Effect of Molecular Weight on Brittle-to-Ductile Transition Temperature of Polyetherimide

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ABSTRACT: The fracture and yield strength of polyetherimide was evaluated over a temperature range of 23 to 140°C for materials with number-average (M_n) and weight-average molecular weight (M_w) ranging from 15.6 to 22.8 and 36.6 to 52.3 kg/mol, respectively. The brittle-to-ductile transition temperature, where an equal probability exists that an impact will result in a brittle or ductile failure, was determined by evaluating the temperature at which fracture and yield strength are equal. The transition temperature decreased from 155 to 60°C with increasing molecular weight and provided a measure of relative ductility between material samples. As a case study, the practical impact strength of an injection-molded food service tray was determined at 20°C and correlated with fracture strength as a function of molecular weight. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1666–1671, 2004

Key words: polyetherimide; ULTEM®; brittle; ductile; fracture strength

INTRODUCTION

Material properties of thermoplastic resins are routinely measured in accordance with ASTM or ISO standards where specimen type, geometry, and test conditions are well defined. The standardized test methods are useful in providing a method of comparing physical and mechanical properties, which facilitate in the selection of a material for a given application. However, in practice, it is extremely difficult to assess and translate material properties measured with test specimens by using controlled test conditions with the unpredictable and uncontrolled environment that an injection-molded article may encounter. This is especially the case when impact properties are considered because the very nature of an impact is an unpredictable event for which the type of impact, load, velocity, and temperature may vary significantly for each molded article.

A material's fracture strength, yield strength, and brittle-to-ductile (B/D) transition temperature are of importance when considering impact performance of a molded article in an application spanning a wide temperature range because fracture behavior depends on molecular weight and temperature, among other factors. Impact testing at a single temperature is insufficient to adequately characterize a material's performance in environmental conditions that are constantly changing.

In addition to demonstrating good practical impact strength, a thermoplastic material should have acceptable melt-viscosity characteristics to ensure melt processibility by the injection-molding process. A low molecular weight resin is generally preferred to improve processibility, production rates, and yields; however, enough practical ductility (or impact strength) must be maintained for end-use application.

Material properties of impact strength and flow are two important characteristics that trend in the opposite direction because polydispersity of polyetherimide remains relatively constant over a wide range of molecular weights. An increase in M_n results in a corresponding increase in M_w, which results in better impact strength but higher melt viscosity and a subsequent reduction in melt processibility. This presents a problem requiring a compromise in M_w (and M_n) to ensure a capable injection-molding process to produce a molded product, while maintaining practical impact properties over the application temperature range.

The B/D transition temperature characterizes the temperature at which a 50% probability exists that a material fracture will result in either a brittle or a ductile failure as a result of an impact.[1] The transition from B/D failure occurs when yield strength decreases to a value below its corresponding fracture strength as a function of molecular weight, temperature, and impact velocity. Similar studies as to the effect molecular weight has on the B/D transition temperature of polyethylene, polypropylene, polycar-

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TABLE I
Molecular Weight Characteristics of Polyetherimide[a]

Resin sample	M_w (Kg/mol)	M_n (Kg/mol)	PDI (M_w/M_n)	MFR[b] (g/10 min)
A	52.30	22.82	2.29	9.3
B	47.25	20.13	2.35	15.3
C	42.70	18.20	2.35	22.0
D	40.17	17.14	2.34	31.4
E	36.64	15.66	2.34	47.4

[a] M_n and M_w reported values in polystyrene standard.
[b] 337°C, 6.6 Kgf.

bonate, polyester, and polyester copolymers have been reported in literature.[2–5] The temperature at which the yield and fracture strength are equal defines a material's B/D transition temperature. As yield strength continues to decrease below its fracture strength with increasing temperature, it becomes more probable a material will fracture in a ductile fashion. This probability continues to increase with temperature until all impact failures result in a ductile fashion. Conversely, as temperature decreases below the B/D transition temperature, the probability increases that a material will demonstrate brittle behavior.

