

Thermochemical Stress Crazeing and Cracking of Thermoplastics

D. G. LEGRAND

Corporate R&D, General Electric Company, Schenectady, New York 12301

SYNOPSIS

A new method of inducing crazing and cracking in thermoplastics is discussed. The method involves the thermal quenching of hot thermoplastics into simple organic liquids or organic solutions. Data are presented for several different thermoplastics and a number of different liquids. The results are interpreted in terms of a model based on the work of Manning and Lineback that incorporates thermal strains and stresses, thermal conductivity, specific interfacial energies, and defects. The specific crazing energy for bisphenol-A polycarbonate when quenched into isopropyl alcohol is determined to be approximately 3×10^5 erg/cm² from this model. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It has been known for many years that when amorphous thermoplastics such as polystyrene are strained either in tension or bending, they undergo crazing and that the strain or stress necessary to initiate crazing may be reduced as a result of contact with some organic liquids.¹⁻⁴ More recently a mechanism of crazing that occurs after yielding at elevated temperatures near T_g has been discussed.⁵ This latter type of crazing produces numerous crazes of a very regular fibrillar structure, and these crazes have been called type II. Excellent reviews of these subjects have been presented.⁶⁻⁹

In this work we discuss crazing and cracking that has been observed when hot amorphous thermoplastics are thermally quenched in simple organic liquids or solutions. Data are presented for several thermoplastics and a number of different crazing and noncrazing liquids. The results are interpreted in terms of thermal stresses, specific interfacial energies, and defects.

EXPERIMENTAL

Injection-molded samples of bisphenol-A polycarbonate (BPAC), polymethyl methacrylate

(PMMA), polyestercarbonate (PEC), polystyrene (PS), 2,6-dimethyl polyphenylene oxide (PXO), and blends of PS with PXO were used in these experiments. Several of the BPAC samples were carefully annealed above their T_g in order to remove residual orientation and then slowly cooled to minimize residual thermal stresses. All other samples were tested as molded.

In a typical experiment, a sample was placed in a forced hot-air oven and allowed to come to thermal equilibrium. The sample was then removed and immediately immersed into the quenching liquid. The sample was left immersed for times varying from 1 s to 2 min. The sample was then removed and visually examined for crazes and cracks.

RESULTS AND CONCLUSIONS

In view of the number of variables involved, an attempt was made to isolate them. The results are summarized in Tables I-IV.

Effects of Different Thermoplastics and Liquids

The data in Table I demonstrate that several thermoplastics, including a blend, are observed to craze when thermally quenched into an organic liquid such as isopropyl alcohol. The principal requirement is that the thermoplastic be heated near T_g . As noted

Table I Upper Temperature Necessary to Cause Crazing in Various Thermoplastics When Quenched into IPA at Room Temperature

Material	T_1 (°C)	T_2 (°C)	Results ^a
BPAC	125	24	Hundreds of fine crazes
PEI	193	24	Hundreds of small crazes
PEC	180	24	Large number of coarse crazes
PXO	195	24	Large number of fine surface crazes as well as edge crazes
PS	99	24	Extensive surface crazing
PMMA	110	-5	No crazing
25PS/75PXO	180	24	Large number of crazes on the edges of the samples

^a Fine crazes are hairlike in thickness while small crazes are short in length, e.g., 0.1–0.2 cm.

Table II Crazing Behavior of BPAC in a Variety of Organic Liquids and Solutions When Quenched from 125°C to Room Temperature

Crazing Liquids	Results
1	
<i>n</i> -hexane	Large number of crazes
<i>n</i> -decane	Few long crazes that look like internal cracks
Methyl alcohol	Large number of crazes
MDM ^a	Few long crazes that look like internal cracks
Glacial acetic acid	Few long crazes
Liquid N ₂	No crazing or cracking
Water	No crazing or cracking
Ethyl acetate	Softens and plasticizes the surface
Acetone	Softens and plasticizes the surface
Glycerol	No crazing or cracking
Ethylene glycol	No crazing or cracking
Carbon tetrachloride	Extensive crazing along edges
Methyl cyclohexane	Extensive surface crazing
Isopropyl alcohol	Large number of fine crazes that extend over the entire surface of the sample
IPA + water	Number of crazes decreases as the concentration of water increases
Ethyl acetate + <i>n</i> -hexane	Changes from softening to crazing as the % hexane increases
Acetone + IPA	Same as ethyl acetate + <i>n</i> -hexane
Acetone + MeOH	Same as ethyl acetate + <i>n</i> -hexane
CCl sub 4 + <i>n</i> -hexane	Same as ethyl acetate + <i>n</i> -hexane

^a Hexamethyl disiloxane.

