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An Investigation into the Fracture Behaviour of Ethylene Propylene Impact Copolymers

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SUMMARY: Injection moulded copolymer specimens containing between 6 to 11 % ethylene were impacted using the drop weight method at 23 °C and – 20 °C. Their response to the impact event was analysed in terms of failure mechanisms by considering their initiation and propagation energies at the respective temperatures. At –20 °C, the results indicated that the multiple shear yielding toughening mechanism is predominant whereas room temperature tests show evidence of multiple crazing behaviour. The peak force sustained by the specimens decreased with the testing temperature.

Introduction

Isotactic polypropylene (i-PP) is a versatile semi-crystalline polymer exhibiting good mechanical properties and an advantageous price-performance ratio. It is also well known due to its ease of processing in various manufacturing methods. However, the PP homopolymer is known to exhibit low impact strength at temperatures below room temperature. Thus the use of polypropylene in engineering structural applications is severely limited. The low impact strength of PP can be attributed to its high glass transition temperature (T_g) of approximately 0 °C.

An improvement in the impact property of isotactic PP can be achieved through modification of the i-PP by incorporating a secondary rubbery phase into its microstructure. This is known as rubber toughening and is done either by copolymerization or blending of two polymer phases together. The copolymerization process changes the polymer structure and morphology, and as a consequence its properties. Ethylene propylene rubber (EPR) is commonly used as the secondary phase in polypropylene systems. The inclusion of ductile rubber particles within the homopolymer matrix lowers the ductile-to-brittle transition temperature of the impact copolymer. However, an improvement in impact strength due to copolymerization is accompanied by a noticeable reduction in the modulus and scratch resistance. The dispersed rubber particles (secondary phase) in the matrix act as stress concentrators and

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thereby initiate mechanisms consuming energy over a large volume. The main dissipation mechanisms have been identified as multiple crazing and shear yielding in the homopolymer matrix, as well as the cavitation or void formation of the rubber particles.[1-3]

Toughening Mechanisms

The multiple crazing mechanism is based on the formation of crazes in the copolymer at a critical stress level. Crazes are defined as regions of localised yielding that consist of microvoids in a plane perpendicular to the maximum principle stress, that are stabilised by fibrillar bridges of plastically deformed and oriented polymeric material. The crazes are observed as a stress whitening effect around the point at which load is applied onto the copolymeric specimen. By acting as stress-raisers, the EPR particles control craze growth and initiate numerous, small energy absorbing crazes. Termination of the initiated crazes for growth control purposes is also achieved by the dispersed secondary phase particles, by the process of arresting the crazes. Thus, the presence of rubber particles as well as the particle size is crucial in the multiple crazing theory. A particle size of about 0.4μm was found to produce optimum results for the PP system.[4]

The shear yielding process interacts with the multiple crazing mechanism to reduce the crack size, thereby increasing the impact strength of the copolymer. Local yielding during deformation induces the formation of shear bands. A minimum amount of stress whitening is observed in this toughening mechanism. The shear bands formed act as barriers placed in the growth directions of the crazes, thereby providing another means of limiting craze size. A reduction of the hydrostatic stress required for craze growth is also observed when shear bands originate at the craze tip, thus preventing craze growth.[4]

The third energy dissipation mechanism, cavitation, occurs within the EPR particle, as opposed to the matrix. Triaxial stresses develop in the rubber particles due to the effect of the stress concentration, provided that adequate adhesion between the two phases exists. This leads to the dilation and elongation of the matrix. Localised plastic deformation occurs within the ethylene propylene rubbery shell and weak shear bands are formed. Thus a higher hydrostatic stress builds up inside the particles. This then leads to void formation through cavitation inside the plastically deformed EPR particles, to relieve the volume strain imposed on the material. These voids continue to grow in size with increasing strain. Debonding of the secondary particles and the matrix may also occur. Following void formation, extensive shear yielding occurs in the matrix as a result of the increase in the shear stress component.[5]

Materials and Experimental Procedure

Injection moulded copolymeric specimens were used in the impact tests. The ethylene content in the specimens ranged between 6 and 11 %. Sasol Polymers Pty (Ltd) supplied two different series of impact copolymers. The "A" series specimens were injection moulded at a melt temperature of 200 °C, using a mold temperature of 30 °C. The "B" series samples were produced by increasing the melt temperature to 230 °C, whilst keeping the mould temperature at 30 °C.