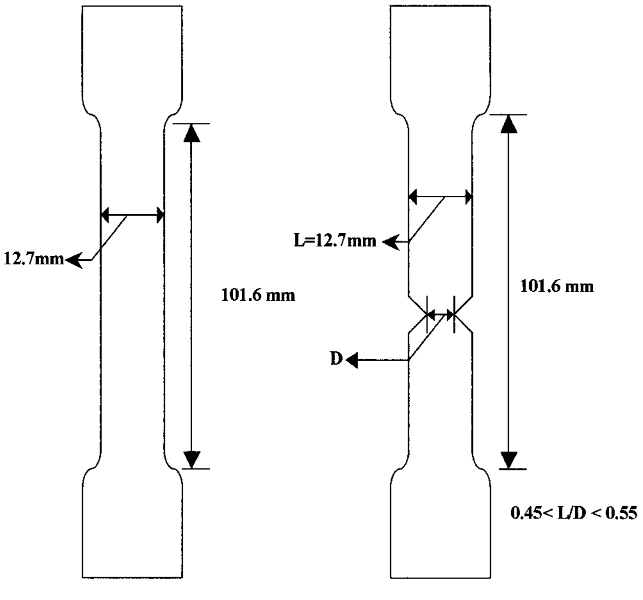
The type of impact, specimen geometry, temperature, molecular weight, and the degree of molded-in stress in test samples may affect the B/D transition temperature. In this study, the effect molecular weight of polyetherimide has on impact properties of fracture strength and its corresponding B/D transition temperature were evaluated and correlated with practical impact of an injection-molded article.

EXPERIMENTAL

Polyetherimide, Ultem® resin, from GE Plastics, with molecular weight (M_w) and number-average molecular weight (M_n) ranging from 36.64 to 52.30 and 15.66 to 22.82 kg/mol were evaluated, respectively. Material samples of intermediate composition were obtained through pellet blending and melt extrusion of high and low M_w resin to achieve additional material compositions for evaluation. Molecular weight was determined by dissolving 0.25 g of each sample in methylene chloride and analyzing with a Waters 2690 HPLC system consisting of two Waters Linear Ultra-Styragel (mixed bed) HR5E GPC Columns with UV detection at 254 nm. The system was calibrated by using monodispersed polystyrene standards ranging from 2000 to 214,000. The polydispersity index (PDI) of each material investigated remained relatively constant and ranged from 2.29 to 2.34. The corresponding melt flow rate (MFR) characterizing flow behavior ranged from 9.3 to 47.4 g/10 min and was evaluated by using a Tinius Olsen MP987 Extrusion Plastometer in accordance with ASTM D1238 test methods at 337°C and 6.6 kgf. Melt density was 1.16 g/mL. A summary of polyetherimide materials evaluated is presented in Table I.

ASTM Type I tensile bars were injection molded by using a 150-ton injection-molding machine, 6 oz. barrel, with mold and melt temperatures of 135 and 365°C, respectively. The tensile properties were evaluated on 3.2-mm-thick samples by using ASTM D527 test standards with an Instron 5566 motor-driven test frame with a hot-air thermal chamber. The thermal chamber was used for temperature-dependent studies from 23 to 150°C with temperature variations of individual samples of ±2°C. Material samples were conditioned prior to evaluation for 2 h at test temperature and evaluated with a fixed displacement rate of 0.254 mm/min.

The fracture strength of each material was evaluated by using ASTM type I tensile bars with two 45-degree v-notches in the test area, as presented in Figure 1. A TMI notch-cutter with tip radius of 0.254 mm cut notches in a sample, reducing test area from 40.3 to 20.6 mm^2. Feed rate and cutter speed were fixed at a constant rate to maintain consistency in sample preparation. Notch dimensions maintained a plane strain condition for all the experiments (i.e., the ligament length-to-width ratio) was between 0.45 and 0.55 so as to induce brittle failure with no sample yielding prior to failure. After notching, the samples were heat soaked for 2 h at test temperature. Each sample was tested in accordance to ASTM D638; the



(a) (b)

Figure 1 (a) ASTM type I tensile bar—yield strength test sample. (b) ASTM type I tensile bar with v-notches—fracture strength test sample.

