# Determination of the Fracture Toughness of Thermoformed Polypropylene Cups by the Essential Work Method

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In this work the anisotropic fracture behavior of neat and rubber-modified polypropylene cups induced by a vacuum thermoforming process is studied. The effect of different draw-ratios is also examined. An elasto-plastic fracture mechanics approach, based on the method of the essential work of fracture, is applied to samples cut from the thermoformed cups both longitudinally and transversally to the drawing direction. For all the products examined a strong anisotropy in the fracture behavior is observed. The fracture resistance for cracks propagating along the drawing direction is lower than in the transverse direction, this fracture anisotropy being enhanced at higher draw-ratio. The presence of the rubber particles results in an increase in the fracture toughness for cracks running transversally to the drawing direction, but, at the same time, it seriously reduces the fracture resistance for cracks propagating along the drawing direction. In order to better understand the dependence of the fracture behavior upon the processing conditions and material structure, dynamic mechanical thermal analysis, transmission electron microscopy, and X-ray diffraction measurements are also carried out.

#### **INTRODUCTION**

Thermoforming offers some advantages over competitive processes such as blow molding, rotational molding, and injection molding. Owing to the relatively low forming pressures, mold costs are low and parts of relatively large size can be economically fabricated. Parts with very small thickness-to-area ratio can be obtained, and for thin-wall parts, the fabrication time is extremely short, making the process very economical for large production volumes (1).

During the thermoforming process, the plastic sheet is stretched to the final shape, at the proper forming temperature. The extent of deformation depends on many parameters, such as the sheet temperature, the level of the applied force, and the material stress-strain behavior. Above the glass transition temperature (Tg), most amorphous thermoplastic polymers have sufficient chain mobility to deform and even to flow under load. If the material flows, it can retain permanent deformation once the load is removed. For semicrystalline polymers above Tg, those chain segments that are not involved in the crystalline domains can deform to an extent that depends on the crystallinity level.

In general, the mechanical behavior of polymeric materials can be strongly affected by the molecular

orientations that usually develop as a consequence of the stretching during the transformation process (2). This effect is particularly marked in semicrystalline polymers owing to possible changes in the orientations and/or in the microstructures of the crystalline domains, which can induce a pronounced anisotropy in the fracture properties. Such a behavior is observed in polypropylene thermoformed products, in which the fracture resistance for crack propagation along the drawing direction may be seriously compromised.

The aim of this work is to study the anisotropic fracture behavior of polypropylene cups obtained by means of a vacuum thermoforming process.

## EXPERIMENTAL

The materials were kindly supplied by Himont Italia S.p.A., in the form of thermoformed cups having two different depths (*d*), 100 mm and 58 mm, respectively, corresponding to different draw-ratios. The cups were obtained from neat and rubber-modified polypropylene sheets, 1.35 mm in thickness, by a vacuum-assisted thermoforming process at a temperature of 160°C. The rubber-modified polypropylene contained 15 wt% rubber as dispersed phase.

Tensile modulus and yield stress were measured on strips cut both along (Y in *Fig. 1*) and transversally (X



Fig. 1. Schematic of the position of SENT-X and SENT-Y specimens in the thermoformed cups.

in *Fig. 1*) to the drawing direction and tested by means of an Instron 4502 tensile tester at a cross-head speed of 10 mm/min. In order to overcome troubles resulting from the cups' curved shape, samples with a high length/width ratio (10–15) were used. The tensile yield stress was evaluated from the zero slope point in the stress-strain curves. In some cases no zero-slope point was observed and the yield stress was determined as the stress where the two tangents to the initial and final parts of the load-elongation curve intersect (3). At least five specimens were tested for each measurement.

Dynamic mechanical thermal analysis (DMTA) was carried out on strips, 4 mm wide and 20 mm long, cut along the X and Y direction, by using a Mk II Polymer Laboratories dynamic mechanical thermal analyzer in the tensile mode, in the temperature range from -100 to  $+150^{\circ}$ C, at a frequency of 1 Hz.

