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Polypropylene filled with flame retardant fillers: Mechanical and fracture properties

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SUMMARY: Two grades of isotactic polypropylene (homopolymer and block copolymer) were filled with magnesium and aluminium hydroxides, and studied focusing the mechanical and fracture characteristics of the composites. As expected, dispersion of such fillers in PP resulted in improved stiffness and reduced tensile yield strength. By one hand, the composites fracture resistance was characterised at low strain rate applying the J-integral concept; the resistance to crack growth initiation (J_{IC}) was found decreasing as the $Mg(OH)_2$ concentration was raised in the copolymer PP matrix. By the other hand, the linear-elastic fracture mechanics (LEFM) parameters were determined by means of instrumented impact tests at 1 m/s on the homopolymer PP filled with uncoated $Al(OH)_3$ particles. The higher the $Al(OH)_3$ mean particle size, the lower the composite fracture energy (G_{IC}). In the opposite, with commercial surface-coated filler grades it was not possible to achieve LEFM conditions to characterise the fracture toughness of filled PP at 1 m/s, because the $Mg(OH)_2$ surface coating, which is applied in practice to improve the melt processing, acts increasing the composite plasticity and reducing the tensile yield strength.

Introduction

Flame resistance is one of the most limiting factors for polymeric materials utilisation. Satisfactory flame retardancy can be achieved through the incorporation of halogen-based additives; however, their use is nowadays reversing due to the corrosiveness of their breakdown products. Harmless fillers like magnesium $Mg(OH)_2$ and aluminium $Al(OH)_3$ hydroxide1) could be a right solution for polypropylene flame retardancy. As a result of the filler endothermic breakdown, the flame is cooled and thus fewer pyrolysis products are formed. Together with the charring products, the oxide formed on the substrate surface acts as an insulating layer. Moreover, the water vapour liberated has a diluting effect in the gas phase and forms an oxygen-displacing protective layer over the condensed phase. The main

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drawback of these flame retardant fillers is that high concentrations are usually required to achieve a good flame retardancy in polypropylene. The aim of this work is to study the influence of several grades of these flame retardant fillers on the mechanical and fracture characteristics of polypropylene. Aspects as the filler nature, filler concentration in the composite, filler mean particle size, particle surface coating, and strain rate in the tests have been analysed in this work.

Experimental procedure

Two different grades of polypropylene, supplied by Repsol Química SA (Spain), were employed: A homopolymer (named APP, with MFI = 5.8 g/10 min at 230°C and 2160 g) and a block copolymer (named BPP, with MFI = 3.3 g/10 min at 230°C and 2160 g). Five different grades of flame retardant fillers were kindly supplied by Martinswerk GmbH (Germany): Three $Mg(OH)_2$ grades having a mean particle size of 1.4 μm and different surface nature (H5 particles having no surface treatment, and H5L and H5KV with polymeric coatings in order to make easy the compounding with the PP), and two $Al(OH)_3$ grades with no surface treatment and different mean particle sizes (1.5 μm and 60 μm for the OL and the ON grade respectively). Compounding was performed using a corrotating twin-screw extruder (L/D = 24, D = 25 mm). The cylinder temperature profile was 160, 180, 185, 190 and 195 °C, and the screws speed was 80 rpm. A circular cross- section die of 3 mm diameter was employed, and the extrudate was cooled in a water bath and pelletised. The name given to the composites prepared is as follows: The first letter (A or B) indicates the nature of the PP matrix (homopolymer or copolymer), the following numbers represent the nominal filler weight percentage and the last letters are the filler's name. Standard tensile specimens (type I according to ASTM D-638) and prismatic bars of nominal dimensions 127 x 12.7 x 6.35 mm^3 were injection-moulded using a Mateu & Solé 440-90 injection moulding machine and a multiple cavity mould, as described in figure 4 of the ASTM D-647 standard.

Tensile tests were carried out at different crosshead speeds (5, 10, 50, 100 and 500 mm/min) using an ADAMEL DY-34 universal testing machine and an optical extensometer (HOUNSFIELD 500-L). From these tests, Young's modulus (E) and tensile yield strength (σ_y) values were obtained.

