Filled PMMA: Mechanical Properties and Fracture Behaviour

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SUMMARY: The aim of this work is to study the influence of the filler fraction and that of the filler/matrix interfacial adhesion on the mechanical properties and on the fracture behaviour of a poly(methyl methacrylate) PMMA (for injection moulding). The variation of the tensile and flexural mechanical properties with the filler volume fraction was determined. The changes in the fracture behaviour produced by the fillers were studied by evaluating the K_{IC} and G_{IC} parameters of the LEFM (Linear Elastic Fracture Mechanics) by carrying out tests with SENB geometry at room temperature and low strain rates. After fracture surfaces examination by SEM (Scanning Electron Microscopy), it was found that the surface treatment had been rather effective and that the fracture toughening mechanism was multiple crazing.

Introduction

Many plastic materials in the market are filled with rigid particles, usually inorganic. They are added to the polymer in order to modify some properties of the matrix or to decrease costs if the price in volume of the filler is lower than that of the matrix. For these reasons, it is very important to know the influence of the volume fraction of mineral phase on the properties of the material in order to optimise the material regarding its properties and cost. It is already known[1] that the dispersion of filler particles has an influence on the tensile and flexural properties, and also on the crack propagation resistance. Particularly, fracture toughness increases when the filler volume fraction and the interfacial matrix-particle adhesion increase. In an earlier study[2,3] the system PMMA – glass beads (GB) was studied using a casting moulded PMMA. The

aim was to find a surface treatment of the glass beads, which gives a good interfacial adhesion grade. For that purpose, different coupling agents were tested, the best results being for the commercial DYNASYLAN MEMO. The main difficulty of this study was the lack of homogeneity in the obtention of moulded plates, since the glass beads have a tendency to decant during the polymerisation process of the mixture, once it is filled in the mould. In the present work, an injection grade PMMA and glass beads treated with the aforementioned coupling agent are used. Mixing was carried out in a twin-screw extruder, obtaining a good homogeneity in the material and solving the problem of the previous study.

Materials

The composite material of this study is made of two phases. The matrix is an injection grade poly(methyl methacrylate) PMMA, provided by ELF ATOCHEM, commercial trade OROGLAS VM. This PMMA has an average molecular weight of 89.200 g/mol and a T_g around 89°C. the second phase consists in glass beads provided by SOVITEC IBERICA S.A. In order to guarantee a good interfacial adhesion between the two phases of the mixture, the glass beads were submitted to a surface treatment with the coupling agent (γ-methacryloxy-propyl-trimethoxysilane) provided by HULS, commercial trade DYNASYLAN MEMO. The mixing process was carried out in a twin-screw extruder. The obtained pellets were dried 4 hours at 90°C before being injected in a mould (figure 4 of the norm ASTM D-647) at 50°C in order to obtain the normalised specimens. In order to study the influence of the fraction of mineral filler glass beads on the material properties, five different mixtures were made. Their volume and weight compositions are shown in Table 1.

Table 1. Volume and weight composition of the studied samples

Material	PMMA-0	PMMA-2.5	PMMA-10	PMMA-15	PMMA-25
GB volume (%) [a]	0	1.10	5.46	7.62	13.5
GB weight (%) [b]	0	2.20	10.5	14.3	24.1

[a] Calculated from components density
[b] Determined by cinders

Experimental methodology

All mechanical and fracture tests were carried out with the universal testing machine Adamel Lhomargy equipped with a 10kN load cell, at a crosshead rate of 1 mm/min and at room temperature (23°C). Three-point bending tests were carried out according to ASTM D-790 with normalised specimens (6.35 x 12.7 x 65 mm) and a span of 50.88 mm. Tensile tests were carried out according to ASTM D-638 (type I specimens). Fracture tests were carried out with SENB (Single Edge Notched Bend) geometry according to the testing protocol for plastic materials of the European Group of Fracture[4]. The specimens (same dimensions as for flexural tests) were notched at different depths (from 3 to 9 mm) with a CEAST motorised notching machine. The notches were measured with an optic device equipped with a micrometer and sharped with a razor blade before carrying out the tests in order to initiate the crack.

Results and discussion

Mechanical behaviour

It is shown in Table 2 that elastic modulus for both flexural and tensile tests, and therefore the material stiffness, increase with an increasing filler volume fraction as expected, as the glass beads are more rigid than the PMMA matrix.

Table 2. Flexural and tensile properties for different filler weight fractions: (V = 1mm/min)(Standard deviation is showed in parenthesis).

Flexural	PMMA-0	PMMA-2.5	PMMA-10	PMMA-15	PMMA-25
E_f (GPa)	2.5 (0.0)	2.6 (0.0)	2.7 (0.0)	2.8 (0.1)	3.0 (0.2)
σ_f (MPa)	90 (10.9)	70 (2.9)	76 (5.2)	76 (2.8)	79 (3.8)
Tensile					
E_t (GPa)	2.0 (0.1)	2.2 (0.2)	2.3 (0.2)	2.3 (0.1)	2.7 (0.1)
σ_t (MPa)	60 (0.7)	57 (0.7)	56 (0.9)	56 (0.9)	52 (1.6)

Regarding to the flexural and tensile strength, the values show that the addition of glass beads makes them decrease slightly until the reach a stabilisation value. The reasons for that can be attributed to the presence of some glass beads without a perfect interfacial adhesion and lead to a decrease of the specimen effective section (note that a non-adhered particle acts as a hole). In the case of the flexural strength it can be noted that the sample PMMA-2.5 (2.5 weight % filler fraction) shows a notable decrease, although this deviation is still in the experimental error range, it may probably related to the high sensitivity to surface defects that has the flexural specimen compared to the tensile one.

