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Effects of recycling on the microstructure and the mechanical properties of isotactic polypropylene

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Polypropylene (PP) was injection moulded several times to mimic the effect of recycling procedures. The influence of the recycling was studied by following changes in chemical structure, melt viscosity, crystallisation behaviour, and tensile and fracture properties. The main effect of recycling is the lowering of the melt viscosity, which is attributed to molecular weight decrease. Recycled PP exhibits greater crystallisation rate, higher crystallinity and equilibrium melting temperature than those measured for virgin PP. Elastic modulus and yield stress increase with the number of recycling steps. However, elongation at break and fracture toughness decrease. © *2001 Kluwer Academic Publishers*

1. Introduction

The last thirty years have seen plastic materials usage grow to the point where they are now an important part of society. This rapid development has coincided with the equally dramatic rise of what is commonly referred to as the 'green movement'. This increased environmental awareness means that now, more than ever, industry has to be concerned with waste-disposal strategies. Traditional methods concentrated largely on disposal in landfill sites. This option is becoming increasingly unpopular, with legislation being introduced to limit its scope and encourage the introduction of environmentally more acceptable options such as recycling.

There are four main approaches to plastics recycling; primary, secondary, tertiary and quaternary recycling [1]. Primary recycling focuses on clean, uncontaminated, single type scrap from processing operations. Secondary recycling aims at the management of mixtures of plastic wastes. Tertiary or chemical recycling has been defined as the cleavage of polymer chains to make chemical products of lower molecular weight distribution or even to recover the original monomer which can be used for another complete cycle of polymerisation. Finally, quaternary recycling comprises the utilisation of plastic wastes as energy sources.

The knowledge of degradation origins and loss of properties is of great importance in order to determine things such as the number of cycles that a polymer might undergo, the most effective experimental techniques to characterise the recycled polymer, the most suitable additives to control degradation, or the conditions under which the polymer will not degrade. Moreover, a usual way to reuse recycled polymers is by blending them with the same virgin polymer [2] to obtain materials with intermediate properties.

This work is included in a study of the fracture behaviour of blends of virgin and recycled PP prepared by the dissolution/reprecipitation technique [3]. In this paper, PP has been processed up to ten times by injection moulding. The main purpose is to determine the effect that successive temperature and shear-stress cycles inherent in melt-recycling have on the chemical and molecular structure, melting and crystallisation behaviour, mechanical properties and fracture toughness. The influence of recycling on the structure and mechanical properties of PP has been partially studied [4–9].

2. Experimental procedure

2.1. Materials and specimen preparation

For this investigation an injection grade isotactic polypropylene (PP) homopolymer (SM6100, Montell) was used. To simulate the recycling steps, PP was processed in a Battenfeld BA 600CDC injection-moulding machine, and the tensile test specimens obtained were granulated in a knife mill for the next recycling step. This procedure was repeated up to ten times. A melt temperature of 200°C and a cooling time of 20 s were used in accordance with practice ASTM D-4101-96a. The injection pressure was fixed at 594 bar following the procedure described in ASTM D-1897-81. The injection time and the screw rotation rate used were 0.43 s and 200 rpm respectively. These injection parameters were maintained for all the recycling steps. The material code is PP–Rx, where x indicates the number of

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injection moulding cycles, and 0 represents the virgin material (pellets). There are no results of mechanical and fracture tests for PP–R0 since the preparation of the specimens implies the injection moulding of the pellets.

Tensile test specimens (ASTM D-638-97, type I) have been obtained as described above. For each recycling step prismatic bars (ASTM D-647) with 12.7 mm × 6.35 mm × 127 mm dimensions were also injection moulded. These bars were cut to 12.7 mm × 6.35 mm × 63.5 mm dimensions and notched to obtain single-edge notched bend (SENB) specimens for impact tests. Crack (a) to depth (W) ratio between 0.3 and 0.54 were used. A pre-crack was also introduced by sliding a fresh razor blade over the tip of the notch. The final value of the notch depth was measured after fracture by using an optical microscope. The specimens were annealed in a fan-assisted oven for 3 h at 145°C (tensile specimen) and 150°C (fracture specimen).

2.2. Characterisation of the microstructure

The Fourier Transform Infrared (FTIR) analysis was carried out in order to study any change in the chemical structure, using a Nicolet FTIR-460 spectrophotometer.

