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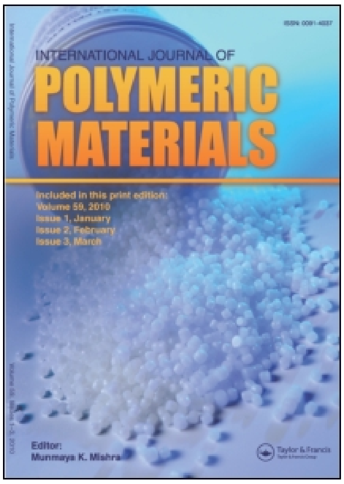

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Correlation of Tensile Properties of Tough Amorphous Polymers with Internal Friction

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Correlation of Tensile Properties of Tough Amorphous Polymers with Internal Friction

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The ultimate stress-strain behavior of five tough amorphous polymers was studied at temperatures from 4.2 to 300°K using an Instron tensile tester which was adapted for cryogenic measurements. The polymers were found to fail by one of three modes depending upon test temperature and sample pretreatment condition. The transition from a general ductile behavior to brittle fracture was accompanied by a maximum in toughness which could be correlated with the γ transition in these polymers. At still lower temperatures there was a change in the brittle failure which correlated with the magnitude of the internal friction intensity of $\Delta = 0.007 - 0.020$. This transition in brittle fracture mode was characterized by a maximum in the brittle fracture stress. It is proposed that the brittle fracture at very low temperature occurs at abnormally low stresses due to stress concentrations factors which can not be relieved since molecular mobility becomes greatly restricted under these cryogenic conditions.

INTRODUCTION

For many years it was generally believed that amorphous polymers were tough and rubbery above the glass transition temperature and brittle at temperatures below T_g. Recently new polymers have been synthesized with large bulky phenyl groups within the main chain. Some of these polymers are very ductile below T_g. It is the purpose of this work to examine the mechanical behavior of several such polymers in the temperature region 4–300°K and to correlate changes in failure mechanism with molecular motion as evidenced by mechanical damping.

At very low temperatures, even the very tough amorphous polymers fail at low elongations in a manner similar to conventional amorphous polymers such as polystyrene at room temperature. Therefore, before considering possible explanations for ductility in tough amorphous polymers, some evidence for microscopic ductility in "brittle glasses" will be reviewed. Berry[1-3] examined PMMA by a cleavage technique and determined the fracture surface energy through the use of the analysis given by Griffith.[4] This experimentally determined fracture surface energy was much higher (by a factor of 1000) than the fracture surface energy calculated from chemical bond strength. When PMMA was freshly broken, it had been noted that the fracture surface reflected colored light. The interference, which causes these reflections, was thought to be due to oriented polymer chains.[2,5] From this evidence, Berry concluded that part of the excess surface energy was due to work of orientation. Such orientation would require chain mobility and drawing on a micro scale. It is well known that when Griffith derived the relationship between brittle strength and crack length,[4] he was considering ideally elastic materials and did not take into account any viscoelastic or plastic behavior which would cause the crack tip to deform and lower the stress concentration. Cessna and Sternstein[6] have shown that the brittle strength of PMMA at 35°C is a function of both crack length and temperature of precracking. The brittle strength was found to increase as the precracking temperature was increased from -70 to 55°C. It was concluded that the greater deformation which occurred at higher precracking temperatures was lowering the stress concentration of the crack and giving higher fracture stress. Therefore, the ultimate strength of a material may be a function of its ability to relax out stress concentration which occurs at flaws.

Kambour has found that many amorphous polymers form crazes prior to fracture, which is further evidence of rather extensive chain mobility on a microscale.[7,8] He noted that the tougher polymers were less likely to craze.

Amorphous homopolymer systems which are tough and ductile will now be considered. In 1963, Boyer[9] noted that many tough polymers had a free volume in the glass state which was larger than normal, and he proposed that impact strength of a polymer varied in proportion to the free volume. The large free volume of tough polymers was also noted independently by Mercier and co-workers in 1965.[10] Litt and Tobolsky[11] defined a new type of free volume $f = (V_a - V_c)/V_a$ called "excess volume", where V_a and V_c are the specific volumes of the amorphous and crystalline phases, respectively. Upon examination of a large number of amorphous polymers, it was found that polymers were ductile at room temperature if $f \geq 0.07$. These observations lead to the speculation that toughness was due to chain mobility which was enhanced by large free volume.