below, this temperature is dictated by many factors, including molecular weight, thermal history, and by the liquids as reported in Table II. These results indicate that other liquids, as well as solutions other than isopropyl alcohol (IPA), can act in conjunction with thermally induced stresses to cause crazing and cracking. The fact that some liquids, which are known cracking agents at room temperature, only cause softening and plasticization is not surprising in view of the temperatures. In contrast, the extensive crazing in the presence of IPA and methyl cyclohexane with lesser amounts of crazing with methyl alcohol, hexamethyl disiloxane (MDM), and other liquids is surprising. In particular, it has been suggested that IPA does not craze BPAC and that thermal shock can be used to increase its craze resistance.¹

In an attempt to determine if this phenomenon was related to the physical properties of the liquid rather than its chemical properties, several samples were coated with 0.1–0.2 μm of aluminum and copper by evaporation and by sputtering. The samples were then thermally quenched into IPA. The metallic coatings were then dissolved and the samples were determined to have crazed. A careful examination of the coatings reveal pinholes. These pinholes were thought to be the cause of the observed crazing. In order to avoid this problem, aluminum foil was wrapped around samples that had been coated with glycerol, and these samples were quenched into IPA. There was a slight amount of crazing that was attributed to a small leak at one of the corners. These results suggest that the liquid and/or its vapor must come in direct contact with the surface of the thermoplastic and that the phenomenon is associated with the properties of the liquids. Unfortunately, an attempt to correlate the number and amount of crazing with the other physical properties of the

fluids, e.g., the cohesive energy densities (CEDs), surface tensions, viscosities, etc. was not initially successful. However, subsequently it was noted that softening of the thermoplastic occurred as the solubility parameter of the test liquid approached that of the thermoplastic, while crazing and cracking occurred either side of this point.

Effect of Thermal Quenching Conditions

The results of different thermal quenching conditions are shown in Table III for BPAC and IPA, and it is clear that as one changes the upper test temperature, the amount and type of crazing changes. In particular, the number of crazes and the amount of crazing increase as the upper test temperature is increased from 105 to 165°C while the quenching temperature is held constant. Visually the number and amount of crazing appears to maximize around 125–140°C as shown in Figure 1. At 164°C, only one very small craze was visible. If one lowers the upper test temperature from 125 to 104°C and also lowers the quench bath temperature from 25 to 4°C, then as reported in the bottom half of Table III, the amount and number of crazes increases. These results suggest that the amount of crazing is partly associated with the magnitude of the thermal stress since as shown in the last entry in Table III when the temperature of the quenching bath was reduced to –32°C, there was no visible crazing.

There are three possible explanations for the observed reduction in the number of crazes at high temperatures. The first one is based on the possibility that crazes are formed; but, because of the rapid inversion of the surface stresses from tensile to compressive, the crazes are closed up. The second one involves the magnitude of the thermal stress at the surface because when the temperature of the thermoplastic is greater than T_g , the sample has a rubbery-type modulus so that when the surface is

quenched to the glass, the stress in the surface is much reduced. The last one is based on the possibility that the liquid plasticizes the surface and is similar to the argument of Kambour et al.²

Effects of Thermal History

Samples of BPAC were annealed at 165°C to remove residual strains and stresses. These samples were then thermally quenched into ice water. Upon heating to 125°C for 20 min and then being quenched into IPA at room temperature, there was no evidence of crazing or cracking. Upon annealing at 125°C for 24 h and then quenching into IPA, the number of crazes was observed to be greater than for the as-molded samples. These results suggest that the residual compressive stresses in the as-molded samples and the samples thermally quenched from 165°C suppress the ability for the sample to craze. This interpretation was further supported by quenching the front and back surface of bent samples and noting that only a few crazes formed on the surface under compression and they were parallel to the compression axis. In contrast, hundreds of crazes appeared on the surface under tension and were perpendicular to the tensile stress. Other thermally quenched samples that had aged overnight at room temperature were also tested and these samples had about the same amount of crazing as the as-molded samples but much less than the samples that had been annealed at 125°C overnight. These results suggest that the residual internal stresses are relaxing and are in agreement with changes observed in the creep compliance upon aging of BPAC at room temperature after thermal quenching.¹⁰

Effects of Molecular Weight

It has been known for some time that many of the properties of polymers are dependent on molecular weight. For this reason, the effect of molecular weight on the thermally induced crazing of BPAC in IPA was investigated. These results are presented in Table IV. It is immediately obvious that as the molecular weight increases, the amount of crazing decreases. This result is similar to previous work wherein it was observed that as the molecular weight increased, the fracture stresses increased.¹¹

Time-Dependent Crazing

The effect of immersion time on thermally induced crazing of BPAC in the presence of IPA was determined, and it was found that extensive crazing can

Table III Effect of Quenching Conditions on the Thermally Induced Crazing of PBAC

