

The J -integral fracture toughness of PP/CaCO₃ composites

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The J -integral method was introduced to investigate the fracture process of PP/CaCO₃ composites. The results showed that the resistance of PP/CaCO₃ composites to crack initiation and propagation was greatly improved with the addition of CaCO₃ filler. Large scale plasticity was caused in PP/CaCO₃ composites, from which a large amount of energy was absorbed by the PP matrix. The reason for the increase in the fracture toughness of PP/CaCO₃ composites was attributed to the partial micro-drawing ahead of the crack tip in the PP matrix, which was formed by the stress concentration caused by the filler particles in the PP matrix and/or by the interfacial debonding between filler particles and the PP matrix. It was indicated that the presence of CaCO₃ filler could augment the ductility of composites locally, resulting in higher fracture energy in the crack initiation and propagation of the PP/CaCO₃ composites in a certain CaCO₃ content range.

1. Introduction

Rigid inorganic fillers (RIF) have been widely used to improve the physical properties of polymers in commercial production for special applications. Recently, RIF toughened plastics became an attractive subject in the polymer materials field. But, up to now, the role of filler in composites and its effect on the fracture toughness of composites has remained unclear. As the toughness of materials sets limits both to the design and safety of engineering components and structures, the criterion for fracture toughness of polymer materials has been extensively investigated from practical and scientific viewpoints. One of the most practically useful criteria for brittle or quasi-brittle fracture of polymers is based on the linear elastic fracture mechanics (LEFM) of materials.

Fracture mechanical characterization of polymer materials was mainly manipulated with the methods and theories developed in metal fields. Recent studies showed that LEFM were applied successfully to the fracture characterization of brittle polymers, such as PS, PMMA, etc. [1]. However, in practical cases, there are many polymers in which the considerable amount of energy put into the material is dissipated to create the large plastic deformation ahead of the crack tip. This problem is often encountered in the testing of toughened polymers, such as HIPS, ethylene-propylene block copolymers (PPB), PP and PE at the temperature above their glass transition (T_g). In these circumstances, the LEFM theory envisages the dimension of the specimens and the crack to be much larger than the size of the plastic zone around the crack tip for valid evaluation of the fracture toughness para-

eters. However, the injecting moulded products are relatively small compared to the size required, invalidating the use of LEFM.

In the case of large scale plasticity, post-yield fracture mechanics, such as the J -integral method, must be used for a quantitative characterization in fracture toughness of polymers. J -integral was firstly proposed by Rice [2] in studying the elastic-plastic materials of the metal fields as an energy input parameter which can be used as a criterion for crack initiation in the fracture of such materials.

There has been little effort to apply the J -integral to polymer materials, except for the few limited attempts of Hashimi and Williams [3] and Narisawa [4] in ductile materials and Vn-Khanh *et al.* [5] in PP/Mica composites, in which satisfactory results have been obtained. In this study, the J -integral method has been used to examine and characterize the fracture process of PP/CaCO₃ composites, the fracture parameters in the elastic-plastic regime are also discussed.

2. Experimental procedure

2.1. Materials

The polypropylene matrix in PP/CaCO₃ composites was homopolymer powder PP 2402 (Yanshan Petrochemical Ltd) with a melt index of 3 g/10 min and a density of 0.91 g cm⁻³. The filler was light CaCO₃ with a diameter of 1–5 μm and a density of 2.65 g cm⁻³. The filler was pre-treated with a coupling agent (OCL 999). As a standard, untreated CaCO₃ filler was used to investigate the effect of the coupling

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agent and its content on the fracture process of PP/CaCO₃ composites.

2.2. Sample preparation

PP/CaCO₃ composites with different filler contents (10, 20, 30 and 40 wt % of CaCO₃ filler) were prepared by melt-mixing. The CaCO₃ filler was firstly dried to 100°C in a dry atmosphere for 12 h, then mixed with powder PP. The pre-mixed products were extruded in SHJ-30 twin-screw extruder. The standard specimen bars for tensile tests were obtained by mould injection according to the ASTM standards.