Three point bending fracture tests were performed on SENB specimens with nominal dimensions B x W x L = 6.35 x 12.7 x 63.5 mm^3, which were obtained by cutting the injected bars into halves. The notches were machined using a 45° V notch broaching tool. These blunt notches were then sharpened with a single cut from a razor blade in order to get an initial sharp crack. Two kind of fracture tests were carried out to determine the materials fracture parameters: By one hand, low-rate (1 mm/min) tests were performed on the copolymer based compounds applying the multiple specimens method^2) (a_0/W = 0.5) to determine the J-integral critical value (J_{IC}). On the other hand, high rate (1 m/s) tests were carried out on multiple specimens with variable a_0/W ratio^3) for determining the critical stress intensity factor (K_{IC}) and the fracture energy (G_{IC}) of the homopolymer based materials. These late tests were realised by means of an instrumented impact pendulum.

The fracture surfaces were examined by scanning electronic microscopy (SEM) in order to investigate the morphological aspects associated with the deformation and fracture processes.

Results and discussion

The obtained values of Young's modulus (E) and the tensile yield strength are shown in Fig. 1. As expected from the higher stiffness of the filler the composite Young's modulus increased progressively with the filler content, and the copolymer-based compounds showed lower values than the homopolymer series due to the difference between the stiffness of both PP matrixes; PP block copolymers are less stiff than homopolymers. As shown in Fig. 2, a good concordance was found between the experimental values of E and those predicted by the classical models^4) for polymers filled with particles under isostres conditions. The best agreement for the homopolymer-based compounds was found to be the Kerner-Nielsen model, and no remarkable influence of the filler nature was found with similar filling rate.

The observed decreasing trend of the yield stress *versus* the filler volume fraction (Fig. 3) matched well with the values predicted by the theoretical model for polymers filled with fibres shorter than the critical length^5), in which the load transmission mechanism acting between matrix and filler is only the interfacial shear:

$$\sigma_{yc} = \sigma_{ym}(1 - V_p) + 2\tau \frac{l}{d} V_p$$

The fibre length to diameter ratio (*l/d*) has been substituted by the ratio between the particle plate equivalent diameter and the particle thickness (~ 5). The results indicate low interfacial adhesion (τ = 0.73 MPa) between H5 particles and PPA matrix. Due to a weak interface, particle debonding occurs at a low stress level, reducing the material effective cross-section and so the yield stress. Using $Al(OH)_3$ and surface-coated grades of $Mg(OH)_2$ even gave lower values of the interface shear strength (τ). Finally, both Young's modulus and tensile yield strength values increased with the strain rate imposed in the test (Fig. 4).

Concerning to the fracture, the resistance J-R curves and the obtained fracture parameters of unfilled and H5L filled PP copolymer are shown in Fig. 5. A decreasing trend of the J_{IC}

values can be observed as the filler content increases in the composite, which indicates that magnesium hydroxide particles act reducing the polymer resistance to crack growth initiation.

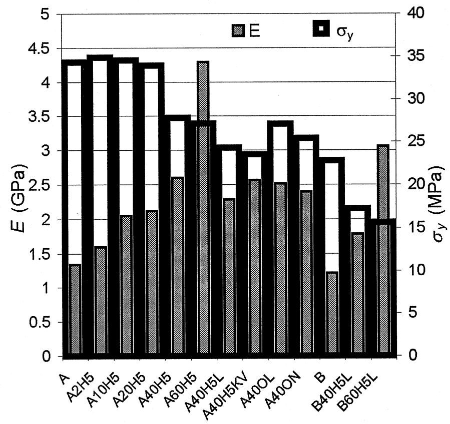

Fig. 1. Tensile properties at 10 mm/min.