T_1 (°C)	T_2 (°C)	Results
100	25	No crazing
113	25	One long fine craze
120	25	Several crazes
125–153	25	Hundreds of fine crazes
164	25	No crazes
102	24	One long craze
102	4	Hundreds of fine crazes
102	–32	No crazing

occur in times of less than 1 s. This observation indicates that the quenching liquid, e.g., IPA does not have time to penetrate surface more than 0.1 μm because the diffusion coefficients are of the order of 10^{-9} cm^2/s . In view of this conclusion and the known thermal stresses, it appears that the mode of failure must involve surface imperfections. This idea is similar to one previously suggested by Argon.¹² As tests of this idea, the surface of BPAC plaques were sealed off in a checkerboard pattern and then crazed by thermal quenching into IPA. Each of the open and the covered squares were checked for crazing. All of the uncovered squares had crazed while none of the covered squares had crazed. As the thermal quenching conditions were reduced, some of the uncovered squares did not show any evidence of crazing.

Nucleation and Growth of Crazes and Cracks

Manning and Lineback have proposed that the number of crazes/cracks that form in ceramic materials as a result of thermal shock is given by an extension of the Griffith equation as discussed by Berry and is similar to one proposed by Hasselman.¹³⁻¹⁵ The derivation is outlined below.

The strain energy (SE) for an elastic body is given by

$$\text{SE} = \sigma\epsilon/2 = E\epsilon^2/2 \quad (1)$$

where σ is the stress, ϵ is the strain, and E is the

elastic modulus. If this equation is equated to the Griffith energy (GE), then it is given by

$$\text{GE} = \sigma^2/2E = \gamma/\pi c \quad (2)$$

where γ is a specific surface energy and c is the size of a flaw. Following Berry, the effective modulus of a body containing N cracks is given by

$$E_{\text{eff}} = E_{\text{int}}/(1 + 2\pi Nc^2) \quad (3)$$

where it is assumed that no interactions occur between the cracks. If all of the cracks in the material were of the same size and they were separated from one another by a sufficient distance, then it can be assumed that the cracks do not affect the Griffith stress. As a result, it is the crack size, the surface energy, and the intrinsic modulus that affect it. Following Manning and Lineback, one may rewrite Eq. (2) as

$$\text{GE} = \gamma \langle 1/\pi c + 2Nc \rangle \quad (2a)$$

which predicts that for constant values of γ and GE the number and size of the cracks are interrelated, i.e., as the number of cracks increase then their size must decrease and vice versa.

If one assumes that the thermal stress is given by

$$\sigma(\Delta T) = f(\beta)E\alpha \Delta T \quad (4)$$

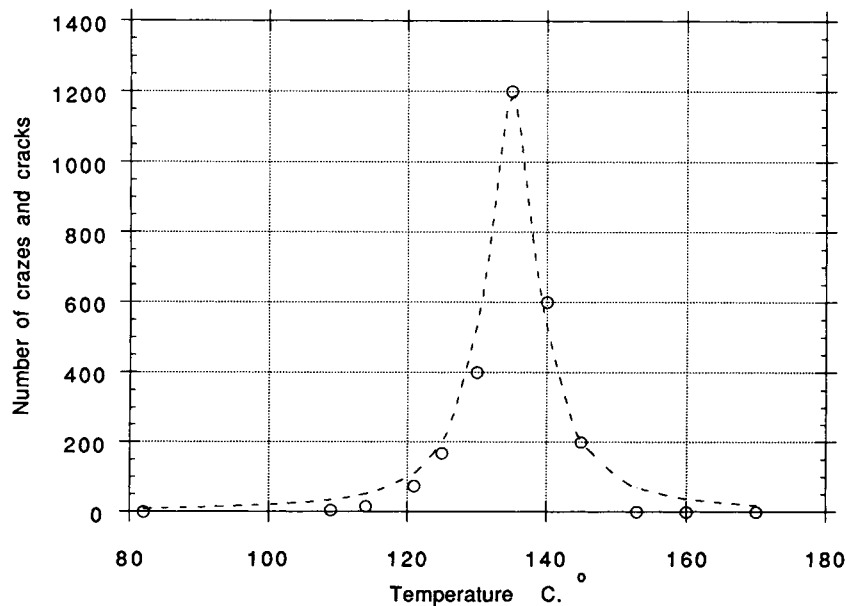


Figure 1 The number of crazes per square inch which form in BPAC vs. the temperature from which the sample was quenched.

Table IV Effect of Molecular Weight on the Thermally Induced Crazing of Bisphenol-A in IPA When Thermally Quenched from 125 to 25°C

Molecular Weight g/mol (10^3) ^a	Results
31.1	Numerous crazes oriented parallel to flow axis
34.1	Approximately the same number of crazes as in the lower molecular weight material
36.2	Few crazes, but again oriented parallel to the flow axis
39.2	Several crazes that are longer than those observed in the lower molecular weight material
42.8 ^b	No crazes

^a Based on polystyrene standard.

