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Effect of ageing on the mechanical properties and the residual stress distribution of hybrid clay–glass fibre–polypropylene injection mouldings

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Abstract The effects of ageing on the mechanical properties and thermal stresses distribution of injection moulded, short glass fibre/clay/polypropylene composites were studied. Two different clays were studied—talc and sepiolite. The results obtained indicate that the incorporation of short glass fibre into clay/polypropylene composites improves the mechanical properties, independently of ageing treatment. Larger elastic modulus values were obtained for talc-filled samples, whereas higher strength values were obtained with the sepiolite-filled ones. The impact strength increased as a result of the incorporation of glass fibre into the sepiolite-filled composite, while a small decrease was detected for the talc-filled polypropylene sample. Sepiolite-filled compounds show higher mould shrinkage in the bar-axis direction than equivalent talc-filled grades. In contrast, the shrinkage obtained on annealing at various temperatures between 100 and 160 °C was generally greater for talc-filled compounds than for the sepiolite-filled compounds. The shrinkage behaviour in the transverse direction was more complex. The residual stress levels of clay-filled polypropylene compounds were generally lower than those reported in the literature concerning short glass fibre polypropylene compounds under similar conditions. Hybrid composites showed much higher stress levels than the corresponding clay-filled samples independently of ageing conditions.

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Introduction

Development of clay/glass fibre/polymer composites is one of the latest evolutionary steps in polymer technology, having attracted great attention due to the potentially large improvements in mechanical and physical properties that can be achieved by incorporating small amounts of clays (<10 wt%) into glass fibre/polymer composites. Clays are commonly added to thermoplastic polymer matrices to reduce cost and at the same time improve the material performance, such as for example the Young's modulus and the heat distortion temperature, but usually with a reduction in other properties such as the strength and fracture toughness. On the other hand, fibres (short or long) improve the stiffness and the fracture toughness when incorporated into the same matrices. The simultaneous use of both clay and fibre fillers, so-called hybridization, leads in many cases to synergistic effects, improving properties such as wear resistance, stiffness, fracture toughness, dynamic response, etc. [1–5].

Injection moulding is the most common procedure in both filled and unfilled thermoplastic polymer manufacturing. This technique usually leads to anisotropy in structure, due to both polymer chain preferential orientation in the flow direction, together with different crystallization regimes towards the sample thickness (skin-core morphology) and the properties, giving rise to a non-homogeneous filler distribution, with fibres and large aspect ratio filler particles oriented in the melt-flow direction at the skin, while no preferred orientation is expected in the core. Other factors to consider when evaluating the end use properties of the final product are the capability of the filler to act as nucleating agent in the polymer crystallization process, and the development of residual stresses, attributed to non-uniform cooling and solidification especially when crystallization processes take place inside the mould during cooling. When the residual stress distribution is asymmetrical about the mid-plane of the wall of a moulding, it can cause warping. Furthermore, residual stresses may have an influence on the fracture behaviour.

In previous articles, we describe a study of the mechanical properties of isotropic compression moulded sepiolite-filled polypropylene [6], as well as the effect of ageing on the mechanical properties and the residual stress distribution of sepiolite, talc and short glass-fibre-filled polypropylene moulded parts [7–9]. The results obtained indicate that the addition of both sepiolite and talc to the polymer matrix leads to an improvement of the elastic modulus, measured in both uniaxial and flexural conditions, and a reduction in impact strength. The residual stress levels measured for particulate-filled polypropylene compounds are lower than those found in short glass-fibre-filled polypropylene under similar conditions, showing at the same time a larger dependence on ageing at room temperature than that found for short glass-fibre-filled polypropylene. In this work, we report on the effect of ageing at different temperatures on the mechanical properties, dimensional stability and residual stresses profile of injection-moulded sepiolite and talc-filled short glass fibre/polypropylene hybrids.

Experimental

The test materials utilized were polypropylene (ICI HWM 25), talc-filled polypropylene (ICI 22T40H) and short glass fibre polypropylene (ICI HW60GR40) based on the same polymer. Sepiolite was supplied by Steetly Minerals Ltd in micronized form. Compounds containing 10 wt% of clay (sepiolite or talc) and 20 wt% glass fibre were made by mixing in a rolling mill at 190 °C, followed by extrusion, and then granulated. The extruder barrel and die were kept at 200 °C for all the batches of material. Table 1 summarizes the composition and sample codes.