The measurements of Melt Flow Index (MFI) were done with a CEAST 6540/010 equipment according to the test conditions of ASTM D-1238-95: 230°C; load 2160 g. MFI is a measure of the fluidity of the material and is strongly influenced by the weight-average molecular weight (M_w). For this reason MFI can be used to obtain rapid information about the change of the molecular characteristics of the PP due to repeated recycling events.

Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer DSC7 thermal analyser under nitrogen atmosphere. Microtomed sections of tensile specimens were used as samples. According to ASTM D-3417-97 the samples typically weighed between 5.5 and 6 mg.

The Avrami analysis method was used to study the kinetics of isothermal crystallisation [10]. DSC samples were maintained as melt at 230°C for 5 minutes. At this temperature self-seeded nuclei disappear because the annealing temperature is higher than the equilibrium melting temperature (T_m^0) of PP (the highest estimation of T_m^0 is 220°C [11]). An isothermal crystallisation temperature (T_c) range from 124 to 134°C was chosen in order to ensure that there is no possible crystallisation occurring during the cooling from the melt to T_c. The cooling rate was 45°C/min.

After each isothermal crystallisation, DSC samples were heated from 50 to 200°C at a heating rate of 10°C/min with the aim of determining the melting peak temperature (T_m) and the degree of crystallinity (X_c). By plotting T_m against T_c, it is possible to obtain a linear plot, which, using the Hoffman-Weeks equation, allowed extrapolation to the point where $T_m = T_c$, i.e., to the equilibrium melting temperature [12]:

$$T_m = T_m^0(1 - 1/\gamma) + T_c/\gamma \qquad (1)$$

where γ is the proportionality factor between initial and final laminar thickness.

The degree of crystallinity (X_c) of the isothermally crystallised samples were calculated using the following equation:

$$X_c = \Delta H_f / \Delta H_f^0 \qquad (2)$$

where ΔH_f is the heat of fusion, derived from the area between the measured curve and the base line in the region of the peak, and ΔH_f^0 is the enthalpy of fusion of a completely crystalline isotactic PP, taken to be 207.1 J/g [13].

The apparent crystallisation temperature (T_{app}) was calculated by taking the peak temperature of crystallisation exotherm. The PP sample was heated to 230°C at a rate of 200°C/min and held for 5 minutes to ensure complete melting. It was then cooled to 50°C at a rate of 10°C/min.

2.3. Mechanical properties

Tensile tests (ASTM D-638-97) were performed on an Instron 4206 standard testing machine at a crosshead speed of 50 mm/min and at room temperature. Elastic deformations were measured by an Instron strain gage extensometer, model No. A1439-1007, having a gage length of 50 mm. A minimum of five specimens was tested for each material.

SENB specimens were tested on a CEAST instrumented Charpy impact pendulum, equipped with a data acquisition unit. Impacting of the specimens occurred under the following conditions: mass of the striker = 2.182 kg, $v = 0.57$ m/s, room temperature, span 50.8 mm. The impact data were analysed according to the linear elastic fracture mechanics approach [14]. The fracture toughness (K_{IC}) was calculated by means of the equation

$$K_{IC} = \frac{3}{2} \cdot \frac{F_{max} \cdot S}{B \cdot W} \cdot \left(\frac{a}{W}\right)^{1/2} \cdot Y\left(\frac{a}{W}\right) \qquad (3)$$

where F_{max} is the maximum load; S the span; B and W are the thickness and the width of the specimen, respectively; a is the initial crack length and $Y(a/W)$ a calibration factor depending on the specimen geometry.

For the determination of the critical strain energy release rate (G_{IC}), the following equation was used

$$G_{IC} = \frac{U_c}{BW\phi} \qquad (4)$$

where U_c is the fracture energy and ϕ is a calibration factor which depends on the length of crack and the size of the sample.

Table I shows a summary of the experimental techniques and samples preparation.