An instrumented drop weight impact tester was used to impact the specimens and observe the response of the specimen during the impact event. The response of the specimen was recorded on a computer by means of a plot of load and energy as a function of the deflection of the specimen. The weight of the impactor used in the tests was 1.152 kg. Tests were done at room temperature and at –20 °C using liquid nitrogen as a coolant. The impacted square specimens had dimensions of 100 mm X 100 mm and a thickness of 3 mm.

The copolymeric specimens were dipped into liquid nitrogen for 15 minutes and fractured. The fractured piece was then heated to 70 °C in a solution of heptane for 30 minutes thus allowing for etching of the rubber particles. Following the etching procedure, the specimens were placed in an ultrasonic bath of methanol. A SEM Coating Unit was used to sputter-coat the mounted specimens before a detailed examination of the surface was carried out by SEM. An accelerating voltage of 10 – 15 kV was used to minimise damage to the polymer specimens. The Joyce Loebl Image Analysis Software package was used to determine the size of the etched rubber particles.

Results and Discussion

Interpretation of specimen impact response graphs

From the instrumented drop weight impact tester, graphs of load and energy as a function of deflection were obtained. Typical graphs of a 6 % ethylene content copolymer tested at a tup height of 2 m are shown below in Figures 1 and 2. These are overlays showing the reproducibility of the impact rig using the same specimen type. The tup reaches an impact velocity of 5.4 m·s^{-1}.

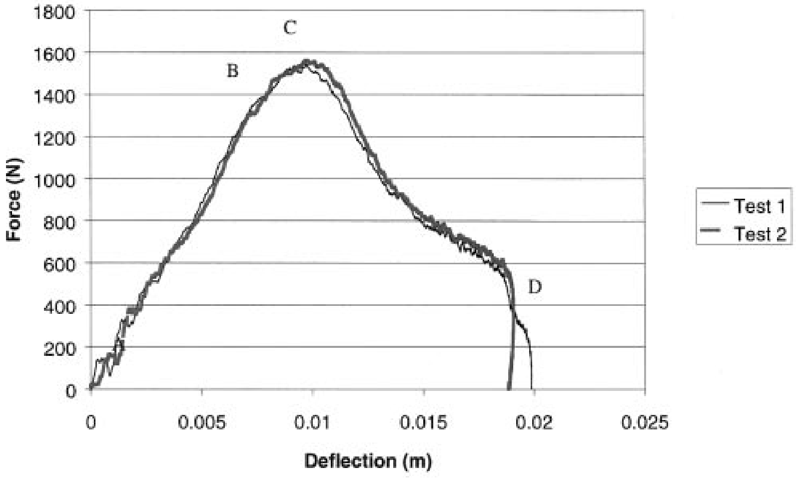

Fig. 1. Graph showing the plot of force versus deflection with the characteristic points in an impact event.

Section A of Figure 1 is known as the dynamic offset and is caused by the loading response being disturbed by the harmonic oscillations generated during the initial collision between the tup and the specimen plate. This section of the graph is insignificant and provides no useful information in terms of response of the specimen to the load exerted onto it by the impacting tup. Point A represents the start of linear load deflection deformation behaviour. This behaviour is characterised by the specimen reacting as an elastically loaded structure.

Point B is the yield point of the specimen and is detected by the deviation of the slope from the elastic linear deflection behaviour. The specimen begins to undergo plastic deformation upon the application of the corresponding load. The first major deformation in the specimen occurs at point C, which is the maximum load the specimen can withstand. This stage is associated with the appearance of deformation characteristics such as cracks, or through penetration on the specimen. It represents the peak load that the specimen can tolerate, under an impact event, before undergoing catastrophic structural damage. The peak load coincides with the initiation of a tear in the centre of the specimen at the point of contact between the hemispherical tup. This stage is usually followed by an obvious reduction in the rigidity of the specimen. The gradual drop in load after the completion of stage C is suggestive of that.