Several authors[12-14] have shown that many polymer systems which are tough below glass transition temperature also have large secondary relaxations at even lower temperatures. This has lead some to conclude that ductility is the result of molecular mobility, which is shown by low temperature relaxations. Data by Turley[15] has shown that transitions are effective in causing ductility only if the relaxation involves main chain motion.

In this paper stress-strain curves are shown for the temperature range 4.2–300°K for five amorphous polymers which contain the phenyl ring within the main chain. The temperature of the maximum energy to failure is correlated with the intense γ relaxation. The failure modes in the temperature range studied are correlated with the level of mechanical damping.

EXPERIMENTAL

Tensile stress-strain measurements were performed in the cryogenic tensile tester shown in Figure 1. During tensile measurements, sample temperatures were maintained by controlling the power to the heater. Under normal conditions the temperature could be controlled to $\pm$ 2°K although tests which

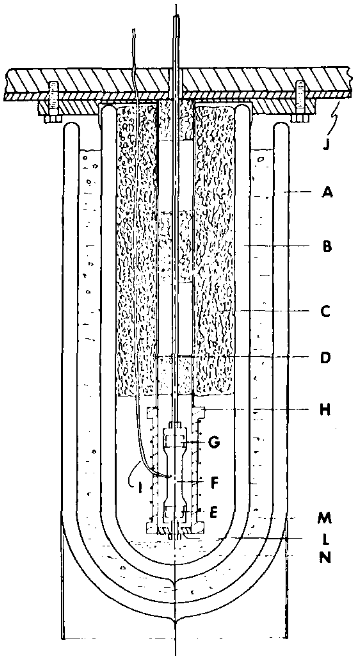


FIGURE 1 Cross section of cryostat for Instron (schematic): (A) outer Dewar (125 mm i.d.) for liquid N_2, (B) inner Dewar (85 mm i.d.) for liquid He, (C) styrofoam plug, (D) stainless steel tube, (E) lower grip, (F) specimen, (G) upper grip, (H) stainless steel rod to load cell, (I) copper-constantan thermocouple, (J) cross head, (K) sample chamber, (L) end cap, (M) liquid N_2, (N) liquid He.

required longer times (when yielding occurred) sometimes resulted in temperature drifts of about 6 degrees. Temperatures were monitored by a thermocouple located adjacent to the sample and could be measured to better than ± 0.5°K throughout the temperature range studied.

The specimens were made from thin films (5–10 mil) cut to the shape shown in Figure 2 and were drawn at a constant rate of 0.05 cm/minute. The polymeric materials used in these experiments are shown in Table I.

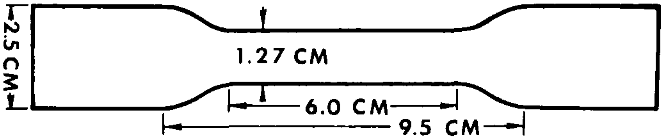


FIGURE 2 Specimen geometry used for tensile test (5–10 mils thick).

RESULTS

Figures 3–9 show the stress-strain behavior of the five polymers studied (PET and PPO were studied with specimens having two physical histories). The mechanical behavior of these seven materials can be divided into three types by failure mode. PCA, CHDMT, amorphous PET and solvent cast PPO all yield at the higher temperatures and fail by brittle fracture at lower temperatures. In each of these four polymers the brittle strength reaches a maxima at some temperature between 4.2°K and the brittle-ductile transition. The details of each polymer will be discussed below.

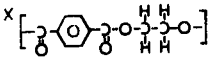
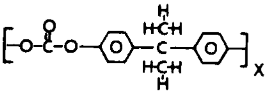
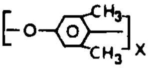
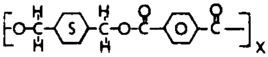
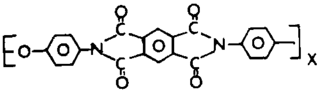
Mylar A (oriented crystalline PET) and KAPTON are both brittle at low temperatures and then become tough at higher temperatures. They are capable of large uniform extension which causes their toughness. Melt cast PPO is brittle at all of the temperatures tested and is in a class by itself.

a) PCA

The tensile stress-strain behavior of amorphous PCA at various temperatures is shown in Figure 3. PCA fails by yielding at 300, 250 and 200°K and fractures just before yielding at 150°K. Ekval[16] has reported the yielding of PCA down to 150°K, but it was necessary to use a special sample geometry to duplicate this result. Because elongation could not be calculated, this geometry was not normally used for this work. Below 150°K, PCA failed by brittle fracture with a maximum in brittle strength at 40°K.