3. Results and discussion

3.1. Characterisation of the microstructure

In general, during recycling the macromolecules are submitted to high temperatures and intensive shearing which promote thermal, mechanical, oxidative or combinations of these degradation mechanisms. The presence of tertiary carbons in the chemical structure of PP induces a rapid oxidation [5]. Fig. 1 contains the FTIR spectrum of the virgin (PP–R0) and ten times recycled

TABLE I Summary of the experimental techniques and sample preparation

Experimental technique	Information	Specimen	Observations
FTIR	Chemical structure	Granulate	
MFI	Indirect measure of molecular weight	Granulate	
DSC	• Kinetics of crystallisation • Degree of crystallinity • Apparent crystallisation temperature	Microtomed section of the tensile specimens	• Before crystallisation samples held at 230°C for 5 min. • Dynamic tests; heating/cooling rate 10°C/min.
Tensile test	E, σ_y, ε_y, σ_b, ε_b	ASTM D-638-97, type I	Annealing 3 h at 145°C
Impact test	K_{IC}, G_{IC}	SENB	Annealing 3 h at 150°C

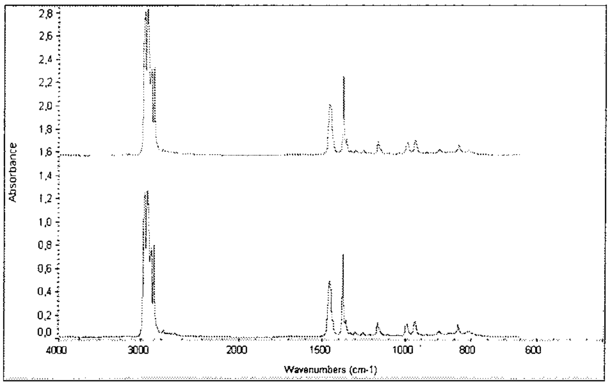


Figure 1 FTIR spectrum of PP—R0 (upper) and PP—R10 (lower).

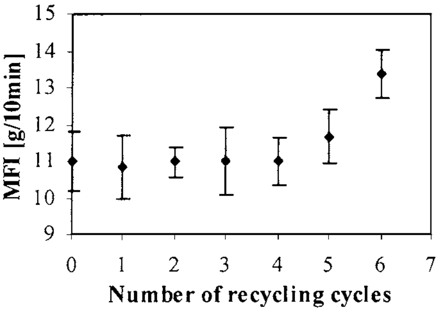


Figure 2 Melt Flow Index (MFI) as a function of recycling cycles.

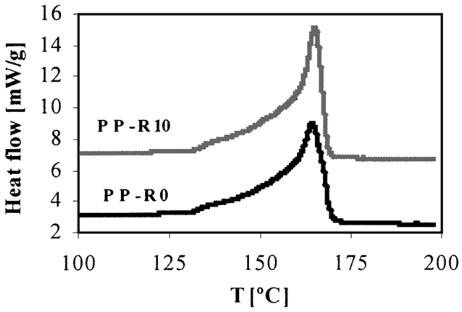


Figure 3 Heating DSC curves for PP-R0 and PP-R10; PP-R10 curve is shifted vertically.

(PP—R10) PP. The lack of variation proves that there are almost no oxidative reactions during the recycling. This behaviour is probably due to the absence of oxygen within the polymer melt.

In Fig. 2 MFI is reported as a function of the number of recycling steps. MFI remains constant up to four cycles, showing an increasing tendency from the fifth cycle. The absence of changes from PP—R0 to PP—R4 is probably due to the presence of stabilisers. The fact that PP degradation starts at the fifth recycling step points out that the previous processing events exhausted the stabiliser required to prevent degradation.

The absence of changes in the chemical structure (Fig. 1) and the increase of the MFI suggest that chain scission, and not oxidation, is the dominant degradation mechanism under the experimental conditions.

Heating DSC curves (Fig. 3) show always a single peak around 164°C, indicating that all the samples have α-form structure [15].

The experimental melting temperature (T_m) is not a material constant; for this reason the equilibrium melting temperature (T_m^0) has been studied. This corresponds to the temperature at which a crystal of the polymer of infinite size heated infinitely slowly melts, and is a true reflection of a polymer's microstructure. T_m^0 as a function of the number of recycling events is plotted in Fig. 4a. T_m^0 is practically constant up to four recycling cycles. PP—R5, PP—R6 and PP—R10 samples have higher and also constant T_m^0. Even if there are no data for samples going from PP-R7 to PP-R9, it could be assumed that their T_m^0 values are very similar to those of PP—R5, PP—R6 and PP—R10. Fig. 4b shows the proportionality factor (γ) for the virgin and recycled PP samples. The proportionality factor decreases for recycled polymers, indicating that the crystal dimensions increase due to recycling. However, it seems that after five recycling steps the lamellar thickness reaches an upper limit, which agrees well with the results referring to the maximum equilibrium melting temperature. Therefore, the observed reduction of the molecular weight with recycling increases the mobility and the ability to fold of the chains [16], allowing the formation of thicker lamellae, and consequently T_m^0 increases.