Point D is indicative of the end of the impact test. This is the failure point at which the specimen loses its structural integrity, fails completely and cannot therefore sustain any more load. At this point, the impact event has ended. The rest of the data is representative of the frictional forces present between the hemispherical tup and specimen as the tup continues to pass through the puncture created in the specimen.

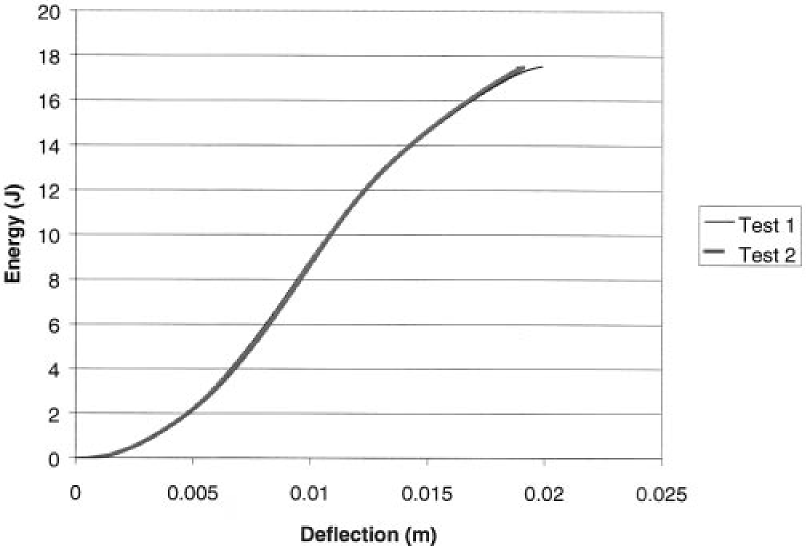

Fig. 2. Graph of the energy absorbed by 6 % ethylene propylene rubber copolymer at a velocity of 5.4m s^{-1}.

At the velocity employed in this impact test, the specimen failed by means of penetration of the tup through the specimen thickness. Through penetration is defined as the entrance of the impactor into the specimen followed by a complete passage through the specimen body. Figure 2 shows the energy response of the same specimen used to obtain the loading response shown in Figure 1. The impact energy of the tup was sufficient to induce a puncture failure of the specimen. Therefore no reduction in the deflection of the specimen is noticed. This indicates that at the point when the impact test terminated, no residual elastic energy was present in the specimen. Thus the energy indicated by the graph at the end of the test is the total energy absorbed by the copolymeric specimen in the process of plastic deformation.

Effect of ethylene content on impact strength

A number of drop weight impact tests were performed on the "A" series specimens. The tests were done at room temperature and at a height of 2 m to ensure complete penetration of the specimens, even at high percentages of ethylene content. Figure 3 represents the peak load sustained by the various specimens during the impact event.

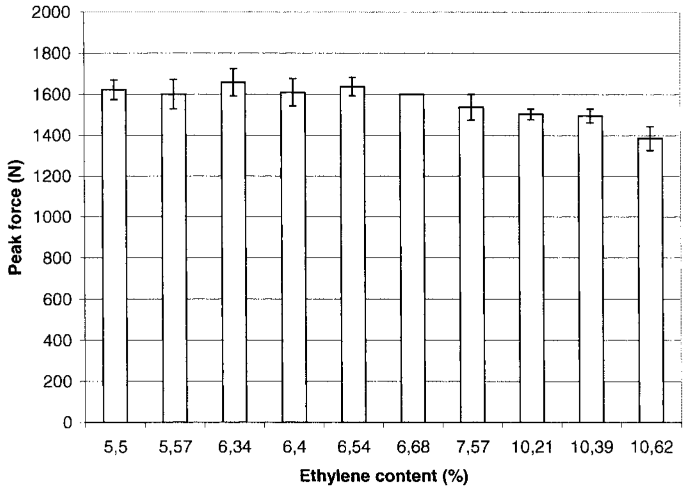

Fig. 3. Plot of peak impact force of the "A" series specimens as a function of their ethylene content.