Single Edge Notched Tension (SENT) specimens were cut from the cups, both longitudinally and transversally to the drawing direction. As schematized in *Fig. 1*, SENT-Y and SENT-X indicate specimens containing cracks propagating along and perpendicularly to the drawing direction, respectively. In order to meet the size requirements for the application of the essential work of fracture (EWF) method (4), the specimens' widths and lengths were chosen equal to 40 and 80 mm, respectively, while the ligament length was varied in the range from 1 to 13 mm. The initial notches were prepared with a sharpened razor blade mounted on a laboratory attachment so that penetration could be carefully controlled. The measurement of the notch length was performed using an optical microscope. At least five specimens were tested for each ligament length at room temperature and a cross-head speed of 2.5 mm/min. During the fracture tests the crack growth was monitored using a B/W Sony video camera connected to a video-recorder and to an image analyzer system.

Transmission electron microscopy (TEM) observations were performed on samples obtained from the cups surface. Samples were cut by a cryogenic ultramicrotome (Ultracut S + CryoFCS, Leica) and treated in a ruthenium tetraoxide aqueous solution in order to evidence the rubber phase.

Wide-angle X-ray diffraction (XRD) patterns (incident X-ray beam perpendicular to the cup surface) were obtained at room temperature using a Chesley microcamera with Ni filtered CuK $\alpha$  radiation, operating at 30 kV and 25 mA.

## The Essential Work of Fracture (EWF)

Because of the ductility of the materials examined, an elasto-plastic fracture mechanics approach, based on the methodology of the essential work of fracture (4–13), was applied. This method, originally proposed by Broeberg (5), is based on the assumption that the total work of fracture,  $W_f$ , consists of two parts: (i) the work expended in the fracture-process zone,  $W_e$ , which is considered to be essential for the fracture process; and (ii) the work responsible for the plastic deformation outside the fracture-process zone,  $W_p$ , which is not essential for the fracture process itself. The total fracture work may therefore be written as:

$$W_f = W_e + W_p \tag{1}$$

Under plane stress conditions,  $W_e$  is proportional to the ligament length, *L*, and  $W_p$  is proportional to  $L^2$  as follows:

$$W_f = LBw_f = LBw_e + \beta L^2 Bw_p \tag{2}$$

and

$$w_f = w_e + \beta w_p L \tag{3}$$

where *B* is the specimen thickness,  $\beta$  is a shape factor for the outer plastic zone, which depends upon the geometry of the specimen and the crack, and  $w_f$ ,  $w_e$ , and  $w_p$  are the specific total, essential, and non-es-

Fig. 2. Locations (•) where XRD and TEM specimens were taken. Letter A and B refer to lower (d = 58 mm) and higher (d = 100 mm) draw ratios respectively, while numbers 1, 2, and 3 refer to positions at 10%, 50% and 90% of the cup depth, respectively.



Determination of the Fracture Toughness



A/2



A/3



A/3

B/3



Fig. 3. XRD patterns of neat polypropylene cups. A/1, A/2, A/3, B/1, B/2, B/3 refer to Fig. 2.

sential work of fracture, respectively. The parameter  $w_{e}$  is regarded as a material property for a given thickness. Equation 3 indicates that parameters  $w_e$  and  $\beta w_p$  can be evaluated by linearly interpolating a number of experimental data of  $w_f$  obtained by testing samples at various ligament lengths. If the ligament is in a state of pure plane-stress,  $w_e$ ,  $w_p$ , and  $\beta$  are

B/3

Fig. 4. XRD patterns of rubber-modified polypropylene cups. A/1, A/2, A/3, B/1, B/2, B/3 refer to Fig. 2.

independent of the ligament length, and consequently *Eq 3* yields a straight line. To generate a state of pure plane-stress, the ligament length must be greater than three to five times the specimen thickness (6, 7). Moreover, in order to avoid the plastic zone's being disturbed by edge effects and to ensure complete yielding of the ligament before the crack starts to propagate, the ligament length should be less than one third of the specimen width or less than the plastic zone size, whichever is the lower (8).



Fig. 5. Stress-strain curves for neat polypropylene specimens obtained from cups with depth of a) 58 mm, and b) 100 mm, respectively.