The analysis of the crystallisation of a polymer is of great importance in understanding structure/properties relationships. The crystallisation isotherms (Fig. 5) have been processed by Avrami's equation between 0.1% and 30% of the final degree of crystallinity. Incubation period is defined as the time interval required at a supercooled state before the critical equilibrium nucleus dimension is established [10], and the induction time is defined as the time to reach the point at which the weight fraction of solid can be detected experimentally to differ from zero, and this is given an arbitrary value of 0.1%. Moreover, the Avrami analysis is likely

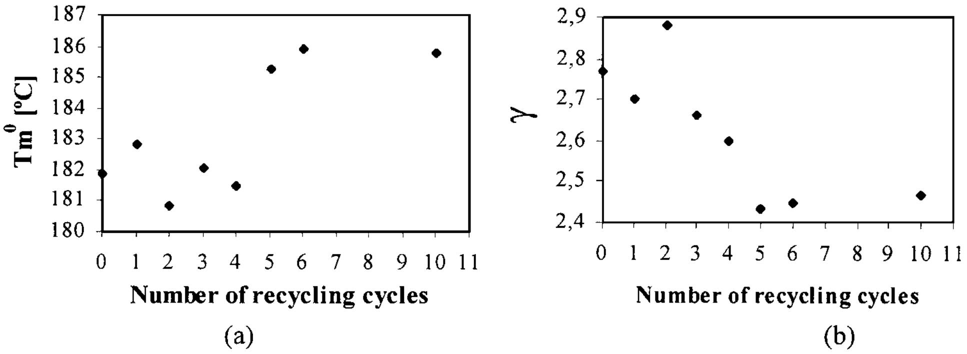


Figure 4 Equilibrium melting temperature (T_m^0) and proportionality factor (γ) of virgin and recycled PP.

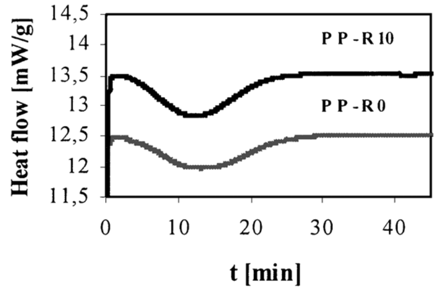


Figure 5 Isothermal crystallisation curves for PP-R0 and PP-R10 ($T_c = 128°C$); PP-R10 curve is shifted vertically.

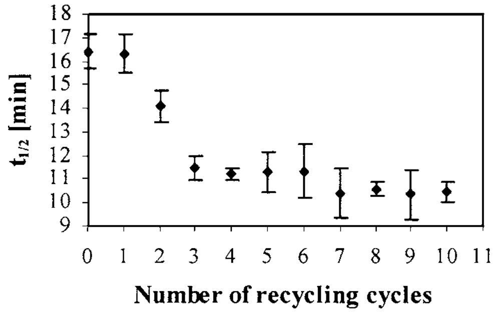


Figure 7 Evolution of the crystallisation half-time ($t_{1/2}$) with recycling cycles.

to fit the observed data adequately for the initial 30% of the crystallisation, where secondary crystallisation do not occur [17].

Fig. 6 shows the values of the Avrami exponent, n, (Fig. 6a) and the kinetics constant, k, (Fig. 6b) for samples crystallised isothermally at 128°C. Avrami exponent (n) is a combined function of the number of dimensions in which growth takes place, and also of the order of the time-dependence of the nucleation process, and should assume integer values. However, it is frequently found by the experimental data that the Avrami exponent takes values between 2.4 and 3.6 [15]. The results for n are between these values, and since n is similar for all samples, the mechanism of crystallisation is not affected by the recycling. The kinetics constant (k) depends on nucleation and growth rates. Under isothermal conditions the growth rate is constant up to high degrees of conversion [15], so k is indicative of the nucleation rate. The increase of k with recycling is probably due to the greater degree of supercooling ($\Delta T = T_m^0 - T_c$), since the crystallisation temperature is the same for all the samples (128°C) but T_m^0 is higher for the more degraded materials. As ΔT increases the number of active heterogeneous nuclei increases, causing rate to increase.