The bar chart above shows a slight decrease in the peak force experienced by the specimens with increasing percentages of ethylene content. However, the 5.5 – 6.68 % range do not show any variation in the results obtained. This could be attributed to the different processing methods and conditions employed in the manufacture of the copolymers, since the raw materials were not obtained from the same source but from various companies. Ideally, however, the ultimate force or strength of the copolymers should decrease with increasing ethylene content. This is due to the associated increase in the ductility of the copolymers as more ethylene propylene rubber is added into the microstructure, since the rubber particles impart toughness to the copolymer through the contribution of the amorphous phase regions present within the EPR particles. This would also explain the drop in the stiffness or Young's modulus experienced by the specimens.

Effect of processing conditions on impact behaviour

The "B" series specimens were also impacted to determine the effect of increasing the melt temperature of the copolymers during the manufacturing stage. Figures 4 and 5 show a comparison of the results obtained from the impact tests in the form of a bar chart. The light and dark bars are representative of the "A" and "B" series respectively.

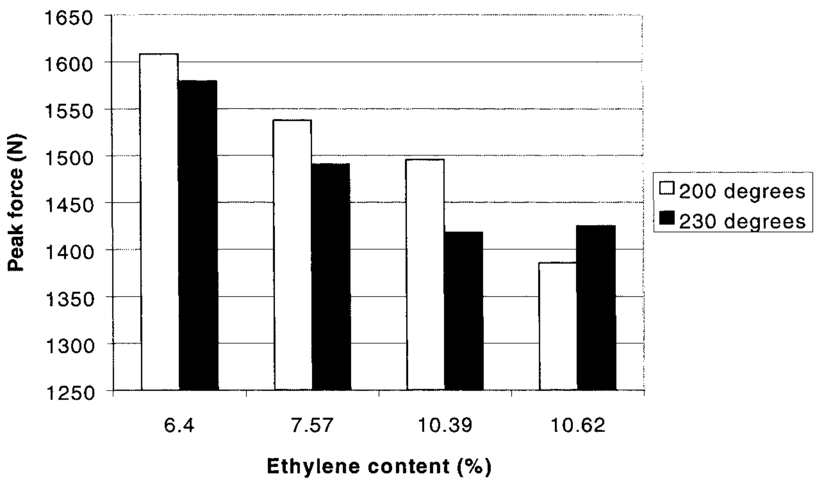

Fig. 4. Bar chart showing the difference in peak force experienced by the "A" and "B" specimens, with increasing percentages of ethylene content.

Evidently, there is a decrease in the peak force of the 230 °C melt temperature specimens. A decrease of approximately 2 – 5 % is observed in the "B" specimens when compared to the "A" series of specimens. The 10.62 % ethylene content samples show an increase in the peak force at 230 °C, instead of a consistent decrease. However, examination of the energy absorption graphs in Figure 5 shows that all the tested specimens, including the 10.62 % ethylene, follow the trend of absorbing a decreased amount of energy during the impact deformation with an increased melting temperature.

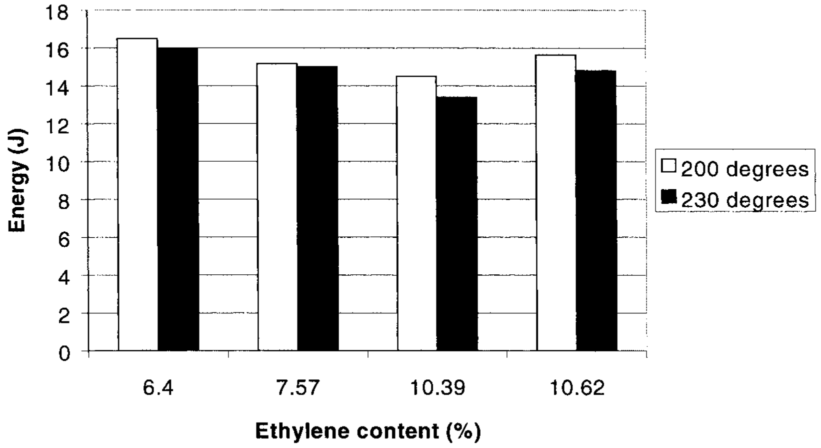

Fig. 5. Plot representing the impact energy absorbed by the "A" and "B" specimens tested.

All the specimens in Figure 5 shows a decrease in the energy absorbed by the specimen during the impact event between the tup and the specimen in the drop weight test. The decrease is however not very pronounced; it is about 6 %.