Materials were injection moulded into ASTM D638 tensile test bars (190 × 12.7 × 3.2 mm) on a Butler-Smith 100/60 reciprocating screw machine with a 26 mm diameter screw. The mould cavity was end-gated, the nozzle temperature 200 °C, the barrel temperature (2 zones) 200/220 °C, injection pressure 161 MPa and mould temperature 35 °C. The specimens were divided into four batches as follows:

(a) Stored at ~20 °C for 22 h before testing.
(b) Stored in a deep-freeze cabinet at −80 °C for 30 days before testing.
(c) Stored at ~20 °C for 30 days before testing.
(d) Stored at ~20 °C for 30 days and then annealed at 160 °C for 6 h before testing.

The choice of −80 °C for low temperature storage was made because a suitable deep-freeze cabinet was available and because the temperature is well below the glass transition temperature of polypropylene and its compounds with inert fillers. Storage at this temperature should freeze all molecular conformational changes that might alter residual stress levels. It is noted, however, that changes might occur during the cooling and re-heating processes and the experiments were designed to provide some insight into the importance of this effect. The elevated annealing temperature of 160 °C is close to the melting temperature of polypropylene and provides an extreme comparator for the possible changes that may occur in residual stress distribution post-moulding; extensive molecular relaxation (that may include a reduction in molecular orientation) and secondary crystallization are expected to take place at this temperature. The choice of 30 days for storage interval is somewhat arbitrary but relates to typical shelf times for polymeric consumer products.

Impact tests were conducted on a Daventest Izod Impact machine using test pieces extracted from the tensile bars. The ends of the bar were sawn off, leaving the central 63.5 mm of the gauge length. Tests were then carried out according to a standard procedure (ASTM D256) for specimens of dimensions 12.7 mm × 3.2 mm, using a Type A notch (2 mm depth with a 45 °C entrance angle and 0.25 mm tip radius) cut across the bar thickness by using a broaching tool just before testing. Uniaxial tension tests were conducted on an Instron 1193 machine using a crosshead speed of 20 mm min^{-1}. Young modulus was determined using an extensometer and a crosshead speed of 0.05 mm min^{-1} and results are presented as the tangent modulus at zero strain. Three-point bending tests were carried out on parallelepipedic samples of dimensions 100 × 12.7 × 3.2 mm, extracted from the tensile bars, using an Instron 1193 machine, 65 mm span length and a crosshead speed of 20 mm min^{-1}. Selected specimens were placed in an oven at elevated temperature for varying periods of time (44 h at 100 °C, 24 h at 120 °C, 16 h at 140 °C and 2 h at 160 °C) to examine the shrinkage characteristics of the mouldings in both mould and transverse

Table 1 Composition of the studied compounds

Sample	Polypropylene (wt%)	Sepiolite (wt%)	Talc (wt%)	Glass fibre (wt%)
PP	100	–	–	–
PPS10	90	10	–	–
PPT10	90	–	10	–
PPS10F20	70	10	–	20
PPT10F20	70	–	10	20

directions. Dwell times were chosen that were expected to be sufficient for the moulding to reach equilibrium, though no independent check was made on this. Mould shrinkage was also determined by comparing the dimensions with those of the mould cavity.

Residual stresses were measured using the layer removal technique. Description of the procedure and discussion of the analysis of the data have been presented in detail elsewhere [10–12]. The technique involves removing thin uniform layers from the test bars by high-speed milling and measuring the curvature ρ of the bar in response to the imbalanced stresses at each removal. The plot of ρ versus the total depth of material removed $(z_0 - z_1)$ was then converted to a stress versus $(z_0 - z_1)$ profile using the Treuting and Read expression [13]:

$$\sigma_{i,x}(z1) = \frac{-E}{6(1-\nu^2)}\left[(z_0+z_1)^2\left\{\frac{\mathrm{d}\rho_y(z_1)}{\mathrm{d}z_1} + \frac{\nu\mathrm{d}\rho_x(z_1)}{\mathrm{d}z_1}\right\} + 4(z_0+z_1)\{\rho_x(z_1)+\nu\rho_y(z_1)\} - 2\int_{z_1}^{z_0}\{\rho_x(z)+\nu\rho_y(z)\}\mathrm{d}z\right] \qquad (1)$$

where $\sigma_{i,x}(z_1)$ is the residual stress in the x direction at the plane z_1 from the mid-plane of the specimen prior to layer removal, E is the Young's modulus and ν is the Poisson ratio, assumed to be isotropic in the x–y plane, and uniform throughout. ρ_x and ρ_y are the components of curvature in the x- and y-directions, respectively.