2.3. Mechanical properties

All tensile tests were performed in the standard testing machine of Instron Model 1122 according to the ASTM standards. The tensile modulus was measured with a cross-head speed of 1 mm min⁻¹ and tensile strength with two different rates of 1 mm min⁻¹ and 50 mm min⁻¹. The strain was measured with the strain gauge extensometer Instron Model 2630-019.

2.4. *J*-Integral measurement

The three-point-bend specimens with a crack ca. 5 mm long were used in the *J*-integral measurement. The specimen size was 15(W) × 10(B) × 60(L). The crack was first made with a band saw to a certain depth and the final 1.5–2.0 mm was done by forcing a razor blade into the specimen. The notch made by the razor blade had a radius of < 50 μm.

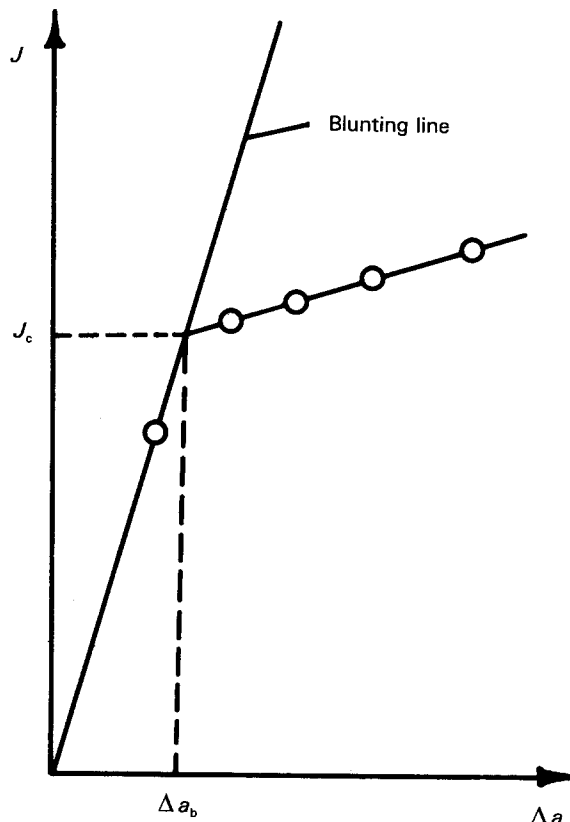


Figure 1 Determination of *J*_c using the *J*-integral method.

An approximate equation for the calculation of *J* in deeply notched, bend type specimens has been introduced by Rice [2], namely:

$$J = 2U/B(D - a) \quad (1)$$

where *U* is the measured area under the load versus load point deflection curve, *a* is the crack length and *B* and *D* are the width and height of the specimen bar, respectively.

This method consists of loading several identical specimens to different values of load point deflection and then unloading. After unloading, the crack advance is marked by a penetrant ink and the specimen was broken open by impact at room temperature. The value of *J* can be determined from Equation 1 for each specimen. The crack growth resistance curve (*R* curve) was obtained by plotting *J* versus Δ*a* (crack growth), from which the fracture toughness at crack initiation (*J*_c) was determined at the intersection of the blunting line which represents the blunting behaviour of the crack tip before real crack propagation with the straight line, as illustrated in Fig. 1. The blunting line was given by the following equation:

$$J = 2\sigma_y\Delta a \quad (2)$$

where Δ*a* is the crack growth length and σ_y is the yield stress of the polymer materials.

3. Results and discussion

3.1. Mechanical properties of PP/CaCO₃ composites

The relationships of the mechanical properties (Young's modulus, yield strength and elongation at break) of PP/CaCO₃ composites with different CaCO₃ contents are shown in Figs 2 and 3.

