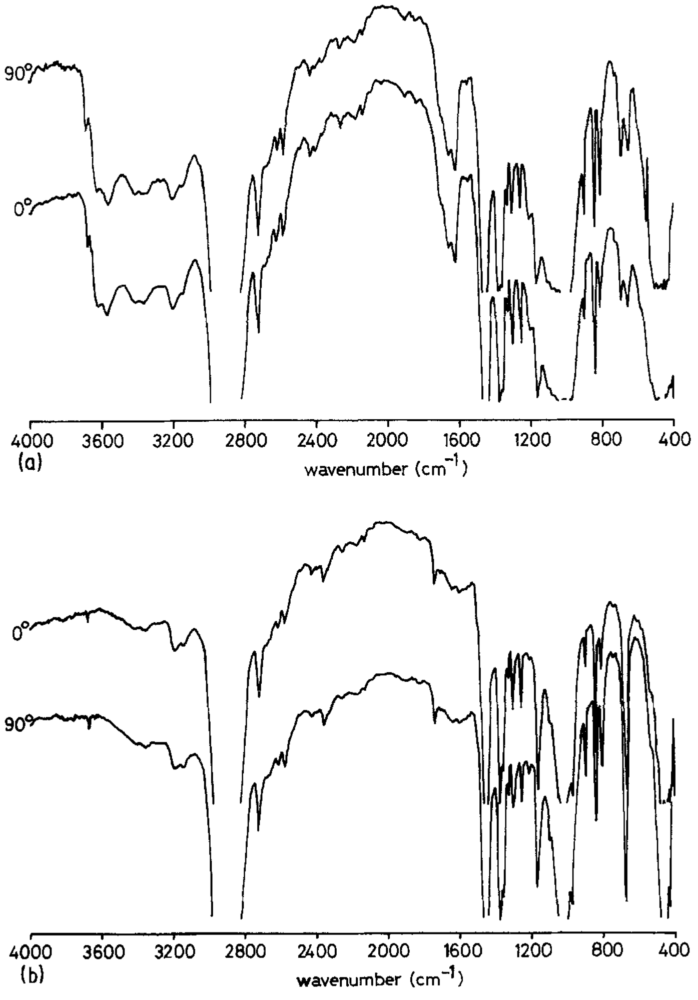

Figure 18 FTIR spectra from skin samples taken with the polarization direction parallel to the moulding direction (0°) and perpendicular to it (90°) for polypropylene compounds containing 10% filler; (a) sepiolite as filler; (b) talc as filler.

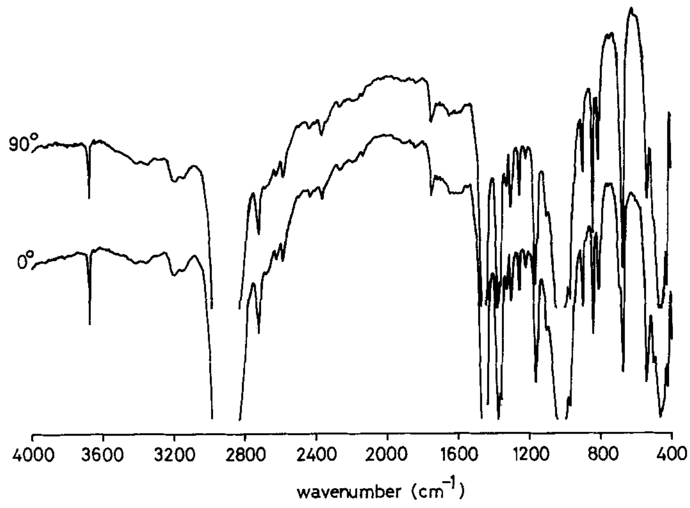

Figure 19 FTIR spectra from a core sample of polypropylene with 10% talc filler, showing results with the polarization direction parallel to the moulding direction (0°) and perpendicular to it (90°).

[23]. Annealing causes shrinkage to occur in the bar axis direction [10] and if the shrinkage of the skin exceeds that of the core this could cause reversal of the stress distribution. Such an effect might be caused either by further crystallization in the skin, by retraction of molecules in oriented conformations originally produced by flow during filling of the mould, or by reorientation of crystals. This is discussed further in the following section.

The residual stress distributions obtained with the talc-filled grades generally show a more anomalous behaviour, often with several reversals of the stress gradient. Even at 10% loading there is significant departure from the parabolic form in all conditions. The talc particles are in the form of platelets and we believe this is why their effect appears to be quite different to that of particles of sepiolite. Glass fibre-filled grades also produce complicated residual stress profiles [3, 21] and again the filler has a distinctive shape and an orientation distribution that is influenced by flow during moulding. The residual stress profiles for polypropylene containing 10% talc, aged at room temperature or at ~80° C all show tensile stresses in the interior but a compressive maximum some way in from the surface (0.3 to 0.4 mm). The stress at the surface in the specimen aged for only 22 h at room temperature was tensile. This is again consistent with the hypothesis that relaxations occur at different rates in the skin and the core and that this is a temporary state reversed again when the slower one catches up with the faster one after it has almost reached equilibrium. Annealing the compound containing 10% talc has again produced weak tensile stresses near to the surface.