Crystallisation kinetics of virgin and recycled materials have been studied by the crystallisation half-time ($t_{1/2}$), since the inverse of $t_{1/2}$ is proportional to the rate of crystallisation. The crystallisation half-time is the time required for the material to reach 50% of its final crystallinity. Fig. 7 shows the variation of $t_{1/2}$ with the number of recycling events. The decrease of $t_{1/2}$ indicates an increase in the crystallisation rate ($\dot{X}$). The increase in $\dot{X}$ with decreasing molecular weight is a general finding confirmed by many researchers [2, 6, 17]. The factor controlling the nucleation and growth rates is not so much temperature itself, as the extent to which the crystallisation temperature lies below the equilibrium melting temperature. The reduction of ΔT produces a decrease in $\dot{X}$. Thus, the increase in $\dot{X}$ with increasing the number of recycling cycles is partly due to the reduction of the molecular weight, and partly to the higher apparent degree of supercooling.

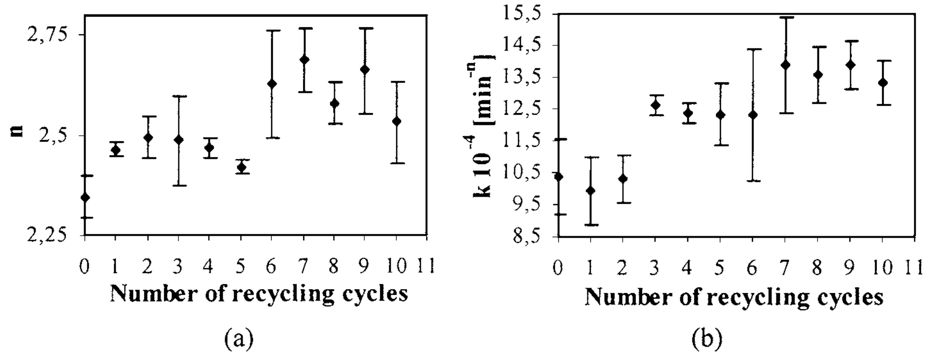


Figure 6 Variation of the Avrami exponent (n) and kinetics constant (k) with the number of recycling events.

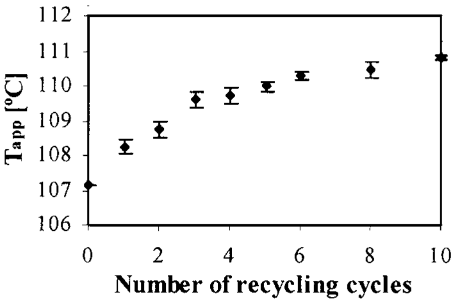


Figure 8 Apparent crystallisation temperature (T_{app}) as a function of the recycling cycle.

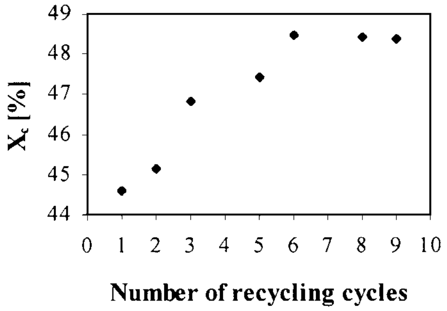


Figure 9 Degree of crystallinity (X_c) of the virgin and recycled PP.

The apparent crystallisation temperature (T_{app}) increases slightly with recycling (see Fig. 8). Recycling a polymer several times introduces impurities. The pre-existing foreign surfaces (impurities) greatly reduce the free enthalpy of the formation of a critical nucleus. This lowers the critical size of the nucleus and results in the formation of heterogeneous nuclei at higher apparent crystallisation temperature [18].

The degree of crystallinity increases with recycling (Fig. 9). As molecular weight diminishes chain mobility increases and crystallisation occurs in a more and more ordered way. Hence the amount of developed crystallinity tends to increase.

3.2. Mechanical properties

The mode of failure of tensile specimens is as follows (see Fig. 10); there is some initial stress-whitening up to the yield point; as soon as this is reached the deformation occurs by necking and finally by fibrillar fracture.