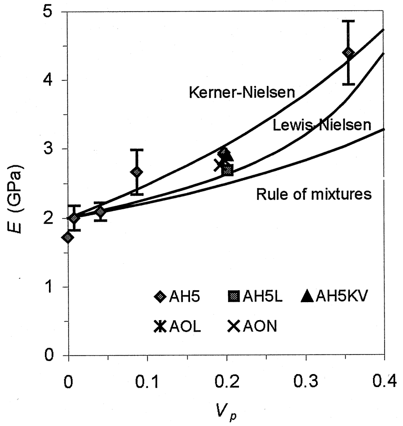

Fig. 2 Obtained and predicted E values.

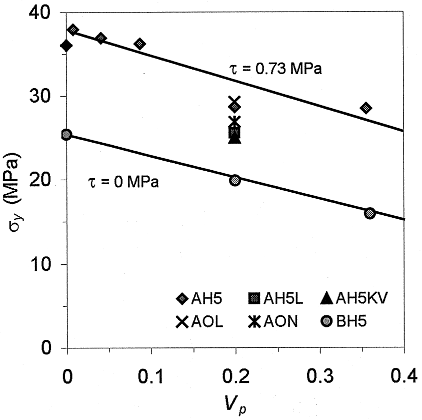

Fig. 3. Obtained values of tensile yield strength.

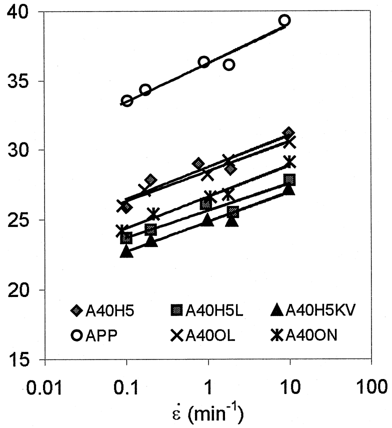

Fig. 4. Strain rate effect on σ_y.

In this sense, the observation of the fracture surfaces by SEM revealed that the crack propagation occurs within matrix ductile tearing. In a first step, microvoids are nucleated in the weakest points of the material, which are the intercrystalline regions in the case of the unfilled copolymer and the particle/matrix interface mainly in the case of the filled samples. The polymer between contiguous microvoids elongates progressively by plastic flow, causing micronecking, and the crack propagates through the progressive failure of this drawn polymer. On the fracture surface, the elongated matrix reminds fibrils or crests when observed by SEM. As shown in Fig. 6, the amount of fibrils on the unfilled PP fracture surface is the lowest of the three studied materials, and the fibril average thickness is found to be the highest. Both characteristics associated with the PP fracture mechanism are in accordance with both the low density of weak points able to nucleate microvoids and the high yield strength of the unfilled PP copolymer with regard to the filled samples. For the same reason, the fibrils in the B60H5L fracture surface are the thinnest and the less elongated of the three samples, due to its high fraction of particles which easily promote the nucleation of microvoids and limit the polymer plastic flow.

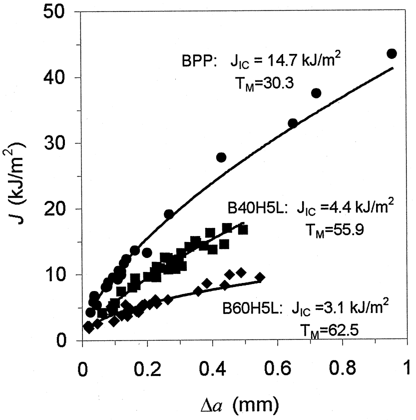

Fig. 5. J-R curves at 1 mm/min.

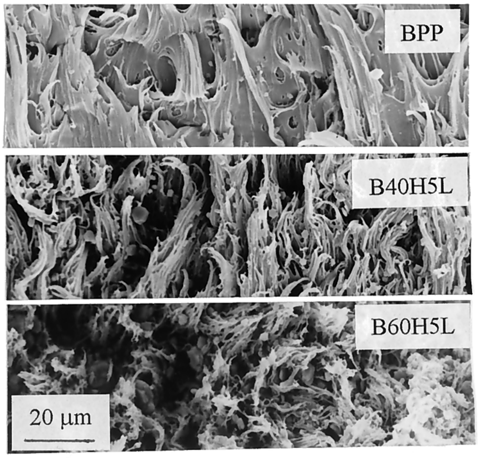

Fig. 6. Ductile tearing on the fracture surfaces.