A plausible justification for the observed decrease in the impact energy of the "B" specimens could be due to a slightly higher degree of crystallinity being achieved in the "B" specimens as the melt temperature is increased. The higher degree of crystallinity could possibly be due to changes that occur in the crystal structure of the specimen thus influencing stiffness and energy absorption. But these factors need to be further investigated by examination of the impacted specimens.

Further, also since a higher degree of crystallinity is achieved in the "B" samples they are more brittle than samples in the "A" series. Due to their comparatively brittle nature the "B" series specimens are unable to plastically deform to the extent of the "A" series, thus limiting their impact energy absorption. However, their limitation with regard to plastic deformation also needs to be investigated.

Effect of test temperature on impact energy

The "B" series specimens were also tested at a cryogenic temperature of –20 °C. Figure 6 shows a plot of the peak force of the specimens; the light coloured bars represent a room temperature test at 23 °C and the dark bars a test at –20 °C.

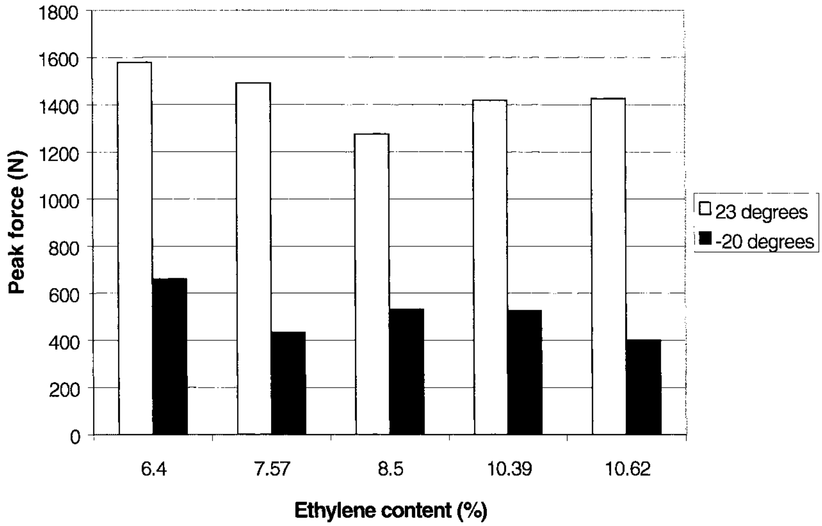

Fig. 6. Graph showing the decrease in peak force of specimens during impact as the test temperature is decreased.

As expected, the peak force decreases quite significantly as the testing temperature is decreased to –20 °C. This trend is observed over the entire ethylene content tested. An average drop of 60 % is observed in this series of tests. This behaviour is also witnessed in the impact energy graphs in Figure 7.

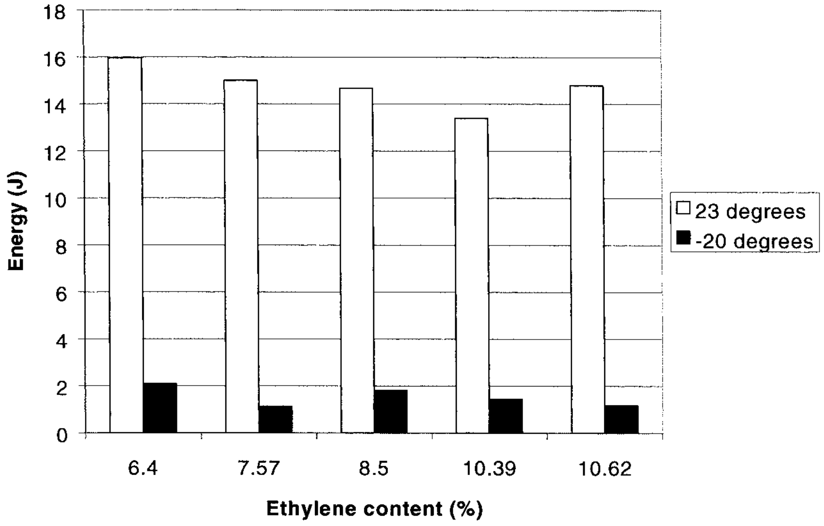

Fig. 7. Graph of the changes in impact energy absorption as the test temperature is decreased to –20 °C.