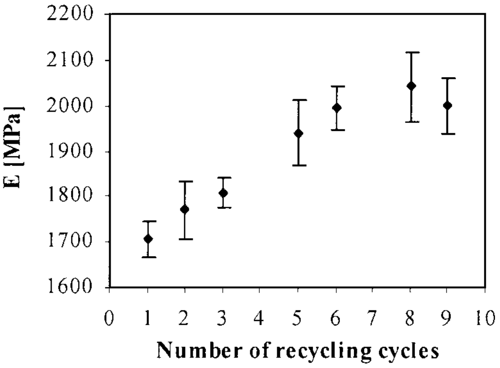


Figure 11 Elastic modulus (E) of the virgin and recycled PP as a function of the number of cycles.

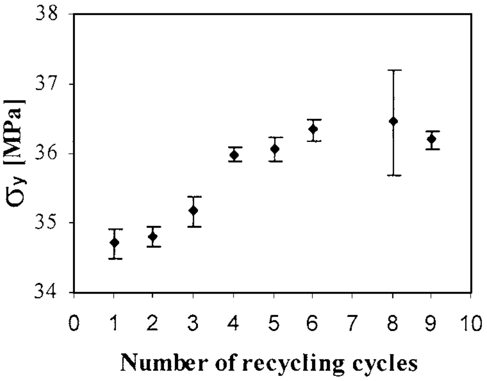


Figure 12 Yield stress (σ_y) after different number of recycling cycles.

The elastic modulus as a function of the number of recycling cycles is plotted in Fig. 11. The modulus increases slightly with recycling due to the higher crystallinity of the recycled PP. The flexibility of a plastic depends basically on the ability of its segments to rotate. Crystalline structures hinder such rotations; therefore, a crystalline material is significantly stiffer than the equivalent plastic in its amorphous condition.

The yield stress (σ_y) increases slightly with recycling (see Fig. 12). As for the modulus, the increase in σ_y is related to the higher crystallinity of the recycled materials. At room temperature the amorphous phase of the PP is above the glass transition temperature (soft), and the crystalline region is below its melting point (stiff), so the higher the crystallinity is the higher material's σ_y is [19].

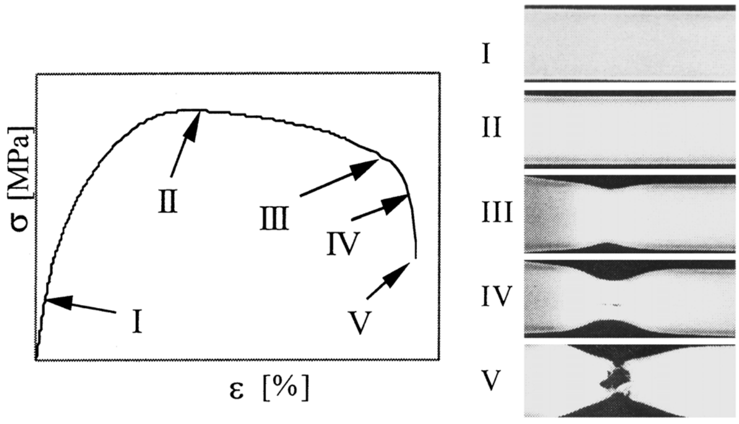


Figure 10 Typical stress-strain tensile curve; elastic deformation (I), stress-whitening (II), necking (III), fibrillation (IV) and fracture (V).

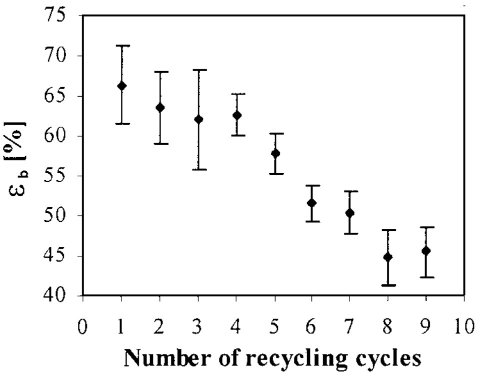


Figure 13 Elongation at break (ε_b) plotted against the number of recycling cycles.

The yield strain is practically constant with recycling (9%). The whitening of the necked region of the tensile yielded PP specimens is associated with the presence of a large amount of micro-voids and a highly fibrillar morphology [20].