The resultant tearing modulus (T_M) of the filled PP was higher than of the unfilled one, indicating higher crack growth resistance once J_{IC} is reached. The cause could be the constraint of the PP plastic flow by effect of the dispersed $Mg(OH)_2$ particles.

Polypropylene filled with magnesium hydroxide showed higher ductility than filled with aluminium hydroxide. A non linear-elastic behaviour was observed in these composites even at relatively high rate (1 m/s). Moreover, the particle surface coating given by the manufacturer to H5L and H5KV grades seems to be the responsible of a remarkable toughening effect of these particles on the homopolymer PP, as it could be observed by the impact tests. The load/time signals recorded by the pendulum sensors indicated fracture with increasing plasticity in the following sequence: A40H5KV > A40H5L > A40H5. Also, as observed during the tensile characterisation of these materials, surface coated fillers allowed higher elongation, which is related to higher toughness. In contrast, composites with aluminium hydroxide satisfied the LEFM conditions and it was possible to characterize their fracture toughness by instrumented impact tests (Fig. 7).

No significant differences were found between the K_{IC} value of the unfilled homopolymer (K_{IC} = 2.36 MPa $m^{1/2}$) and those of the $Al(OH)_3$ filled samples (2.43 and 2.22 MPa $m^{1/2}$ for

A40OL and A40ON respectively). Nevertheless, the fracture energy of these composites (G_{IC} = 2.07 and 1.82 kJm^{-2} respectively) resulted clearly lower than of the unfilled polymer (G_{IC} = 2.40 kJm^{-2}) because of the higher stiffness of the filled samples.

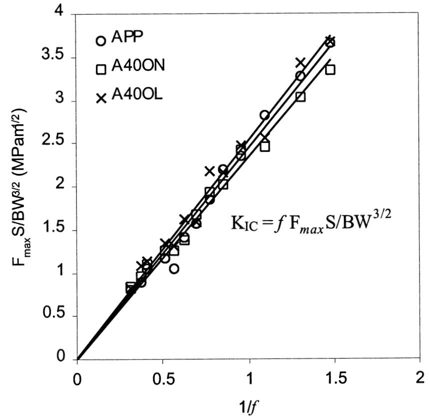

Fig. 7. Linearization of impact data to calculate K_{IC}.

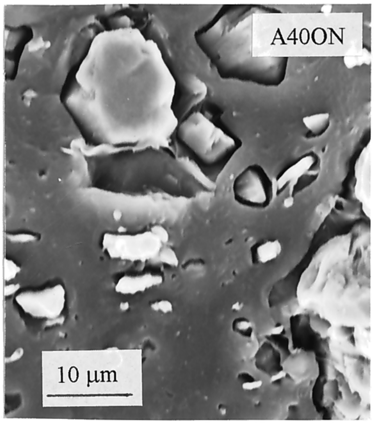

Fig. 8. Fracture surface at 1 m/s.

The slightly lower fracture toughness of the A40ON sample could be justified if we consider the $Al(OH)_3$ particles as inner defects in the matrix (Fig. 8); the bigger the particle mean size the more important the defects are, which act as a crack propagation starter.

Conclusions

Filling PP with flame retardant fillers, such $Mg(OH)_2$ and $Al(OH)_3$, resulted in improved stiffness and reduced yield strength and fracture toughness. The fracture resistance (J_{IC}) of $Mg(OH)_2$ filled block copolymer PP decreased when the filler concentration was raised. Also, the higher was the $Al(OH)_3$ mean particle size the lower the fracture energy (G_{IC}) of homopolymer PP-based composites. Other factors like the filler coating and the strain rate also influenced both tensile and fracture behaviour.

References

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