If the curvature after layer removal in the transverse (y) direction is very small, (i.e. $\rho_y = 0$), then Eq. 1 becomes:

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

This equation has been used in the literature in the analysis of residual stresses of injection moulded polymer samples [14–18], and is the one used in this study. This is because the bars did not show any pronounced curvature in the transverse direction and because it is very difficult to make an accurate measurement of curvature in this direction when the bars are narrow, as in the experiments reported here. It is noted that the furthest departure from this assumption that is likely to occur in the case studied here is that in which equibiaxial stresses develop, causing ρ_x and ρ_y to be equal, in which case the factor $(1 - \nu^2)$ in Eq. 2 should be replaced by $(1 - \nu)$, giving a corresponding decrease in the calculated value for the residual stress magnitude of a factor of ~1.4 (considering $\nu = 0.4$). In view of the considerable orientation produced during injection moulding and the corresponding anisotropy of residual stresses it is extremely unlikely that such a large departure would be present. The effect of anisotropy in residual stresses is much more important in moulded plaques than in bars and it is also more easily measured (though it is still challenging to conduct the experimental and computational analysis). This has been discussed at length elsewhere [9, 12, 19]. Another problem that is often overlooked when measuring residual stresses in polymers is the gradient in Young modulus that is sometimes present. This topic has been studied extensively by White and co-workers who have developed methods to measure the Young modulus distribution [20–22] and to conduct a modified Treuting and Read analysis using this data [17, 23–25]. It can be deduced that for the class of samples studied in the work presented here the effects of anisotropy and depth-varying Young modulus will not have a major effect on the results presented below.

Tests were performed directly on the aged injection moulded tensile bars. Thin layers (0.1 mm) were removed from bars using a single-point cutter on a high-speed milling machine, measuring the resulting curvature by a laser reflection technique based on the optical lever principle [26]. Residual stress values were calculated using Eq. 2 with $\nu = 0.4$ and E values experimentally calculated from uniaxial tests (Table 2).

Results

Sepiolite is a high surface area (~200–300 $\mathrm{m^2\ g^{-1}}$) fibrous magnesium silicate with $[\mathrm{Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4{\cdot}8H_2O}]$ as the unit cell [27], whose structure is composed of two bands of silica tetrahedrons linked by magnesium ions in octahedral coordination. The discontinuous octahedral layer provides infinite channels along the fibre axis with a cross section of about $1 \times 0.4\ \mathrm{nm}^2$. This clay has been used to reinforce different polymers such as polypropylene [28–31], poly(hydroxyethyl acrylate) [32], epoxy [33, 34], nylon-6 [35], polyurethanes [36], polyacrylic acid [37], natural rubber [38], etc. Results indicate that sepiolite changes the kinetics of crystallization of PP matrix in nanocomposites, acting as heterogeneous nuclei and increasing the crystallization temperature, without changing the crystalline structure and crystal polymorphism [28–30, 39, 40].

The mechanical properties of isotropic, compression moulded, sepiolite-filled polypropylene indicate that the incorporation of low concentrations (10 wt%) of sepiolite leads to an improvement in flexural modulus and strength and in the uniaxial tensile Young modulus, with a decrease in impact strength, and tensile strength. Increasing filler concentration leads to a continuous decrease in the impact strength, while the tensile strength increases up to a value higher than that obtained for unfilled polymer [6]. The mechanical properties of compression moulded sepiolite/short glass fibre/polypropylene hybrid composites (10/20/