Similar to the typical filler-reinforced materials, with the addition of the CaCO₃ filler, both the yield strength and the elongation at break of the composites

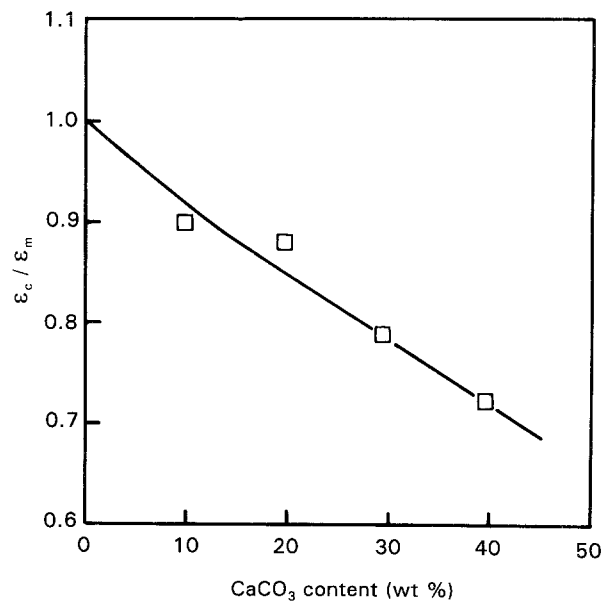


Figure 2 Effect of CaCO₃ content on the relative elongation at break (ε_c/ε_m) of the PP/CaCO₃ composites (ε_c and ε_m are the elongation at break of the composite and the matrix, respectively).

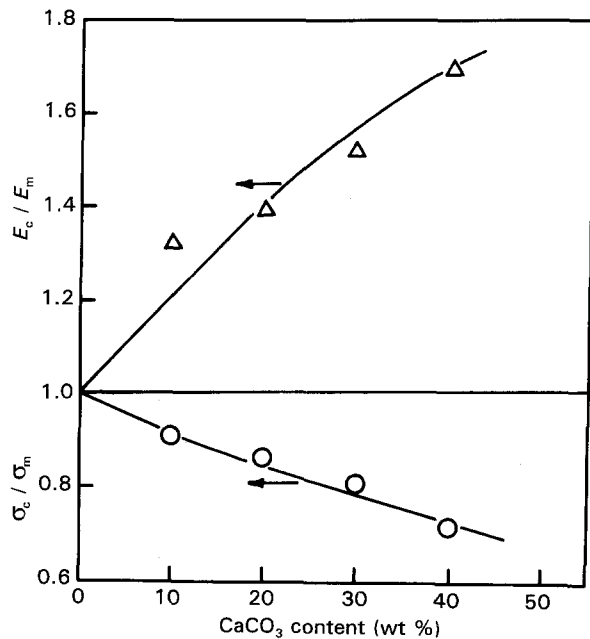


Figure 3 Effect of the CaCO₃ content on the relative Young's modulus and yield strength (E_c/E_m and σ_c/σ_m) of the PP/CaCO₃ composites (E_c and E_m , σ_c and σ_m are Young's modulus and yield strength of the composites and the matrix, respectively).

decreased, but the tensile modulus of the composites increased, which showed that the presence of the CaCO₃ filler lowered the fracture energy of the composites.

3.2. J-Integral measurement

3.2.1. Crack initiation

Contrary to the tensile properties, the stress-strain curve of the three-point-bend specimen bar with a prepared sharp notch showed a surprising result. Virgin PP exhibited purely brittle behaviour. Fracture occurred at a small deflection with a smooth fracture surface and only a small stress whitening zone existed. However, all the PP/CaCO₃ composites showed similar ductile behaviour. With an increase in CaCO₃ filler content the composites became more and more ductile. Both the amount of plastic deformation and stable crack growth increased. The plastic deformation accompanied by stable crack growth can be represented by the non-linear region of the load versus deflection curve. Since the area under these curves increased, so the energy absorbed by the specimen to fracture increased with the increase of CaCO₃ content for all the specimens tested having the same crack length and dimensions.