TABLE I

Polymeric materials used in this work

PET	Amorphous poly(ethylene terephthalate) —  Melt cast commercial film, M_n = 15,000 with 1% low molecular weight (xylene extractable) species and no crystallinity by x-ray diffraction.	(a)
Mylar A (d)	Oriented and heat set PET	(a)
PCA	Bisphenol A polycarbonate —  Melt cast commercial Lexan (e) film Amorphous: As received Lexan film Crystalline: Crystallized by exposure to acetone vapor for 24 hours at room temperature. 28% crystalline by x-ray diffraction. Oriented: Drawn 220% at 151°C.	(b)
PPO (e)	Polyphenylene oxide —  Melt cast: Molded from powder at 300°C and rapidly cooled. Solvent cast: Received as film cast from $CHCl_3$ and contained 0.5% residual solvent.	(b)
CHDMT (d)	Poly(1,4-Cyclohexylene dimethylene terephthalate) —  Received as molding pellets with M_w = 24,000. Samples molded at 310°C and cooled at various rates.	(c)
Kapton (d)	Polyimide: Received and tested as 5 mil film — 	(a)

(a) Received from E. I. duPont de Nemours and Co.
(b) Received from G.E.
(c) Received from Eastman Kodak Co.
(d) Trade mark of DuPont
(e) Trade mark of G.E.

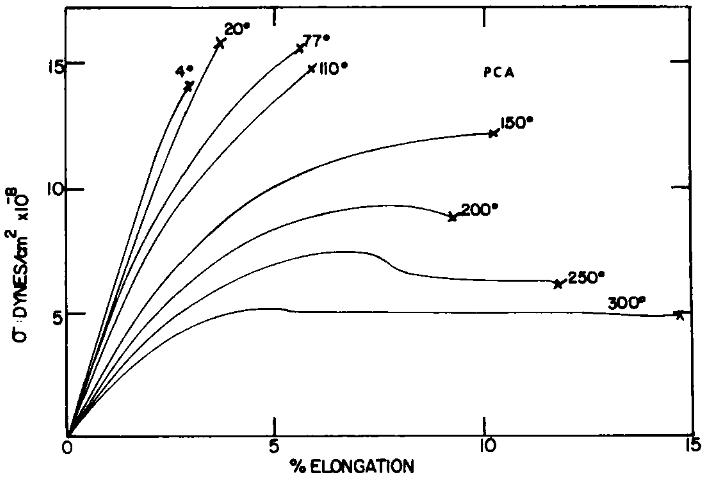


FIGURE 3 Tensile stress-strain behavior of amorphous PCA at various temperatures, °K.

b) CHDMT

As is shown in Figure 4, amorphous CHDMT undergoes a ductile-brittle transition around 200°K and has a maximum in brittle strength occurring at 95°K.

c) Melt Cast PPO

The stress-strain behavior of melt cast PPO in tension is shown in Figure 5. Melt cast PPO failed by brittle fracture throughout the temperature region 4–300°K. At 4, 110 and 200°K the melt cast PPO failed at a constant 4%

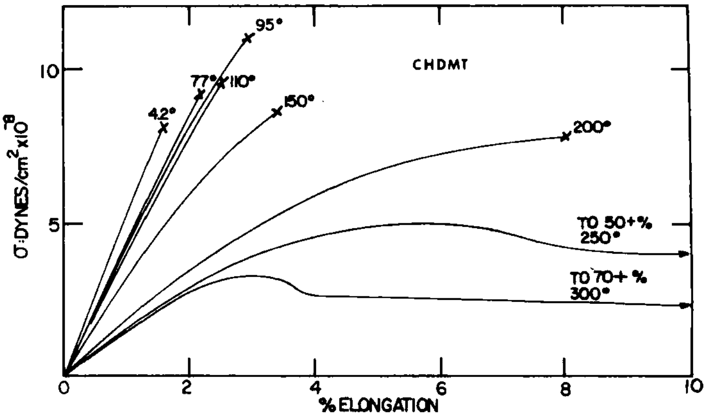


FIGURE 4 Tensile stress-strain behavior of CHDMT as a function of temperature, °K.