Table 2 Mechanical properties of the samples as a function of ageing

Sample	Impact strength (kJ m^{-2})	Uniaxial tension		Three Point Bending	
		Modulus (GN m^{-2})	Strength (MN m^{-2})	Modulus (GN m^{-2})	Strength (MN m^{-2})
PP aged 22 h 20 °C	3.74	0.98	29.3	1.27	56.7
PP aged 30 days −80 °C	4.33	1.00	28.9	1.32	54.3
PP aged 30 days 20 °C	3.58	1.05	30.2	1.45	62.4
PP aged 30 days 20 °C + 6 h 120 °C	7.24	1.04	31.9	1.34	58.3
PPS10 aged 22 h 20 °C	2.87	1.33	29.5	1.47	60.4
PPS20 aged 30 days −80 °C	3.28	1.24	29.1	1.41	59.1
PPS10 aged 30 days 20 °C	2.90	1.26	25.9	1.80	64.8
PPS10 aged 30 days 20 °C + 6 h 120 °C	3.77	1.45	31.2	1.58	63.8
PPT10 aged 22 h 20 °C	4.10	1.77	22.3	1.59	46.4
PPI10 aged 30 days −80 °C	3.31	1.75	29.8	1.79	63.0
PPT10 aged 30 days 20 °C 20	2.79	1.89	32.0	2.08	67.7
PPT10 aged 30 days 20 °C + 6 h 120 °C	5.92	1.60	31.7	1.87	67.9
PPS10F20 aged 22 h 20 °C	5.48	4.57	49.4	4.08	101.5
PPS10F20 aged 30 days −80 °C	5.05	4.40	49.8	4.10	104.0
PPS10F20 aged 30 days 20 °C	4.54	4.71	51.6	4.44	105.0
PPS10F20 aged 30 days 20 °C + 6 h 120 °C	5.97	4.68	54.5	4.29	110.8
PPT10F20 aged 22 h 20 °C	3.72	4.93	43.9	4.09	92.6
PPS10F20 aged 30 days −80 °C	3.65	4.38	43.9	4.41	93.6
PPS10F20 aged 30 days 20 °C 20	3.52	5.35	48.4	5.16	104.4
PPS10F20 aged 30 days 20 °C + 6 h 120 °C	4.55	4.47	47.2	4.44	94.4

70 wt% relative concentration) show a large decrease in the impact strength, and a large improvement in the Young modulus (160% compared to the unfilled polymer), and flexural modulus and strength [41]. The mechanical properties (impact strength, and modulus and strength both in uniaxial tension and three-point bending tests) of the polypropylene hybrid clay/glass fibre/polypropylene composites in the form of injection moulded samples are presented in Table 2. Data for pure polypropylene and for 10 wt% sepiolite and talc-filled polypropylene aged under the same conditions are also shown for comparison. Results indicate that the impact strength of the sepiolite/glass fibre/polypropylene hybrid aged 22 h at 20 °C is 46% higher than that of unfilled polypropylene, and 91% higher than that of the 10 wt% filled sepiolite/polypropylene composite. The values obtained for the aged samples follow the same behaviour though the improvement in the impact strength is not so high. Different behaviour was detected with the annealed samples, where the highest value for impact strength was obtained with the polypropylene sample. Regarding talc-filled samples, the impact strength of polypropylene and the hybrid composite aged 22 h at 20 °C were practically identical, and lower than the value obtained for the talc-filled polypropylene sample. Again a different behaviour was detected for samples aged for 30 days at ambient temperature, for which the highest values corresponded to unfilled polypropylene. Annealed samples showed the highest impact strength values, however, the lowest value corresponded to the hybrid composite.

The Young modulus of the composites, both hybrid and particulate-filled, was higher than that of unfilled polypropylene, the highest values corresponding to the talc-filled samples. Ageing for 30 days at 20 °C led to an improvement in the Young modulus, with a small increase observed for the annealed samples. Filled samples showed the same behaviour, except for the sepiolite/polypropylene compound, for which a decrease in the value of the Young modulus was detected, in agreement with data obtained for isotropic compression-moulded samples [31]. Samples aged at low temperature showed in all cases values of the Young modulus lower than those of the samples aged at 20 °C. The uniaxial tensile strength of polypropylene and the sepiolite-filled samples are of the same order, and higher than those measured for the talc-filled samples. Again the higher values correspond to the hybrid samples, independently of the ageing treatment. Regarding aged samples, an increase was observed in the uniaxial tensile strength values, except for the sepiolite-filled polypropylene composite. Annealing led to increase in the strength values of polypropylene and sepiolite-filled samples, whereas a small decrease was detected for the talc-filled ones.

The flexural modulus of the composites is, as expected, higher than that for unfilled polypropylene. Ageing at −80 °C, increased the value of the modulus, except with the sepiolite/polypropylene sample. The talc particles and glass fibres orient parallel to the flow direction and enhance the bending stiffness. The highest flexural strength values correspond to the sepiolite-filled systems, whereas for the talc-filled samples the values are even lower than those obtained for unfilled polypropylene. Again, ageing caused higher strength values, except for the polypropylene and sepiolite-filled polypropylene samples.