Figs 4-6 show plots of the relationships of J_c of the composites versus Δa (the length of stable crack growth), CaCO₃ content and the coupling agent content (with constant CaCO₃ content: 40 wt %), respectively.

The results in Fig. 5 show that J_c of the composites increased up to 20 wt % CaCO₃ content and reached a maximum at 20 wt % CaCO₃. Above 20 wt % the stable fracture in the composites still occurred, but J_c decreased with further increase in CaCO₃ content, which indicated the decrease of the energy absorption

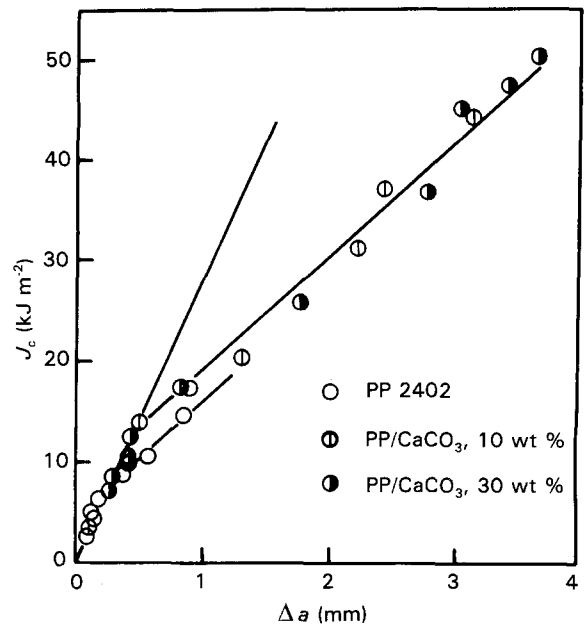


Figure 4 Experimental resistance curves of the PP and PP/CaCO₃ composites.

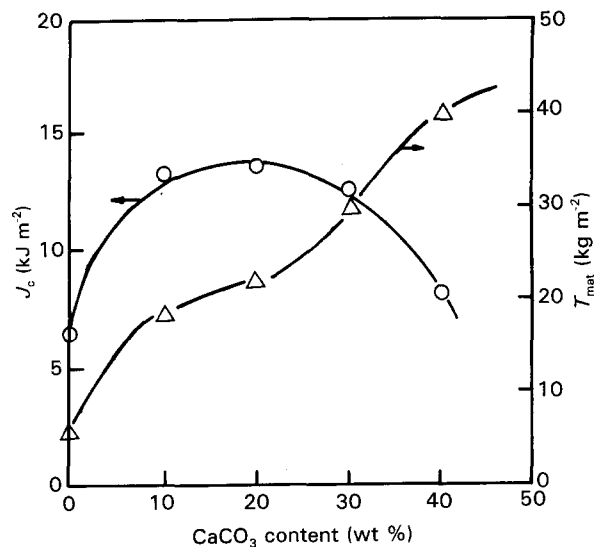


Figure 5 Effect of the CaCO₃ content on the J_c and T_{mat} of the PP/CaCO₃ composites.

of the specimen. But, at an even higher (40 wt %) CaCO₃ content, J_c of the PP/CaCO₃ composite was still higher than that of virgin PP. These results show that the crack growth resistance of PP/CaCO₃ composites at the initial stage increased with the addition of CaCO₃ filler. It was attributed to the changes in the behaviour of energy absorption for PP matrix in the presence of CaCO₃ filler, since there was almost no energy absorption for the RIF in the deformation process of the composites. So, CaCO₃ filler in composites has a promoting effect on the energy absorption of the PP matrix.