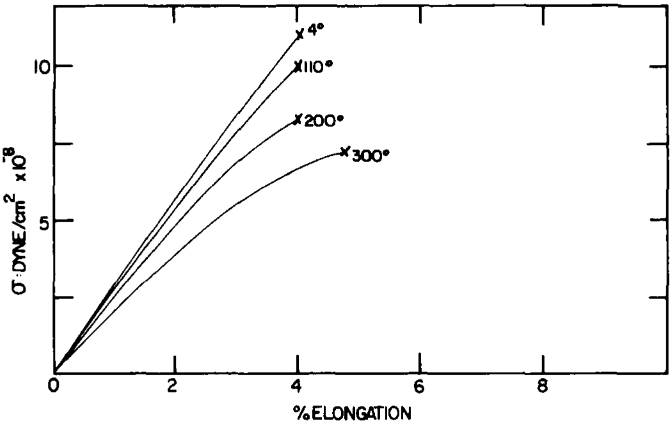


FIGURE 5 Tensile stress-strain behavior of melt cast PPO as a function of temperature, °K.

strain. Only slightly greater elongation occurred at 300°K, which is the temperature of the γ relaxation.

d) Solvent Cast PPO

Figure 6 shows the stress-strain behavior of solvent cast PPO. At 250 and 300°K solvent cast PPO is ductile which is probably due to the plasticization effect of the residual $CHCl_3$. Below 250°K solvent cast PPO is brittle, but the $CHCl_3$ still tends to increase the elongation at 200°K. Below the brittle maximum at 150°K, solvent cast PPO fails at a shorter elongation than the melt cast PPO (see Figure 5).

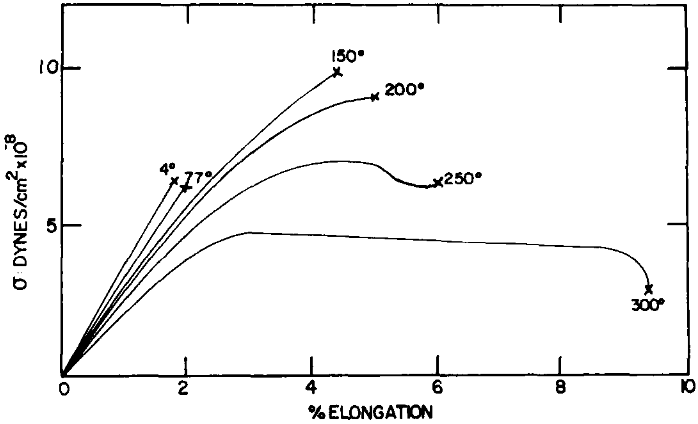


FIGURE 6 Tensile stress-strain behavior of solvent cast PPO at various temperatures, °K.

e) Amorphous PET

The tensile stress-strain behavior of amorphous PET is shown in Figure 7. This PET seems to be ductile only at 300°K. The brittle strength of amorphous PET reaches a maximum at 110°K.

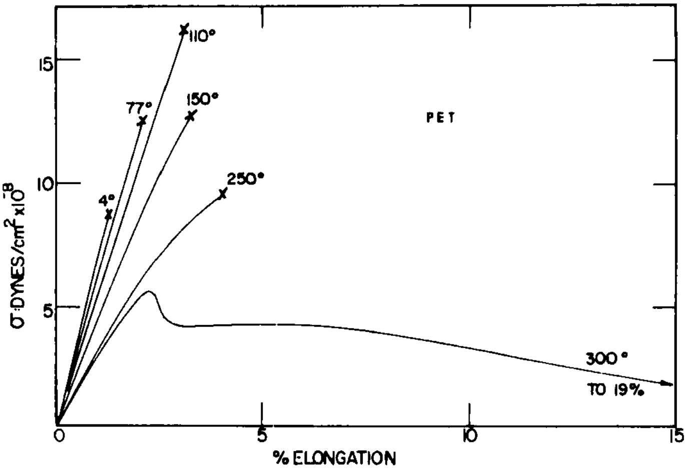


FIGURE 7 Tensile stress-strain behavior of amorphous PET at various temperatures, °K.

f) Mylar A—Oriented Crystalline PET

Figure 8 shows the tensile behavior of Mylar A as a function of temperature.