The elongation at break (ε_b) for virgin and recycled PP is seen in Fig. 13. ε_b is practically constant up to four recycling steps, and decreases with recycling above this point. This decreasing is related to the higher crystallinity of the recycled PP [21] and to the reduction of the molecular weight with repeated processing cycles. Lower molecular weight inserts more chain ends into the structure, resulting in fewer chains completely integrated into the crystal to sustain stress during tensile loading, causing failure at lower elongation. Moreover, shorter molecules have less entwining and less C-C linkages to stretch.

The break stress is practically constant (22.6 ± 1.6 MPa) up to ten recycling steps. As is shown in Fig. 14, K_{IC} and G_{IC} decrease with recycling. In this paper only the results for PP-R1, PP-R2, PP-R4 and PP-R6 are reported in order to show the effect of recycling on the fracture parameters. Nevertheless, a more exhaustive study is actually being carried out.

Tie-molecules act as local transmitters of stress among lamellae and are broken during deformation and fracture. The density of tie-molecules being incorporated in at least two crystalline lamellae (intraspherulitic link) and also the number of those connecting the spherulites (interspherulitic link) increase with molecular weight [22, 23]. Furthermore, an increment in the molecular weight enhances the probability of chain entanglements in the amorphous phase [22, 23], resulting in a more connected structure. At increasing molecular weight, a higher elongation at break of fibrils is observed [24], increasing the energy required for crack propagation, and consequently improving fracture toughness. The concentration of the tie-molecules can also be varied by the crystallisation temperature [23, 24]. As the crystallisation temperature is lowered the material becomes more and more compact, since the degree of connection between lamellae and spherulites increases. This is due to the fact that at lower T_c, the nucleation and density rates, as well as the overall crystallisation rate, increase. This effect trends to freeze somewhat the melt configuration of the molecules, allowing only for local lamellae formation. This provides in the fully crystallised sample a number of tie-molecules between lamellae which is higher the lower is T_c. Thus, it could be assumed that the tie-molecule density decreases with recycling due to shorter molecules and higher crystallisation temperatures.

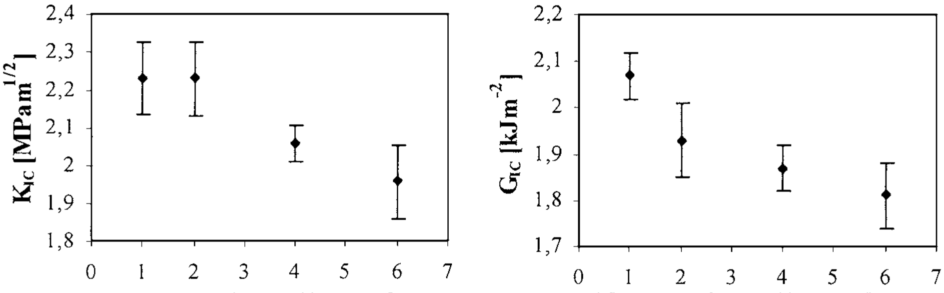
The lowering of the toughness with recycling may also be due to the increase in yield stress [25] (see Fig.12). It has been reported that the fibrillated damage zone ahead of the notch can be initiated more easily in a lower-yield-stress material [26], and that the amount of dissipated energy is proportional to the extension of this plastic zone, whose size depends on the yield stress of the material [27].

4. Conclusion

The effects of recycling on the structure and mechanical properties of isotactic polypropylene have been investigated. The absence of changes in the chemical structure and the increase of the MFI suggest that chain scission, and not oxidation, is the dominant degradation mechanism under the experimental conditions.

The observed reduction of the molecular weight with recycling increases the mobility and the ability to fold of the chains, allowing the formation of thicker lamellae and higher degree of crystallinity. The crystallisation rate also increases with recycling due to the shorter molecules and higher apparent degree of supercooling.

The higher elastic modulus and yield stress of the recycled PP seems to be correlated with higher degree of crystallinity, and the lower elongation at break with the decrease of the molecular weight. Fracture toughness also decreases for the recycled materials due to the higher yield stress and the lower tie-molecule density.



(a) (b)

Figure 14 Effect of recycling on (a) fracture toughness (K_{IC}) and (b) strain energy release rate (G_{IC}).

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