The results in Fig. 6 show that the effect of the coupling agent content on J_c of the PP/CaCO₃ composite is not significant. J_c did not change with different coupling agent content from 0.5 wt % to 3 wt %, although J_c of the PP/CaCO₃ composites in which the filler was treated with coupling agent were slightly

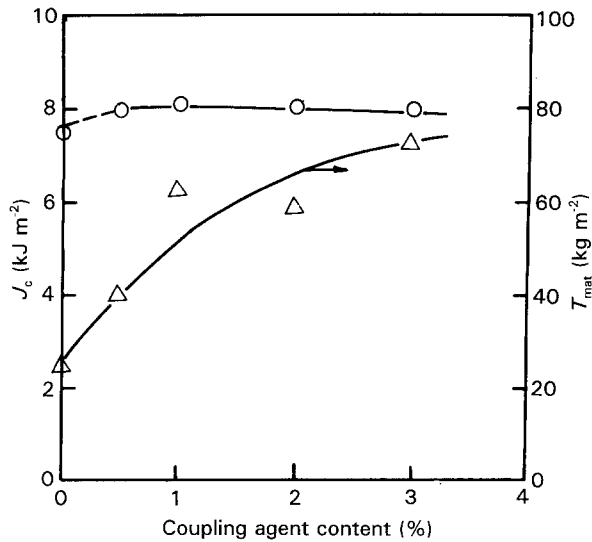


Figure 6 Effect of the coupling agent content on the J_c and T_{mat} of the PP/CaCO₃ composites (CaCO₃ content 40 wt %).

higher than that for untreated CaCO₃ filler. The results of modulus-strain gauge and axial tensile volume strain measurement indicated that the coupling agent had little effect on the interfacial adhesion of the composites but played only the role of promoting the uniform dispersion of CaCO₃ fillers in the composites.

3.2.2. Crack growth (propagation)

J_c (critical initial J value) was used to characterize the energy absorption of polymer materials at the initial stage of crack and the resistance for crack initiation. In addition, the J curve of J versus Δa can also be used to characterize the resistance of polymer materials for crack propagation, in which the resistance of materials to stable crack growth was expressed by $dJ/d\Delta a$, proposed by Paris *et al.* [6]. A material parameter named tearing modulus (T_{mat}) was defined as:

$$T_{mat} = (dJ/d\Delta a)E/\sigma_y^2 \quad (3)$$

where E is Young's modulus and σ_y is the yield stress of the polymer materials. T_{mat} can be obtained from the slope of the J resistance curve of the polymer materials.

The relationships of T_{mat} for PP/CaCO₃ composites with CaCO₃ filler and coupling agent content were also plotted in Figs 5 and 6.

The results show that T_{mat} increased consistently with the increase of both filler and the coupling agent content, which indicated that the fracture mode of the PP matrix changed with the addition of the filler. A more pronounced effect of plasticity occurred in PP matrix of composites, resulting in higher energy absorption in crack initiation and propagation process of the composites. T_{mat} increased with the increase of the coupling agent content, which indicated that the crack propagation process of the materials is closely associated with the interfacial layers of the PP matrix with the CaCO₃ filler. The coupling agent had the effect of reinforcing plasticity on the PP matrix.

3.3. Stress analysis

Above partial micro-drawing of PP/CaCO₃ composites was attributed to the change of the stress field and the stress concentration around the filler particles in PP matrix with the addition of the CaCO₃ filler. If the CaCO₃ filler was simplified as a spherical filler, the stress concentration zone caused by a filler can be described as shown in Fig. 7.

At the initial stage of the tensile deformation (before interfacial debonding), the stresses of the PP matrix to filler were tensile stress at two polars and the compressed stress at equator of the filler particles. In addition, there was a stress of filler to the PP matrix due to the stress interaction.

Based on the Von Mises yield criterion:

$$(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 = 6K^2 \quad (4)$$

where σ_x , σ_y and σ_z are the three axial stresses, respectively, and K is the material parameter.