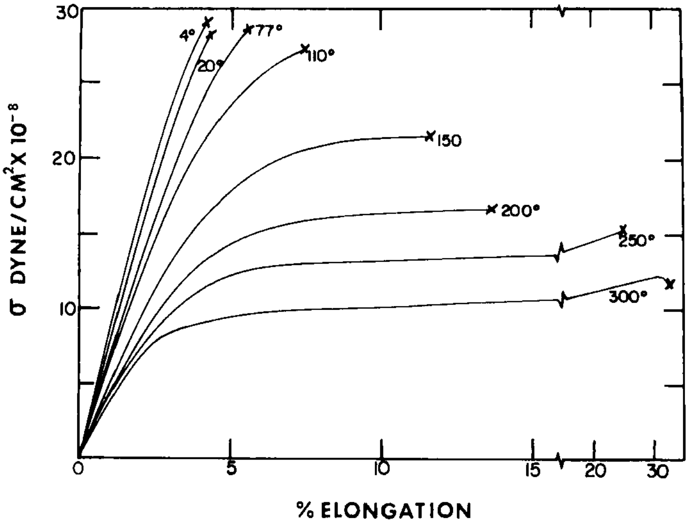


FIGURE 8 Stress-strain behavior of Mylar A in tension at various temperatures, °K.

Comparison with amorphous PET (Figure 7) shows that Mylar A has a higher modulus and elongation at all temperatures. In the temperature region 150–300°K, Mylar A is very tough because it is capable of long uniform extensions and below 110°K it becomes brittle with a constant brittle strength from 4.2 to 77°K.

g) KAPTON

The tensile stress-strain behavior of KAPTON is shown in Figure 9. KAPTON is quite brittle at 4.2°K, but above 77°K it draws to relatively high extensions with uniform extension at 250 and 300°K.

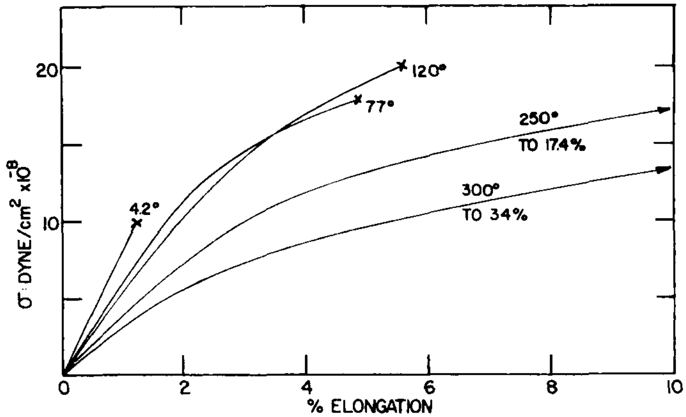


FIGURE 9 Stress-strain behavior of KAPTON in tension as a function of temperature, °K.

DISCUSSION

Several methods have been used by various investigators to evaluate the toughness of polymers below the glass transition temperature. Naturally, the toughness of a polymer is strongly dependent upon its elongation at failure which in turn is dependent upon the failure mode. For each of the polymers studied, failure occurred by from one to three modes. The failure mode can be correlated with internal friction which is a measure of molecular mobility.

There are two low temperature failure modes which appear on a macroscopic scale to be brittle fracture, but their maxima in brittle strength are governed by separate criteria. Figures 10 and 11 show the fracture stress of various polymers plotted as a function of tensile modulus (E). For each polymer, there is a temperature region where σ_F increases with increasing E. This is to be expected, for Vincent has shown empirically that for many

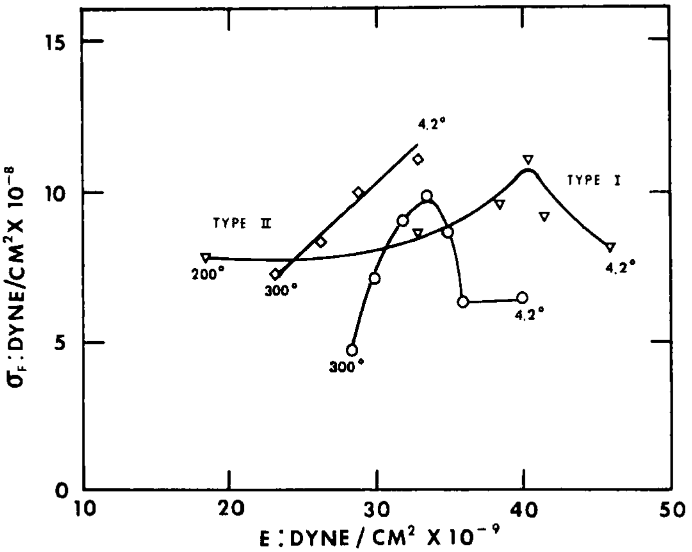


FIGURE 10 Fracture stress of polymers as a function of tensile modulus showing the transition from Type I to Type II brittle fracture.