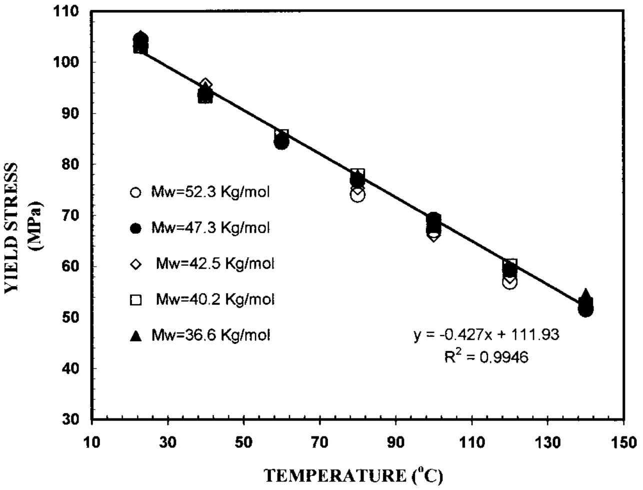


Figure 2 Polyetherimide yield strength as a function of molecular weight and temperature.

resulting tensile strength at break was reported as fracture strength.

A 610 × 152 × 25.4 mm center-gated cold sprue food service tray was injection molded by using a 550 ton, 48 oz. barrel, Krauss–Maffei molding machine to a part weight of 402 g. The tray had a nominal wall thickness of 2.97 mm. Melt temperature varied from 350 to 375°C, corresponding to an increase in melt viscosity of high molecular weight resin as a result of increased mechanical shear during plastication. Resin was dried for > 4 h at 150°C prior to molding. The mold surface temperature was measured by using a contact surface pyrometer as 137 and 143°C for cavity and core sides, respectively. During processing, the molding machine pack pressure was increased to compensate for polyetherimide melt viscosity differences between samples to produce a food service tray of constant weight.

The injection-molded trays were evaluated for impact strength by dropping a 4.6 kg weighted aluminum tup measuring 25.4 mm in diameter on a tray handle with a 2.54 mm wall thickness that extended 25.4 mm vertically above the tray surface for a length and width of 50.8 and 38.1 mm, respectively. Each tray had two handles located along the width of the tray that were susceptible to impact in practical application. To simulate a severe impact of a tray striking the floor when dropped, a fixture was developed to hold a tray at a 45-degree angle for which the tup would strike a handle, which acted as stress concentrator. The tup was dropped in increments of 6.35 mm from a starting height of 254 mm as measured from the location on the tray surface where impact occurred. The test method identified the average height where a part fails when impacted with a 4.6 kg load and subsequently the average impact energy to failure was determined. The methodology used was in accordance with Bruceton Staircase Test Method per ASTM D2463-95.

RESULTS AND DISCUSSION

The yield strength as a function of temperature for polyetherimide with molecular weight ranging from 36.6 to 52.3 kg/mol is presented in Figure 2 for each material investigated. Yield strength decreased linearly from 103 MPa at 23°C to 50 MPa at 140°C with a regression coefficient (R^2) of 0.99. Yield strength decreased at a rate of 8.5 MPa for every 20°C increase in temperature. In contrast, yield strength remained constant as a function of molecular weight, M_w, over the temperature range investigated.

The experimental result was typical of shear yielding, which is independent of molecular weight once the critical entanglement molecular weight was exceeded. Theoretical models discussing the effect molecular parameters have on yield strength are left for literature review.[6,7] In addition, yielding of amorphous polymers such as polyetherimide as a function of temperature and strain rate are described by Eyring's model.[8] The model describes yielding as viscous flow in which an activation barrier for local shear displacements is decreased by applied stress.