It was especially beneficial for matrix yielding if tensile and compressed stress coexisted among the triaxial stresses in the stress fields of the matrix. So, with the addition of the CaCO₃ filler, the yielding of the PP matrix in PP/CaCO₃ composites can easily occur.

If the interfacial adhesion of the filler with the PP matrix is weak, interfacial debonding will occur first at the two polars of the filler, then propagate on the filler surface, forming a flaw around the filler after interfacial debonding. It is known from the stress analysis of a flaw [7] that there was a tensile stress at the equator of the flaw and its magnitude was three times that of the partial bulk stress of the PP matrix. So, the partial yielding of the PP matrix had been caused before the bulk stress was equal to the matrix yield stress, which also indicated that the flaws played the promoting roles in the yielding of the PP matrix.

The above results are qualitatively described in Fig. 8, namely, from interfacial debonding of the fill particles with the PP matrix, partial micro-drawing of

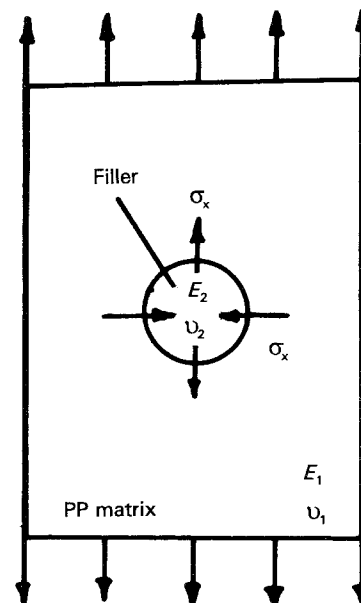


Figure 7 Schematic of the stress concentration caused by a filler in PP matrix ($E_2 > E_1$, $\nu_2 > \nu_1$).

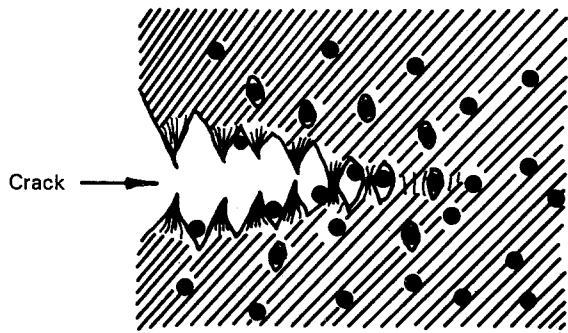


Figure 8 Schematic of the fracture process of the PP/CaCO₃ composites.

the PP matrix to the large plastic deformation in PP matrix, then to ultimate failure of the composites.

It can be concluded that the addition of the CaCO₃ filler to the PP matrix can augment crack initiation and propagation resistances of the PP matrix in both the static and impact test. This type of behaviour is attributed to the micro-ductility of the PP matrix ahead of the crack tip caused by the CaCO₃ filler particles. The *J*-integral results in fracture mechanics show that the fracture toughness of the PP/CaCO₃ composites can be greatly improved at the moderate CaCO₃ content range.

4. Conclusions

1. *J*-integral was a more effective method for characterizing the fracture process of PP/CaCO₃ composites than general tensile tests in which the fracture energy of the composites decreased with the addition of CaCO₃ fillers. It was confirmed that with the addition of the CaCO₃ fillers, the fracture mode of

the PP matrix in the PP/CaCO₃ composites with *J*-integral measurement changed from the brittle fracture for virgin PP to the ductile fracture for the composites, which was attributed to the changes of stress fields in the PP matrix around the filler particles. In addition, interfacial debonding also played a promoting role in the yielding of the PP matrix.

2. The crack initiation and propagation resistances of the PP matrix were increased with the addition of CaCO₃ fillers in both the static and impact tests, which was attributed to the micro-ductility of the PP matrix ahead of the crack tip, caused by the filler particles and flaws from the interfacial debonding. The fracture toughness of the PP/CaCO₃ composites can be greatly improved over a certain CaCO₃ content range.

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