◇ Melt cast PPO
▽ Solvent cast PPO
○ CHDMT

polymers $E = \sigma_F\,(40 \pm 10)$ over a wide range of temperatures.[17] Except for melt cast PPO, each polymer has a maximum in σ_F at some temperature between 4.2°K and its γ relaxation temperature. Failure at temperatures below the σ_F maximum temperature will be called Type I failure.

In the temperature region of Type I failure, σ_F increases with increasing temperature although the modulus is decreasing. It is proposed that at very low temperatures a polymer will break below the brittle strength predicted from the modulus, due to stress concentration effects around flaws. The increase in σ_F with increasing temperature is attributed to a decrease in effective stress concentration which is caused by increased molecular mobility. The proposed decrease in stress concentration at higher temperature due to relaxation around flaws is further substantiated by Figure 12 which shows that elongation at failure is increasing with increasing internal friction.

It is thought that the maximum in σ_F represents a transition from Type I to Type II failure. We propose that this transition could take place when the molecular mobility is large enough to substantially relieve stress concentration at flaws to such an extent that the polymer reaches its inherent brittle strength without premature cracking. Table II shows that the transition from Type I to

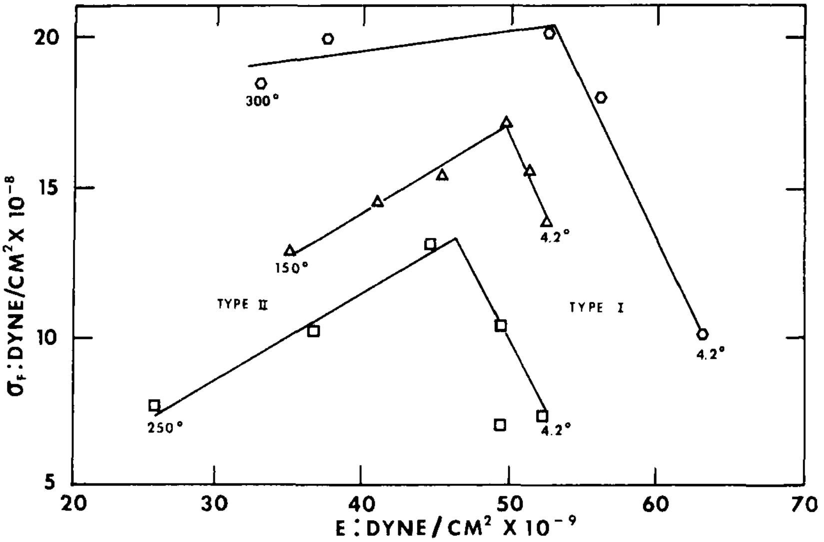


FIGURE 11 Fracture stress of several tough polymers as a function of tensile modulus showing the transition from Type I to Type II brittle fracture.

○ KAPTON
△ PCA
□ PET

Type II failure can be correlated with an internal friction of $\Delta = (7\text{–}20) \times 10^{-3}$. The process by which stress concentration is relieved in the Type II region may be local yielding at flaws. From the present work it is not possible to state definitely that yielding is occurring, for the surfaces were not examined by microscopy. However, Kambour[8] has examined fracture surfaces of PCA specimens broken at 77°K and has found crazing.

A similar concept of stress relaxation at flaws was proposed by Cessna and Sternstein to explain failure behavior in PMMA.[6] PMMA was precracked at 55, 30 and −77°C and then broken at 35°C. A large increase in brittle strength was found when the precracking temperature was increased from 30 to 55°C. The greater brittle strength was attributed to a reduction in stress concentration caused by chain mobility near the flaw tips.

The increasing elongation with temperature in the Type II region causes an increase in toughness. As is shown in Figure 13, some polymers have a maximum in toughness (area under stress-strain curve) which can be associated with the γ relaxation. These maxima occur because the failure mode changes from Type II to ductile near the γ relaxation. Ductility occurs when chain mobility is high enough to allow continuous yielding. The decrease in toughness with increasing temperature in the ductile region is caused by decreases in both modulus and yield strain.