Table 3 shows the values of the moulding shrinkage along the flow direction of the injection moulded samples, calculated by measuring the difference between a linear dimension of the mould at room temperature and that of the moulded part. Unfilled polypropylene showed a moulding shrinkage of 1.41%, a characteristic behaviour of semi-crystalline polymers, associated with the volume reduction process exhibited during cooling [42]. The addition of 10 wt% of sepiolite had little effect on the shrinkage of the samples, suggesting that there is no preferential orientation of the sepiolite particles during the injection moulding process, the small difference probably being the result of changes in the polypropylene crystallization due to the nucleating effect of the filler, but the incorporation of the same amount of talc decreased the shrinkage up to 28%. These results agree with those reported in the literature [43] and have been explained as the result of the flake-shaped talc particles orientation along the flow direction during the injection process coupled with interfacial contact effects between the talc particles and the polymer matrix. Hybrid composites show much lower shrinkage values, independently of the type of clay, due to the orientation of the glass fibres in the flow direction. Table 4 reports the shrinkage in the moulding and transverse direction of annealed samples, obtained by measuring the length of the bar before and after being annealed at different temperatures, and then left at 20 °C for 24 h. It is notable that the values are lower than those measured for non-annealed samples, specially for the unfilled and clay-filled polymer. The annealing shrinkage values measured for unfilled polypropylene increased with heat treatment in both moulding and transverse directions. Regrettably the moulding surfaces were not sufficiently planar to enable accurate measurements to be made of the thickness of the mouldings and the shrinkage/expansion in this direction could not be monitored. The shrinkage of talc-filled polypropylene was larger than that displayed by sepiolite-filled polypropylene, independently of the thermal treatment, while this relation was not so clear for the sepiolite-filled polypropylene sample. Again lower values were obtained for the hybrid samples.

Table 3 Mould shrinkage of the samples in the bar-axis direction

Sample	Shrinkage (%)
PP	1.41
PPS10	1.51
PPT10	1.01
PPS10F20	0.25
PPT10F20	0.23

The analysis of the residual stress distributions in injection moulded polymeric materials (amorphous, crystalline, fibre and particulate-filled) have become the subject of an increasing number of studies due to their effect on the mechanical properties, dimensional stability and chemical resistance [44, 45]. The residual stress distributions in clay-filled and clay/short glass-fibre-filled polypropylene stored for 30 days at −80 °C before conducting the layer removal test, are shown in Figs. 1 and 2. Unfilled polypropylene showed a slight departure from the classical parabolic profile, with a maximum tensile stress of 1.2 MN m^{-2} at 0.5 mm from the bar centre, and a compressive stress of approximately 1.2 MN m^{-2} near the surface. It has to be pointed out that the residual stresses begin to decay immediately after moulding as the result of molecular relaxation processes, so a reduction in stress levels is expected, even if

Table 4 Effect of heat treatment on the annealing shrinkage in the flow and transverse direction

Sample	Shrinkage (%)							
	44 h, 100 °C		24 h, 120 °C		16 h, 140 °C		2 h, 160 °C	
	MD	TD	MD	TD	MD	TD	MD	TD
PP	0.21	−0.24	0.63	−0.16	0.66	0.02	0.83	3.17
PPS10	0.33	0.48	0.42	0.57	0.12	−0.57	0.71	0.41
PPT10	0.55	0.78	0.45	2.60	0.62	2.06	0.94	3.48
PPS10F20	0.14	−0.40	0.17	−0.08	0.42	−0.64	0.16	0.72
PPT10F20	0.16	−0.81	0.20	−0.08	0.16	−0.65	0.08	−0.57

Negative shrinkage values indicate that expansion occurred

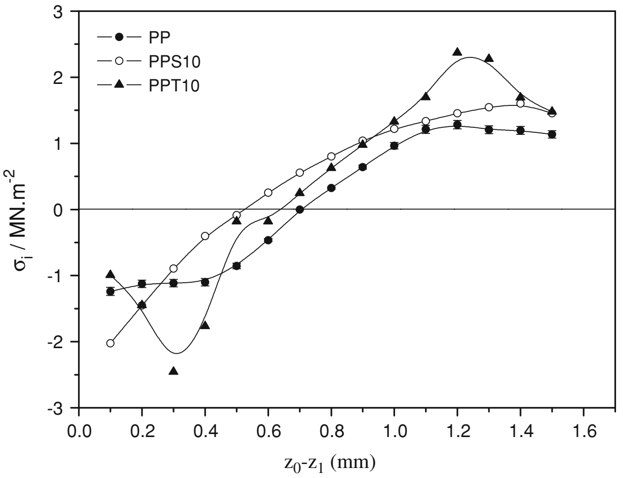

Fig. 1 Residual stress analysis for 10 wt% filled clay/polypropylene composites aged 30 days at −80 °C