Fracture behaviour

In case of plane strain, with the sample geometry condition S=4W and 0.25W<B<W[5)], the critical stress intensity fracture K_{IC} is determined experimentally by the relation:

$K_{IC} = \dfrac{P_c}{B} \cdot \dfrac{1}{\sqrt{W}} \cdot Y\left(\dfrac{a}{W}\right)$ (Fig. 1a) where P_c is the maximal load at rupture, B is the sample

thickness, W is the width and Y(a/W) is an adimensional function depending on the notch depth. In these conditions, the critical energy release rate G_{IC} can be determined

using the relation: $G_{IC} = \dfrac{U}{B \cdot W \cdot \Phi\left(\dfrac{a}{W}\right)}$ (Fig. 1b) where U is the absorbed energy up to

rupture, ϕ is an adimensional function depending on the notch depth and B, W are the specimen cross-section dimensions.
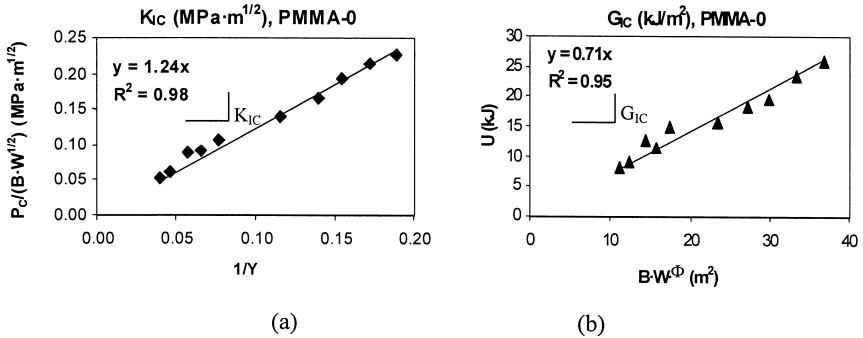

Fig. 1: Determination of the fracture parameters for the sample PMMA-0; (a) K_{IC} (MPa.m$^{1/2}$); (b) G_{IC} (kJ/m^2).

In Table 3, it can be noted that K_{IC} increases with an increasing filler volume fraction and seems to remains constant from 7 % (around 15% filler weight fraction) filler volume fraction on. This result shows that K_{IC} does not seen to follow a linear dependence with the filler volume fraction, as a small filler amount is enough to reach a maximal toughness. The same trend is observed for G_{IC}. It can be verified that experimental G_{IC} values are nearly the same, considering experimental error, than the calculated G_{IC} values, using the following relation between G_{IC} and K_{IC}:

$$G_{IC} = \frac{K_{IC}{}^2 \cdot \left(1 - v^2\right)}{E_t}$$ where v is the Poisson ratio, which in case of PMMA is 0.38, and

E_t is the tensile modulus. These results confirm that the experimental values are correct and the fracture test for this type of material is adequate.

Table 3. Fracture properties for different filler weight fractions (v = 1mm/min)

	PMMA-0	PMMA-2.5	PMMA-10	PMMA-15	PMMA-25
K_{IC} (MPa.m^{½})	1.24	1.26	1.32	1.63	1.65
G_{IC} (kJ/m^2) experim.	0.71	0.72	0.79	1.02	1.07
G_{IC} (kJ/m^2) calculated	0.66	0.62	0.65	0.98	0.87

Scanning microscopy

It may be noted in the SEM micrograph, shown in Fig. 2a, that the interfacial adhesion between the particles and the matrix has been rather effective. In Fig. 2b, it can be noted that the fracture toughening mechanism was multiple crazing, indicating brittle fracture (the fracture surface shows the typical *patch* or *mackerel patterns*), and that a low percentage of filler is enough to create a maximal crazing capacity of the matrix. These detached crazes zones tend to decrease in size in the crack direction since crazes tend to get thinner toward the craze tip[6].
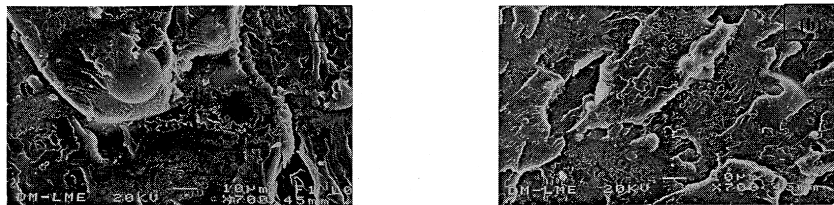
Fig. 2: SEM micrographs of the fracture surface of a PMMA; (a) PMMA-2.5 (2.5 % filler weight fraction): good interfacial adhesion between matrix and a filler particle; (b) PMMA-10 (10 % filler weight fraction): typical *patch* or *mackerel patterns* on the fracture surface.

Conclusions

Elastic modulus for both flexural and tensile tests increase by 20 and 35% respectively with a 13.5% filler volume fraction. Flexural and tensile strength decrease by 12 and 13.5% respectively with an increasing filler volume fraction. The values of flexural strength are nearly double higher than values of tensile strength. The fracture parameters K_{IC} and G_{IC} increase by 33 and 50% respectively with the addition of filler and remain nearly constant from 7 % filler volume fraction, indicating that around this value the maximal plastic deformation capacity of the matrix is reached. Adhesion between particle and matrix has been rather effective with this surface treatment. Toughness fracture increase can be attributed to multiple crazing mechanism.

References

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