Together with the decrease in peak force, a substantial drop of about 80 % in the impact energy of the specimens occurs when the test temperature is dropped to –20 °C. The decrease in peak force in the samples can be explained by the occurrence of a transition in the specimens, from a ductile to brittle phase, due to the cryogenic test temperature (-20 °C) employed. This embrittlement is also responsible for the dramatic drop in the impact energy, since the specimens can no longer absorb energy due to a reduced ability for plastic deformation in the specimens. In addition, the stress whitening effect is absent in the low temperature tests which indicates that multiple crazing does not take place, thus providing further rationalisation for the decrease in the impact energy of the specimens.

Energy distribution in specimens

The "B" specimens tested at 23 °C and –20 °C were also investigated in terms of the energy distribution that occurs during the impact event. The pre-maximum load energy is known as the crack initiation energy (lightly coloured section) and initiates the formation of cracks in the specimen. The post-maximum load energy is responsible for crack propagation and is thus known as crack propagation (dark section). Figures 8 and 9 show a comparison between the distribution of energy in the specimen at two different temperatures. Clearly, there is a difference in the manner of energy absorption of the specimens associated with a temperature change. The results from the 23 °C test temperature specimens show that crack propagation energy utilizes between 45 to 55 % of the total energy absorbed by the specimen during the impact event. Comparatively, Figure 9, the sub-zero specimens show that an average of only 20 % of the total impact energy can be attributed to the crack propagation energy, whilst 80% is utilised in crack initiation.

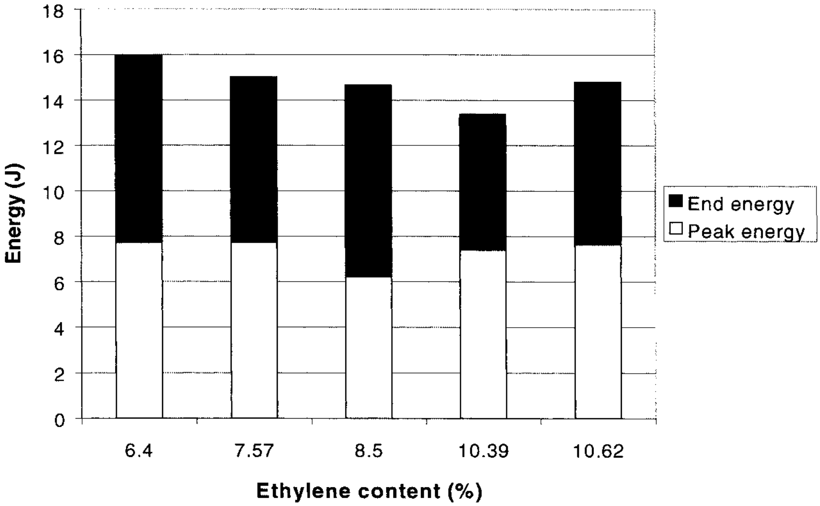

Fig. 8. Energy distribution of the "B" series copolymeric specimens at room temperature (23 °C).

This is a characteristic requirement for the occurrence of the multiple shear yielding toughening mechanism. This would account for the absence of the stress-whitening zone due to crazing at the impact point between the tup and the specimen. The absence of the crazing mechanism lowers the ability of the material to absorb energy thus contributing to the effect of decreased energy absorption seen in Figure 7.

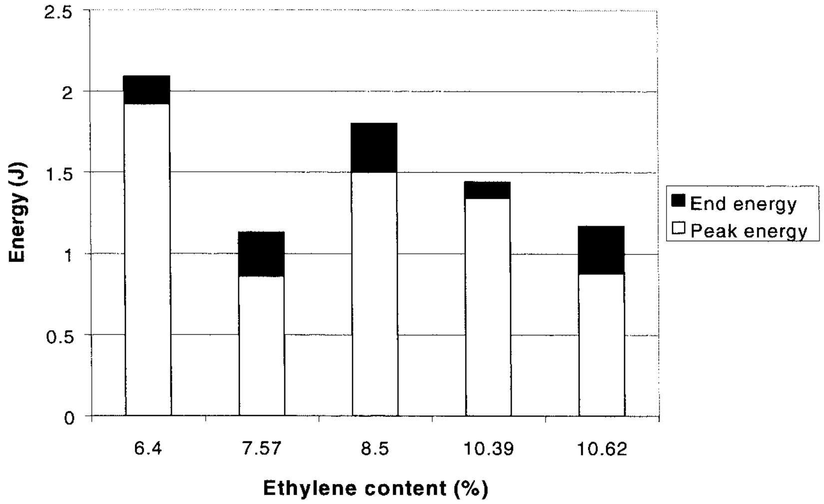

Fig. 9. Energy distribution of the “B” specimens at test temperature of –20 °C.