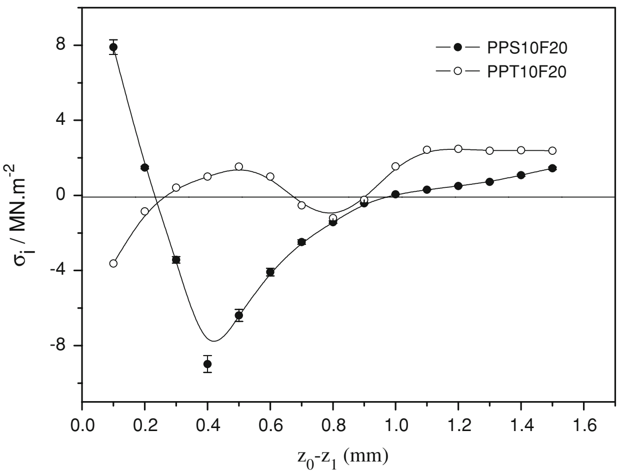

Fig. 2 Residual stress analysis for hybrid clay/glass fibre/polypropylene composites aged 30 days at −80 °C

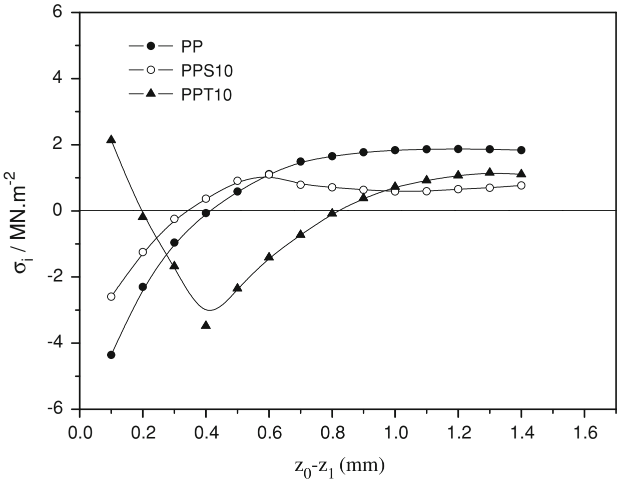

Fig. 3 Residual stress analysis for 10 wt% filled clay/polypropylene composites aged 22 h at 20 °C

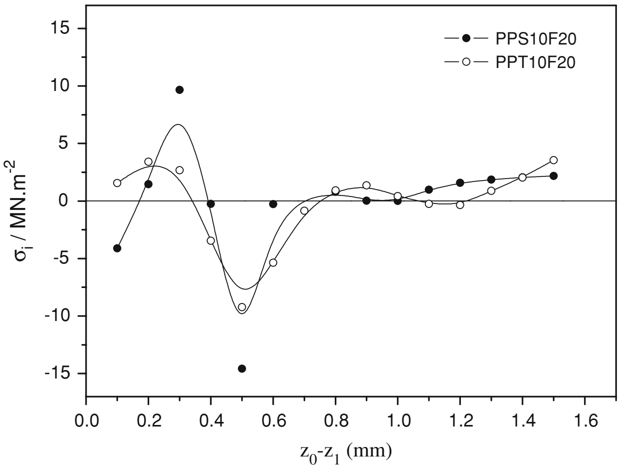

Fig. 4 Residual stress analysis for hybrid clay/glass fibre/polypropylene composites aged 22 h at 20 °C

the moulding is stored for a period at −80 °C. The stress profiles for sepiolite-filled polypropylene samples agree well with the expected parabolic shape, with a maximum tensile stress value of 1.5 MN m^{-2} at the bar centre, and a compressive stress of the order of 2.6 MN m^{-2} at the bar surface. The residual stress distribution of the talc-filled sample displayed a different behaviour, with a maximum tensile stress of 2.3 MN m^{-2} located at 0.3 mm from the bar centre, and a compressive stress of 2.4 MN m^{-2} at 0.3 mm from the bar surface.