## **RESULTS AND DISCUSSION**

It is well known that the biaxially constrained stretching during a thermoforming process yields to a nonuniform chain orientation along the drawing direction (1). This phenomenon has been investigated with XRD measurements performed at various locations along the cups' axis, as indicated in *Fig. 2*. The XRD patterns are reported in *Figs. 3* and 4 for the neat and rubber modified polypropylene cups, respectively. A/3 and B/3 (in both *Figs. 3* and 4) show the characteristic continuous circular pattern of the nonoriented isotactic polypropylene (14): from the center,  $\langle 110 \rangle$ ,

 $\langle 040 \rangle$ ,  $\langle 130 \rangle$ ,  $\langle 111 \rangle$ ,  $\langle 131 \rangle$ ,  $\langle 041 \rangle$ , and  $\langle 060 \rangle$  reflections of the  $\alpha$  monoclinic cell can be observed (15). The other patterns present some spots of higher intensity located especially on the  $\langle 110 \rangle$  reflection, thus indicating a certain degree of orientation along the drawing direction. As can be concluded from the patterns, going from the upper to the lower part of the cups, a progressive reduction of the crystalline chains orientation occurs. Moreover, the higher the draw-ratio the greater the chain orientation. Thus, in order to compare the results, specimens for the mechanical testing were always cut at the same position in the thermoformed cups. For the same reason it has been very important to ensure that this was the case for crack propagation in the fracture tests.

The anisotropic mechanical behavior of the thermoformed cups is clearly evident from the stress-strain curves of the neat polypropylene specimens, as reported in Fig. 5. Samples obtained transversally to the drawing direction show a well-defined zero-slope yield point, which is not the case for the specimens cut along the drawing direction. It is important to observe that in the drawing direction, the stress-strain behavior should be considered representative of an average behavior of the material due to the nonuniform chain orientation. From the results of the tensile tests, reported in Table 1, we can observe that for the neat polypropylene, the elastic modulus is higher in the drawing direction, with a more pronounced effect for the higher draw-ratio. For the rubber-modified polypropylene, the tensile modulus in the drawing direction is only slightly higher than in the transverse direction and almost the same for the different drawratios. In all cases the yield stress is higher along the drawing direction.

Dynamic mechanical thermal analysis confirms the anisotropy of the mechanical properties at low strains. DMTA thermograms reported in *Fig. 6* and *Fig. 7* show that the tensile storage modulus and the loss factor are higher along the drawing direction. Moreover, the loss factor is higher for the rubber-modified than for the neat polypropylene. It is interesting to observe that at low temperatures (below  $-50^{\circ}$ C) the rubber is in the glassy state and consequently there is almost no difference between the behavior of the neat and the rubber-modified polypropylene specimens.

Table 1.	Tensile Elastic Modulus and Tensile Yield Str	ess, Along the Drawing	g Direction (Y) and	Transversally (X).	The Standard		
Deviation is Reported in Round Brackets.							

Material	Cup Depth (mm)	Tensile Modulus X Direction (GPa)	Tensile Modulus Y Direction (GPa)	Tensile Yield Stress X Direction (MPa)	Tensile Yield Stress Y Direction (MPa)
PP	58	1.6 (0.1)	1.9 (0.1)	33.9 (1.9)	38.3 (2.3)
	100	1.3 (0.1)́	2.3 (0.1)	28.7 (0.8)	48.9 (1.3)
					(*)
PP+ 15% rubber	58	1.2 (0.1)	1.4 (0.1)	28.3 (1.2)	38.4 (0.9)
	100	1.1 (0.1)	1.3 (0.1)	24.7 (0.6)	41.6 (0.8)
PP+ 15% rubber	100	1.1 (0.1)	1.3 (0.1)	28.3 (1 24.7 (0	.2) ).6)

(\*) Stress evaluated at the intersection of the two tangents to the initial and final parts of the load-displacement curve.



0

0

1

2

ament length of 4 mm. Cup depth = 58 mm.

3

4

Displacement (mm)

Fig. 9. Load-displacement and crack growth-displacement

curves for a neat polypropylene SENT-Y specimen with a lig-

5

6

Fig. 6. Tensile storage modulus, E', and loss factor,  $\tan \delta$ , as a function of temperature for neat polypropylene specimens cut along the drawing direction (----) and transversally (- - -) at the highest draw ratio (cup depth = 100 mm).

Fig. 7. Tensile storage modulus, E', and loss factor,  $\tan \delta$ , as a function of temperature for rubber-modified polypropylene specimens cut along the drawing direction (—) and transversally (- - -) at the highest draw ratio (cup depth = 100 mm).