Ethylene propylene rubber (EPR) particle analysis

The etching procedure was followed to obtain the structure shown in the micrograph in Figure 10 below. Table 1 represents the particle size results obtained from the image analysis software for the “A” series specimens.

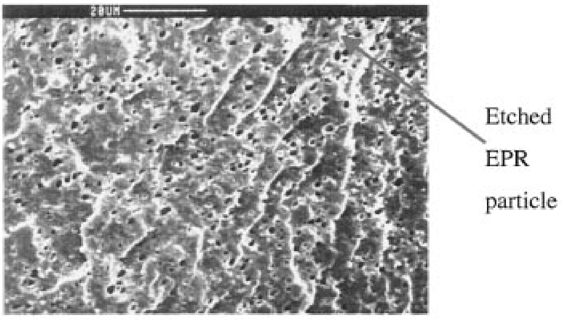

Fig. 10. Micrograph of the 6.4 % (ethylene content in copolymer) specimen showing etched pores in the copolymeric microstructure.

The pores present in the microstructure suggest that the etching technique used to etch away the rubber particles was successful and provide evidence to the existence of the secondary dispersed phase within the polypropylene matrix.

Table 1. Results of the secondary phase analysis done on the "A" batch of specimens.

Specimen	Ethylene content (%)	Particle size (μm)	Interparticle distance (μm)
A2	5.5	0.26	0.35
A1	5.57	0.39	0.49
A4	6.34	0.33	0.36
A3	6.4	0.36	0.49
A6	6.54	0.41	0.71
A5	6.68	0.34	0.62
A13	7.57	0.32	0.41
A9	10.21	0.20	0.19
A11	10.39	0.54	0.56
A12	10.62	0.28	0.33
	Average value	0.34	0.45
	Standard deviation	0.09	0.15

The interparticle distance was calculated from the obtained particle size and volume fracture during the image analysis. The following equation, known as Wu's equation, was used to calculate the interparticle distance present between the dispersed rubber phase.

$$\text{Interparticle Distance} = d^{*}\, k\left\{\left(\frac{\Pi}{6(V_r)}\right)^{\frac{1}{3}} - 1\right\}$$

where d → Particle size diameter

and k → Geometric constant

and V_r → Particle volume fraction

k is factor dependent on the lattice type. A cubic lattice has a k value of 1 whereas a body centred lattice has a value of ($\sqrt{3}/2$).

The large interparticle distance counteracts the effect of toughening due to a larger {interparticle distance/particle size diameter} ratio. This could be a result of agglomeration or coalescing of the EPR particles, which also increases the particle size.

Increasing either the matrix viscosity or the shear rate applied to the matrix can reduce the EPR particle size while keeping the capillary number (Ca) constant. This is seen from the capillary number equation below.

$$Ca = (\eta_m * \gamma * R)/\sigma$$

where η_m → Matrix viscosity

and γ → Shear rate applied to the matrix

and R → EPR particle radius (0.5*d)

and σ → Interfacial tension between EPR particles and matrix

Conclusion

It has been shown that the peak force is dependent on two factors: the ethylene content present within the copolymer and the test temperature employed in the drop weight impact test. An increase in the percentage of ethylene or a drop in the test temperature negatively affects the peak force of the ethylene propylene copolymers.

In addition, the dominant method of energy dissipation within the copolymer changes from multiple crazing to mutiple shear yielding as the test temperature is dropped to -20 °C. Multiple shear yielding results in the specimen having a low crack propagation energy and a lower amount of total energy absorbed by the copolymer. A substantial drop of approximately 80 % was observed in the absorbed impact energy. Stress whitening behaviour at impact point in the specimen plaques was absent in tests carried out at low temperature.

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