The residual stress distributions in clay-filled and clay/short glass-fibre-filled polypropylene stored for 22 h at room temperature before conducting the layer removal test are shown in Figs. 3 and 4. Unfilled polypropylene shows the classical parabolic profile, with a maximum tensile stress close to 2 MN m^{-2} and a compressive stress rising to 4.5 MN m^{-2} near the surface. Sepiolite-filled polypropylene also shows a parabolic shape, with a tensile stress close to 0.8 MN m^{-2} near the bar centre, a maximum tensile stress of 1 MN m^{-2} at 0.6 mm from the bar surface and a compressive maximum of 3 MN m^{-2} near the surface, lower than that measured for unfilled polypropylene. The residual stress profile obtained for the talc-filled composite departs significantly from the parabolic form, showing tensile stresses at the bar surface close to 4 MN m^{-2}, a maximum compression stress of 3.5 MN m^{-2} located at 0.4 mm from the bar surface and a tensile stress rising to 1 MN m^{-2} near the surface. Hybrid composites show different profiles, with larger residual stresses than the corresponding glass fibre free samples; the sepiolite-based hybrid shows large compression stress at the surface, a maximum tensile stress located at 0.3 mm from the bar

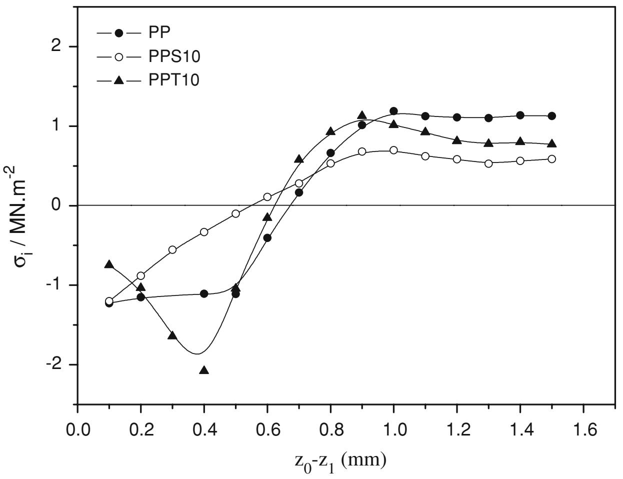

Fig. 5 Residual stress analysis for 10 wt% filled clay/polypropylene composites aged 30 days at 20 °C

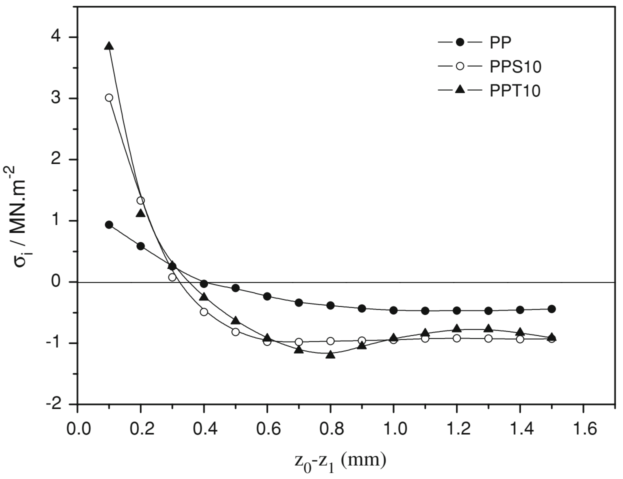

Fig. 7 Residual stress analysis for 10 wt% filled clay/polypropylene composites aged 30 days at 20 °C, then annealed 6 h at 120 °C

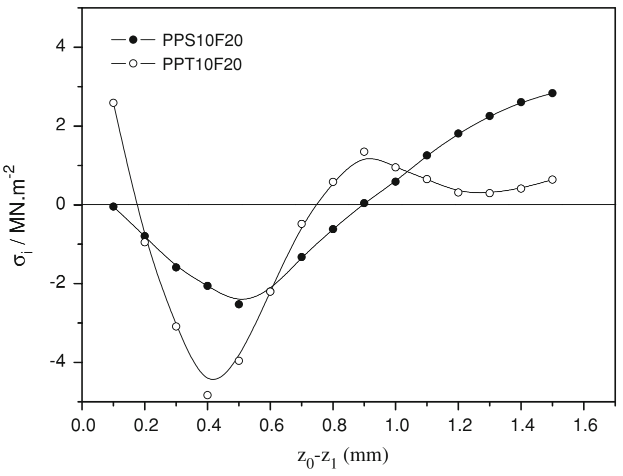

Fig. 6 Residual stress analysis for hybrid clay/glass fibre/polypropylene composites aged 30 days at 20 °C