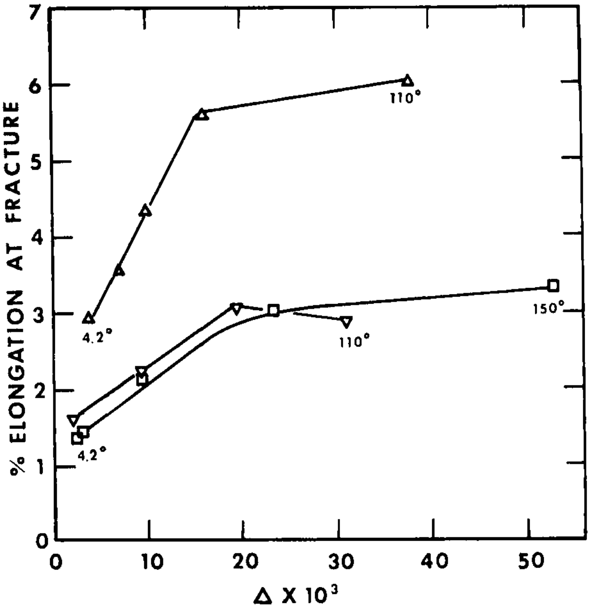


FIGURE 12 Percent elongation at fracture as a function of internal friction for various polymers showing the dependence of elongation on molecular mobility in the Type I brittle region.

△ PCA
□ PET
▽ CADMT

TABLE II

Temperature of transition and internal friction at transition from Type I to Type II failure mode

Material	Temp. of Transition °K	Δ at Transition
PCA	20–40	7–10
PET (A)	77–110	9.6–24
PPO (SC)	110–150	16–18
PPO (MC)	—	—
CHDMT	77–95	10–20
Mylar A	77–120	10–20
KAPTON	77–120	6–7

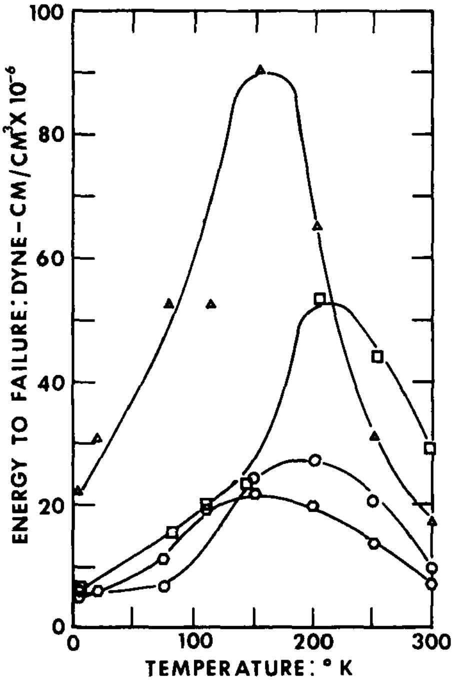


FIGURE 13 Energy to failure for amorphous polymers which yield below T_g showing correlation between toughness and damping.

△ PCA
□ CHDMT
⬡ PET
○ PPO (solvent cast)

CONCLUSIONS

PCA, PET, CHDMT and solvent cast PPO failed in tension by one of three modes depending upon test temperature. In order of increasing temperature, these failure modes were called Type I brittle fracture, Type II brittle fracture and ductile yielding. Type I brittle fracture occurred at very low temperatures where molecular mobility is greatly restricted and was characterized by an increasing fracture stress with increasing temperature and decreasing modulus. It was proposed that premature fracture occurred in this temperature region because of stress concentrations which could not be relieved due to the low molecular mobility. At intermediate temperatures, the above mentioned polymers failed by the more normal Type II brittle fracture. In this case fracture stress varied directly with modulus as is to be expected. The transition from Type I to Type II brittle fracture, which occurred at the maximum in the brittle fracture stress, could be correlated with an internal friction of $\Delta = 0.007 - 0.020$. The change in failure mode from Type II brittle fracture to ductile yielding could be correlated with the γ relaxation and it was accompanied by a maximum in toughness.

KAPTON and Mylar A failed by brittle fracture at low temperatures and deformed by uniform extension above 250 and 150°K respectively. Although there was a less clear cut difference between the types of brittle fracture in these polymers, fracture stress did reach a maximum at temperatures above 4.2°K.

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