A stress–strain curve typical of thermoplastic materials describes the fracture stress behavior of a double-notched polyetherimide sample. The stress–strain curve is characteristic of a brittle failure (induced by the notches) that causes a break without a distinctive yield point or tensile elongation. The v-notches in the test area accentuate brittle failure, unlike a standard ASTM D527 tensile strength test in which polyetherimide in an unnotched geometry demonstrates elongation at break in excess of 50%. As presented in Figure 3, high molecular weight resins have fracture strengths that are larger than low molecular weight

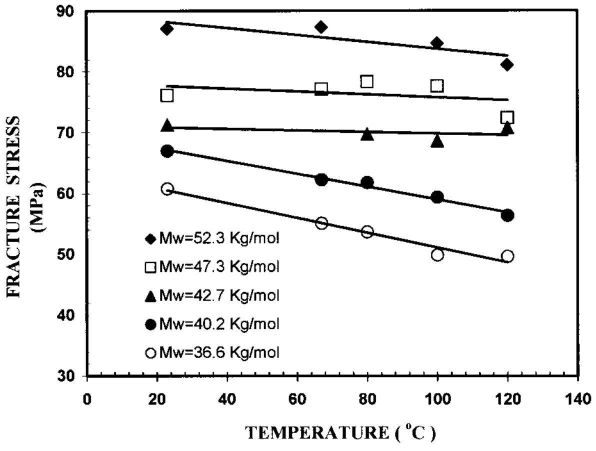


Figure 3 Polyetherimide fracture strength as a function of molecular weight and temperature.

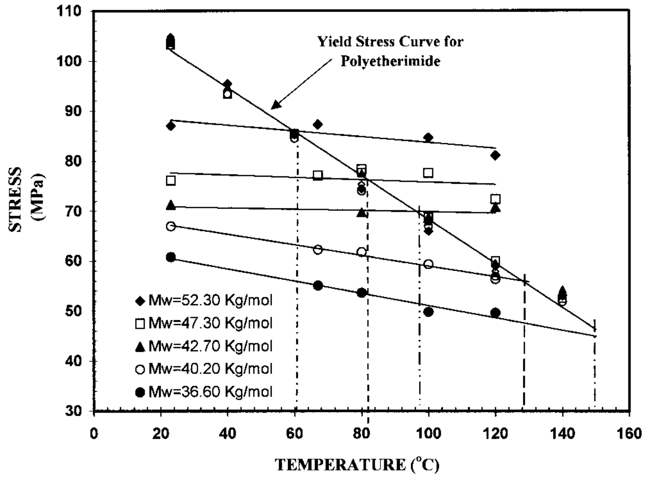


Figure 4 Graphical determination of polyetherimide brittle-to-ductile transition temperature as a function of molecular weight.

materials at any given temperature. For polyetherimide with the highest molecular weight, the fracture strength demonstrated less than a 4% change over the temperature range investigated. However, as molecular weight decreases, temperature dependency became more significant as presented in Figure 3. The fracture strength of the lowest molecular weight material evaluated, 36.6 kg/mol, decreases by 16% as temperature increased from 23 to 120°C. It was reported in literature that brittle failure in glassy polymers occurs by crazing and resistance to craze increases with molecular weight because there are more entanglements between neighboring molecular chains and coils.[9,10] This increase in craze stability with molecular weight is primarily responsible for the observed increase in fracture strength.

The B/D transition temperature in a polymer is the temperature for which a 50% chance ductile deformation may result upon an impact. The transition from B/D failure may be described as two competing but independent stresses, brittle stress and yield stress. Fracture stress, associated with brittle failure, is defined as the stress at break for which crazing is the failure mechanism. In contrast, yield stress is associated with shear yielding and yield strength that results in ductile deformation because a material elongates under the applied stress. The failure mode in a material is determined by these two competing stresses and their magnitude relative to each other. If a material's fracture strength is greater than its yield strength, the failure mode is more likely to be by shear deformation and hence by ductile failure. This results because a material is under yield stress prior to obtaining stress levels required to result in brittle failure. In a similar fashion, if yield stress is greater than brittle stress, the resulting failure will be in a brittle fashion because this stress level was obtained first. In either situation, as the difference between yield and fracture stress increases, the driving force to result in either a brittle or ductile fracture increases.