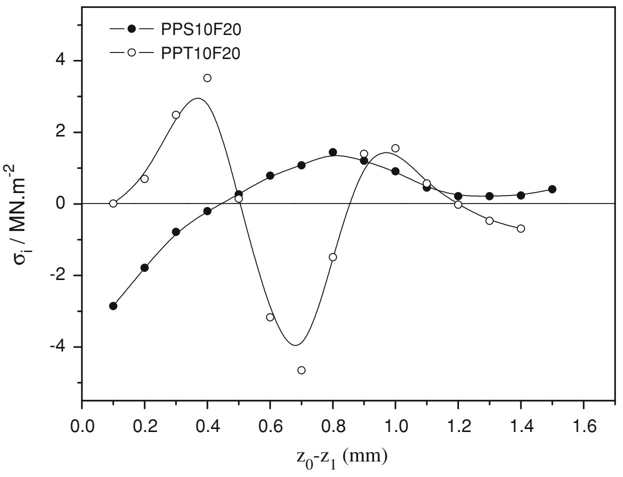

Fig. 8 Residual stress analysis for hybrid clay/glass fibre/polypropylene composites aged 30 days at 20 °C, then annealed 6 h at 120 °C

surface, followed by a large compression stress located at 0.5 mm from the bar surface. Talc-based hybrid composite shows a similar profile, but the stress magnitudes are smaller than those obtained for the sepiolite based hybrid.

Ageing at 20 °C for 30 days led to only minor changes in shapes of the stress distribution profiles of the clay-filled and hybrid polypropylene samples (Figs. 5, 6), showing as a general rule decreases in both compression and tensile stress magnitudes. The large stress magnitudes and sudden variations observed in hybrid samples after 22 h ageing (Fig. 4) were reduced considerably for the samples aged for 30 days (Fig. 6). Annealing at 120 °C led to a reversal of the sense of the stress at most locations through the sample thickness for PP, PPS10 and PPT10 (Fig. 7, c.f. Fig. 5). A similar reversal was obtained with the sepiolite–glass hybrid (Fig. 8). The stress distribution in the talc–glass hybrid was more complex and the effect of annealing on the change in residual stress sense and magnitude varied from one location to another.

The results obtained indicate that immediately after moulding the residual stresses in injection moulded polypropylene samples were at the maximum magnitudes but begin to decay at once, even when stored for a period at temperatures as low as −80 °C, in good agreement with results previously reported in the literature [26, 46]. Ageing at room temperature is expected to lead to a significant reduction in stress levels, due to localized molecular relaxation [26, 46]. Annealing at high temperature led to a marked reduction in stress levels, coupled with the development of weak tensile stresses near to the surface and a reversal in the stress sense. These effects may be explained in terms of further crystallization in the skin layer, by the relaxation of molecules in oriented conformation or by reorientation of crystals. Addition of 10 wt% sepiolite to the polypropylene matrix led to similar residual stress profiles to the one obtained for unfilled polypropylene, though the magnitudes of the stresses were lower. The residual stress distribution obtained for the talc-filled sample was different to that of the unfilled or sepiolite-filled polymer, mainly due to some kind of molecular orientation induced by the platelet-like talc particles in the flow direction. The residual stress behaviour of the sepiolite–glass fibre hybrid samples is similar to that of glass-fibre-filled polypropylene [19], indicating that the development of the residual stresses is governed by the molecular orientation in the flow direction induced by the glass fibre (i.e. transcrystallization), and not by the sepiolite nucleation effects; on the other hand, talc-filled glass-fibre hybrid samples stresses reflect molecular orientations induced by both the glass fibre and the talc particles.

Conclusions

The effects of ageing on the mechanical properties and the residual stresses distribution profile of injection moulded hybrid sepiolite and talc/short glass fibre/polypropylene composites have been studied. The results obtained indicate that the incorporation of short glass fibre to clay/polypropylene composites improves the mechanical properties, in terms of the elastic modulus and strength, measured in both uniaxial and three point bending tests, independently of any ageing treatment. Larger modulus values were obtained for talc-filled samples, due to the orientation of the particles in the flow direction during the moulding process, whereas the highest stress values were measured for the sepiolite-filled ones. The impact strength increased as a result of the incorporation of glass fibres into the sepiolite-filled composite, whereas a small decrease was detected for the talc-filled polypropylene sample, this behaviour being explained in terms of the higher nucleation capability of sepiolite compared with talc. Sepiolite-filled compounds show higher mould shrinkage than equivalent talc-filled grades, whereas the shrinkage obtained on annealing at various temperatures between 100 and 160 °C was generally greater for talc-filled compounds than for the sepiolite-filled compounds. The shrinkage behaviour in the transverse direction was more complicated. The residual stress levels of clay-filled polypropylene compounds were generally lower than those reported in the literature for short glass fibre polypropylene compounds under similar conditions [9], indicating superior dimensional stability. Hybrid composites show much higher stress levels for the corresponding clay-filled samples independently of ageing conditions.

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