Higher talc loadings produced residual stress profiles that apparently have less pattern to them. Pursuing again the idea that in the as-moulded state the material is far from equilibrium and that relaxation occurs at different rates at different depths within the bar, profiles such as those obtained after ageing at room temperature or at − 80° C are not easy to predict, but are not, perhaps, unreasonable. After annealing, the stresses appear to follow a smoother profile, as might be expected, for at such an elevated temperature most of the processes that contribute to ageing at the lower temperatures should quickly go to completion. At 25% talc loading the stress at the surface was tensile after annealing whereas at 40% loading it was compressive. Thus, the tendency to form tensile stresses at the surface dropped as the filler content increased, a trend also found with the sepiolite-filled compounds, though in the latter case the reduction was not sufficient to prevent the development of a net tensile stress at the surface. Because the filler cannot contribute to this phenomenon directly, it must be associated exclusively with the polypropylene phase. Thus, the reduction in the tendency to develop tensile stresses near the surface may simply reflect the reduction in volume fraction of the polymer, and there is no need to look for any subtle interplay between filler and polymer.

Viewing the results overall, it seems that considerable ageing occurs in particulate-filled polypropylene and that significant changes take place in the residual stress distribution, especially in the first day (probably the first few days) after moulding if stored at room temperature. A more complex pattern of changes is evident in mouldings made from talc-filled polypropylene than with sepiolite-filled polypropylene, and that leads to the prediction that sepiolite-filled mouldings should be less prone to warping and distortion than those made from talc-filled compounds with similar loadings. This is particularly so at high loading levels: at 10% loading the ageing behaviour is not very different to that found with unfilled material, a not unreasonable result when it is remembered that 10% by weight corresponds to approximately 4.7% by volume (sepiolite in polypropylene) and 3.6 by volume (talc in polypropylene), respectively.

4.2. Structural studies

The optical sections reveal a skin–core boundary 0.05 to 0.2 mm from the surface. In the case of unfilled material the skin–core boundary has been shown to correspond to the presence of different morphologies [7]. The skin has been found to contain two distinct regions in agreement with results obtained before in injection-moulded polypropylene. In the filled specimens the skin–core boundary is not so clearly visible, probably due to the presence of the filler. The skin thickness seems to increase to a value of 0.12 mm in the case of the 10% sepiolite-filled and

0.17 mm in the talc-filled compound with the same level of filler.

The differences in skin thickness observed between the sepiolite and talc compounds can be explained as a result of the much smaller aspect ratio of the sepiolite particles compared with the talc, as well as following from the differences in the nucleating ability of both fillers. Although the orientation of the filler particle has a direct effect on the properties of the compound, there will be an additional contribution to the properties from the polypropylene. Thus, if the polypropylene orientation relates in any way to the orientation of the filler particles then the filler particle orientation distribution will have a second, indirect, influence over the properties of the moulding.

X-ray diffractograms again show differences between the skin and core morphologies. A small fraction of the material was present as β-crystals in the skin, even after annealing at 120° C, whereas the core samples contained only α-crystals.

A decrease in the relative intensity of the (0 4 0) reflection at $2\theta \simeq 16.8°$ has been found after annealing in the case of the skin samples, whereas the changes obtained with the core samples were hardly significant.

The molecular orientation functions, f_c and f_{av}, show lower values for the polypropylene compounds than for the unfilled polypropylene in the case of the skin samples aged at room temperature. Both functions decrease in the sepiolite-filled compounds when increasing the level of filler and the opposite effect is found with the talc-filled ones. This can be explained to be the result of the orientation of the talc particles when flowing into the mould cavity. The same extent of orientation is not present in the case of the sepiolite particles. The effect of increasing the level of filler restricts the motion of the molecular chains in the melt, during subsequent cooling, and, eventually, in the solidified moulding. This may explain why low values of f_c were obtained for the 40% filler level with both sepiolite and talc compounds and seems to indicate that high levels of filler lead to a more isotropic crystal nucleation pattern, even with talc with a high aspect ratio.

The core samples gave negative f_c values in most cases indicating a preference for transverse orientation, but the f_c values were generally so small that the orientation distribution is indicated to be close to random. Annealing at 120° C caused both orientation functions (f_c and f_{av}) to decrease significantly in skin samples of unfilled polypropylene and polypropylene with 25% filler (sepiolite or talc). With the core, the results from polypropylene seem to indicate that annealing promoted enhanced transverse orientation whereas in the filled compounds the degree of orientation was practically non-existent both before and after annealing. The reduction of the orientation function could be caused either by crystal reorienting, developing a more random orientation distribution, or by the growth of new crystals from previously non-crystallized material that may or may not have possessed orientation, the new crystals forming in directions inclined to the moulding direction. The reorientation of crystals would cause the skin to contract in the bar axis direction, and because no such effect is suspected to be present in the interior (core) region, this would shift the residual stress distribution in the direction observed, ultimately causing tensile stresses to develop near the surface. Alternatively, if new crystals grow from disorganized (non-crystallized) polymer to take up transverse orientation this also would cause a contraction in the skin in the bar axis direction. Although orientation functions were not measured for the 40% compounds after annealing, it is clear that, because they have very small orientation functions before annealing, there is less scope for contraction by either of these mechanisms.

5. Conclusions

The residual stress levels in the particulate-filled polypropylene compounds studied here are generally lower than those found in short glass-fibre-filled polypropylene injection moulded under similar conditions [3]. This is encouraging from the point of view of dimensional stability, for there is less scope for distortion to develop through non-uniform relaxation of residual stresses. On the other hand, the residual stress distributions in these particulate-filled polymers show a greater inclination to change on ageing at room temperature than is found with short glass-fibre-filled polypropylene [18]. The changes are more severe and less predictable with the talc-filled compounds than those with similar loadings of sepiolite.

With sepiolite compounds the molecular orientation levels decrease as filler content increases, leading to the expectation that distortion caused by molecular reorientation will decrease as the filler content increases. This is additional to the effect that a high concentration of filler has in inhibiting molecular relaxation. Annealing promotes changes in orientation, especially in the skin, and this appears to correlate with the development of tensile residual stresses near to the surface.

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