Figure 4 presents fracture and yield strength as a function of molecular weight and temperature. The temperature at which the two curves intersect defines a theoretical B/D transition temperature. A B/D transition temperature for polyetherimide with M_w of 52.3 kg/mol was determined as 60°C, whereas a material with M_w of 36.6 kg/mol was determined by extrapolation to be ~ 155°C because it extended beyond the temperature range investigated. The remaining intermittent molecular weight samples evaluated ranged between 60 and 155°C. As previously discussed, B/D transition temperature of a resin at a given molecular weight may also be affected by test speed.[3,11] In this work, test speed was held constant over the temperature range investigated.

Figure 5 depicts the B/D transition temperature as a function of molecular weight as determined by the intersection of fracture and yield stress curves. The transition temperature decreased with increasing molecular weight, indicating the material is increasing in toughness with molecular weight. An increase in M_w from 42.7 to 52.3 kg/mol decreased transition temperature from 97 to 60°C, resulting in increasing the material's impact resistance. Although the M_w increase improves ductility, it reduces the melt flow rate from 22.0 to 9.3 g/10 min; therefore, melt processibility of the resin decreases. Polyetherimide materials with M_w ranging from 42.7 and 52.3 kg/mol are usually considered materials suitable for most injection-molding applications.

The standardized impact tests as described were compared with a severe practical impact test of a large

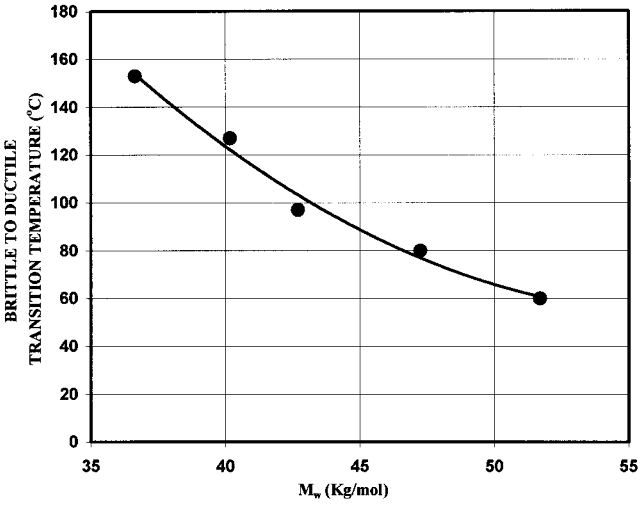


Figure 5 polyetherimide brittle-to-ductile transition temperature as a function of molecular weight.

injection-molded part. The average impact energy to failure of a 4.6-kg load striking an injection-molded food service tray on its handle at room temperature as a function of molecular weight, M_w, is presented in Figure 6. In this specific test, all molded parts evaluated fractured in a brittle fashion. The average impact energy required to fracture a tray increased linearly with M_w with a correlation coefficient of 0.91. The average impact energy ranged from 11.9 to 15.3 J for resins with molecular weight of 36.6 to 52.3 kg/mol, respectively. An increase in polyetherimide molecular weight resulted in a 28.5% increase in impact strength of an injection-molded tray. In actual use, trays made with high molecular weight material resin often show longer service life in demanding applications.

As presented in Figure 7, the average impact strength to fracture a molded part increased linearly with fracture strength with a correlation coefficient of 0.95. The result of this work does show a correlation between severe practical impact testing and the double-notched tensile test. In this test, a 35.5% change in fracture strength from 60.8 to 82.4 MPa translated to a 28.5% change in impact strength of a food service tray from 11.9 to 15.3 J.