Fig. 8. Load-displacement curves for neat polypropylene SENT-Y specimens with various ligament lengths (L1 = 2 mm, L2 = 4 mm, L3 = 6 mm, L4 = 8 mm, L5 = 10 mm). Cup depth = 100 mm.

0

7



Fig. 10. Plots of the specific total fracture work,  $w_f$ , as a function of the ligament length, L, for SENT-X ( $\bigcirc$ ) and SENT-Y ( $\bigcirc$ ) specimens obtained from neat polypropylene cups at a) lower draw ratio (cup depth = 58 mm) and b) higher draw ratio (cup depth = 100 mm).

Typical load-displacement curves obtained by SENT-Y specimens with various ligament lengths are reported in *Fig. 8* for 100-mm-depth neat polypropylene cups, the shape of the curves being similar for all the samples considered. It is readily seen that these curves are geometrically homothetic and that the area under the curves increases as the ligament length increases. The total work of fracture can be easily measured by evaluating the area under the curves. By analyzing the tape-recording of the fracture tests, it is possible to establish that the onset of crack growth always occurs very close to the maximum load (see point A in *Fig. 9*). The crack propagates at constant rate up to the point B, after which a faster crack propagation is observed until breakage.

Plots of the specific total work of fracture versus the ligament length are reported in *Figs. 10* and *11*. Accordingly to *Eq 3*, the intercept of the regression line interpolating the experimental data represents the specific essential work of fracture,  $w_e$ , and the slope of this line gives a measure of  $\beta w_p$ , which is the nonessential specific work term. *Table 2* summarizes the  $w_f$  and  $\beta w_p$  values obtained. For all the samples, anisotropy in the fracture behavior can be observed. This effect is more pronounced for the highly drawn cups (depth = 100 mm). In fact, for these specimens the



Fig. 11. Plots of the specific total fracture work,  $w_f$ , as a function of the ligament length, L, for SENT-X ( $\bigcirc$ ) and SENT-Y ( $\bigcirc$ ) specimens obtained from rubber-modified polypropylene cups at a) lower draw ratio (cup depth = 58 mm) and b) higher draw ratio (cup depth = 100 mm).

value of  $w_e$  is much lower for cracks propagating parallel to the drawing direction (SENT-Y specimens), thus indicating a lower crack resistance along this direction. This anisotropic fracture behavior is more pronounced for the rubber-modified polypropylene cups. In fact, whereas for the neat polypropylene cups at the lowest draw-ratio (cup depth = 58 mm) almost no difference exists between  $w_e$  values along the X and Y directions, a strong anisotropy results for the rubber-modified cups at the same draw-ratio. It is also interesting to note that the presence of rubber promotes toughening only for cracks running along the X direction, whereas it drastically impairs the fracture toughness for cracks that propagate along the Y direction.

Anisotropic effects are also very pronounced in the nonessential work term  $\beta w_p$ , thus indicating that the size and the shape of the plastic zone are strongly dependent on the direction of the applied load, though practically unaffected by the degree of drawing.

The effect of the rubber inclusions on the fracture behavior of the polypropylene thermoformed cups can be better understood by looking at the TEM micro-

Material	Cup Depth (mm)	w <sub>e</sub> SENT- X (kJ/m²)	w <sub>e</sub> SENT- Y (kJ/m²)	β w <sub>p</sub> SENT-X (MJ/m³)	βw <sub>p</sub> SENT-Y (MJ/m³)
PP	58	17.1 (2.6)	22.9 (2.7)	36.5 (3.0)	12.1 (3.0)
	100	43.3 (4.1)	27.2 (3.3)	40.9 (4.6)	11.0 (1.8)
PP+ 15% rubber	58	53.5 (1.8)	13.3 (1.2)	32.5 (1.9)	17.3 (1.3)
	100	57.4 (2.1)	13.8 (1.0)	35.1 (2.1)	11.7 (1.3)

Table 2.  $w_e$  and  $\beta w_p$  Values for SENT-X and SENT-Y Specimens. Errors in Round Brackets Were Evaluated by Considering the 95% Confidence Bands.

graphs in *Figs. 12* and *13*. It is clearly evident that the shape of the rubber particles is markedly elongated in the drawing direction, and, similarly to the chain stretching, the particles result in a higher degree of orientation in the upper part of the cups.