While fracture strength may be used to predict impact strength of an injected molded part when evaluating materials of different molecular weights, other important factors must be considered. Molecular weight is a significant aspect in material impact strength; however, practical impact will also be affected by stress in the molded part. A part molded with high injection speed with a cold mold will have more molded-in stress, therefore, resulting in lower impact than a part made from identical resin made with a slower fill into a hot mold with a longer injection cycle. Measuring molded-in stress of part, which can be done on transparent resins such as polyetherimide by using polarized light, can help determine molding conditions that will give parts with the best impact at any given molecular weight.[12,13] In this study, care was taken to mold trays with low molded-in stress. In other related investigations, we have observed that mold release agents incorporated into the polyetherimide may improve part impact by allowing molding of parts with less stress.[14,15] As mentioned, part geometry will also affect practical impact. Parts designed with gradual radii without stress concentrators demonstrate better impact than poorly designed parts. In addition, it is important to mold materials without thermal degradation so molecular weight is retained. As shown, high molecular weight resins demonstrate better impact properties than a lower molecular weight polymer. Drying the material prior to molding and processing in the recommended melt temperature range of 355 to 400°C with limited use of recycle resin will further optimize practical impact of the molded part by retaining molecular weight.

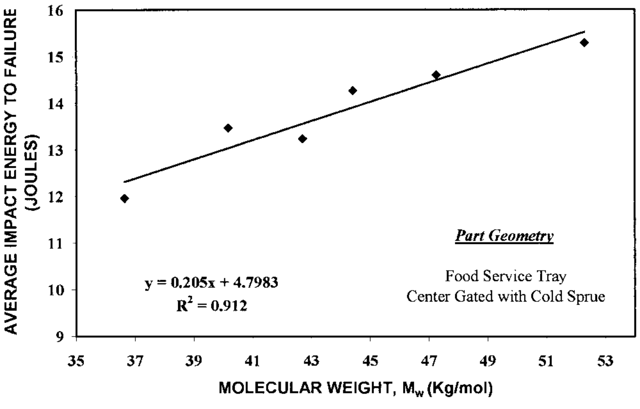


Figure 6 Average impact energy to failure of a polyetherimide injection-molded tray as a function of molecular weight at 20°C with 4.6 kg weight.

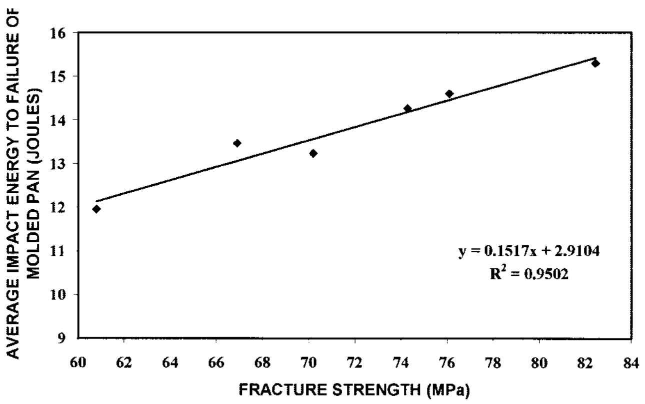


Figure 7 Average impact energy to failure of polyetherimide injection-molded tray as a function of fracture strength at 20°C.

CONCLUSION

The B/D transition temperature of polyetherimide was measured in terms of fracture strength and yield stress as a function of molecular weight and temperature. Over the range studied, as M_w increased, a corresponding increase in fracture strength resulted, while yield stress showed no dependency on the material's molecular weight. In addition, high molecular weight polyetherimide materials generally have lower B/D transition temperatures and are inherently tougher than low molecular weight materials. An increase in molecular weight from 36.0 to 52.3 kg/mol results in a more ductile material with B/D temperature decreasing from ~ 155 to 60°C, hence, showing the effect molecular weight has on ductility. In addition, fracture strength correlated well with the average impact energy to fracture an injection-molded tray.

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