It may be supposed that, owing to their high aspect ratio, the rubber particles play a distinct role along the X or Y directions. In fact, the rubber particles should produce a higher stress localization and concentration for loads applied along the X direction, and, at the same time, they should have a much higher efficiency to stop the cracks that propagate along this direction. This could justify that the rubber toughening develops only for cracks growing in the X direction, whereas for cracks that propagate along the Y direction the rubber particles act only as flaws resulting in a decrease of



Fig. 12. TEM micrographs of rubber-modified polypropylene cups at a magnification of  $55,000 \times$ . Specimen was taken from the upper part of the cup (B/1 in Fig. 2). The rubber particles appear as black regions.

the fracture toughness compared with neat polypropylene.

Since the glass transition temperature range is near room temperature (see Figs. 6 and 7), a strong dependence of the fracture toughness upon temperature and deformation rate is likely to be expected. EWF experiments performed on neat polypropylene SENT specimens at a higher cross-head speed (25 mm/min) confirmed that  $w_e$  is sensitive to the testing rate (see Fig. 14). For cracks propagating both longitudinally and transversally to the drawing direction,  $w_e$  values result in a decrease at higher testing rates. It can be observed that the crack resistance is more sensitive to the testing rate for cracks propagating along the Y direction than the X direction. Further experimental work regarding this effect is in progress.



Fig. 13. TEM micrographs of rubber-modified polypropylene cups at a magnification of  $55,000 \times$ . Specimen was taken from the lower part of the cup (B/3 in Fig. 2). The rubber particles appear as black regions.



Fig. 14. Essential specific work of fracture as a function of the testing rate for neat polypropylene cups at the higher draw ratio (depth = 100 mm) for SENT-X ( $\bigcirc$ ) and SENT-Y ( $\bigcirc$ ) specimens.

## CONCLUSIONS

The anisotropic fracture behavior of thermoformed polypropylene cups was studied through an elastoplastic fracture mechanics approach, based on the method of the essential work of fracture. The fracture resistance for cracks propagating longitudinally and transversally to the drawing direction was investigated for both neat and rubber-modified polypropylene cups. The effect of different draw-ratios was also examined.

In general, the fracture resistance for cracks running along the drawing direction is lower than in the transverse direction. This anisotropic behavior is enhanced as the thermoforming draw-ratio increases.

The presence of rubber as the dispersed phase leads to an increase of the fracture toughness for cracks growing transversally to the drawing direction, but, seriously impairs the resistance to the crack propagation along the drawing direction. This behavior could be tentatively explained by taking into account that the rubber particle is markedly distorted in the drawing direction, as clearly evidenced by transmission electron microscopy.

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#### REFERENCES

- 1. J. L. Throne, *Thermoforming*, Hanser Publishers, Munich (1987).
- I. M. Ward, Mechanical Properties of Solid Polymers, p. 246, John Wiley & Sons 2nd Ed., Chichester, England (1985).
- 3. Idem., ibid. p. 337.
- B. Cotterel and J. K. Reddel, Int. J. Fract., 13, 267 (1977).
- 5. K. B. Broeberg, Int. J. Fract., 4, 11 (1968).
- 6. Y. W. Mai and B. Cotterell, Int. J. Fract., 13, 105 (1986).
- Y. W. Mai, B. Cotterell, R. Horlyck, and G. Vigna, *Polym. Eng. Sci.*, **27**, 804 (1987).
- A. S. Saleemi and J. A. Nairn, Polym. Eng. Sci., 30, 211 (1990).
- 9. Y. W. Mai and P. Powell, J. Polym. Sci. Part B: Polym. Physics, **29**, 785 (1991).
- C. A. Paton and S. Hashemi, J. Mater. Sci., 27, 2279 (1992).
- 11. S. Hashemi, J. Mater. Sci., 28, 6178 (1993).
- S. Hashemi and D. O'Brien, J. Mater. Sci., 28, 3977 (1993).
- W. Y. F. Chan and J. G. Williams, *Polymer*, **35**, 1666 (1994).
- S. Bruckner, S. V. Meilee, V. Petraccone, and B. Pirozi, Prog. Polym. Sci., 16, 361 (1991).
- G. Natta, P. Corradini, Nuovo Cimento Suppl., 15, 40 (1960).

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