^b Thermal quenching from 125 to 0°C causes several crazes to be observed.

where β is the Biot number and is equal to ht/K , h is the heat transfer coefficient, K is the thermal conductivity, α is the thermal coefficient of expansion, and ΔT is the difference between the temperature of the oven and that of the quenching bath. By combining Eqs. (2), (3), and (4), then the critical value of ΔT is given as

$$\Delta T^2 = \frac{2\gamma}{\alpha^2 E} \left(\frac{1}{\pi c} + 2Nc \right) \quad (5)$$

and the number of cracks formed is given as

$$N_c = \frac{\alpha^2 \Delta T_c^2 E_{int}}{4\gamma c} - \frac{1}{2\pi c^2} \quad (6)$$

For the cases where $N = 0$ and where $dN/dc = 0$, one recovers the classic Griffith equation. Equation (6) indicates that the number of crazes that form is a function of several factors. In particular, Eq. (6) indicates that if one keeps the quenching fluid and the thermoplastic constant and assumes that γ is constant while varying only ΔT , then the number, N , of crazes would be a measure of the effect of temperature on c . However, the surface tensions of both the thermoplastics and the liquids are known to be temperature dependent, so that the number of crazes was expected to reflect changes in both γ and c . As a test of this hypothesis, the number and lengths of crazes that were formed in BPAC as a function of ΔT for isopropyl alcohol were measured. Assuming a value of 2 MPa for the modulus, the values of γ at 109 and 135°C were determined and

are, respectively, 4.4×10^5 and 1.2×10^5 ergs/cm². The values for γ are smaller than those previously measured on dry BPAC,¹⁶ but are certainly consistent with the idea that the adsorption/absorption of IPA reduces the energy to initiate and propagate crazes and cracks and that the values are temperature dependent. On this basis, it is obvious that as the fluids are changed, the value of γ may also change, but at this point in time we have not been able to find a direct correlation of the crazing behavior with the surface tension of the fluids, their wettability, or contact angles. This problem reflects as noted above the fact that crazing is not a function of a single variable and that there can be competing mechanisms involved. For example, Kambour, Gruner, and Romagosa² have presented data that indicate quite clearly that some liquids have a high solubility in BPAC, and these liquids tend to plasticize the surface. A similar observation has been made in the case of polyether imide (PEI).⁴ This plasticization of the surface causes the modulus and correspondingly the thermal stresses to be reduced. A second set of liquids appear to cause BPAC to crystallize. As a result of this crystallization internal voiding occurs and may lead to the formation of crazes and cracks. Other liquids are absorbed by BPAC to a much lesser extent and result in varying degrees of crazing and cracking. On the basis of Eq. (6), it appears that the primary variable for these latter liquids is the value of γ , which is a consequence of the interaction of the liquid with the surface and/or defects within the surface. Of course, γ has been defined as the energy to create two new unit areas of surface and to include any work due to plastic deformation adjacent to the surface.^{14,15} If this surface area is created in the presence of an adsorbed and/or absorbed liquid or vapor, how and why is γ changed? It is possible that the liquid serves only to reduce the stress necessary to nucleate crazing and cracking around surface defects and is similar to stress-sorption cracking of metals.^{17,18} For example, Langmuir demonstrated that only a monolayer of adsorbate is needed to reduce the affinity of surface metal atoms for themselves or their environment.¹⁹ Similarly, thermochemical crazing may involve a decrease of surface affinities, with the distinction that only those specific adsorbates are effective that decrease the attractive forces of adjoining species near the stress concentration point around surface defects. There are several types of surface defects that need to be considered. The primary type of defects would be geometric and would be any type of surface roughness including surface scratches. A second type of defect would involve a heterogeneity,

which might be a dust, catalyst, or some other foreign particle and would be located at the interface. Other types of defects associated with end groups and molecular conformations at the surface may also be involved. It is obvious that there is a critical need to be able to identify these defects prior to crazing in order to further our understanding of this mechanism of failure.

SUMMARY

It has been shown that surface crazes can be induced in a variety of amorphous thermoplastics by thermally quenching them into simple organic liquids such as isopropyl alcohol. It is observed that the number of crazes and their length are dependent on the immersion liquid, the difference in the temperatures, the molecular weight of BPAC, and the thermal history. The results are interpreted in terms of a model that incorporates the effects of thermal stresses, the surface properties of the solid in contact with the immersion liquid, and defects in the surface. The surface energy for BPAC in the presence of IPA is determined to be smaller than for dry BPAC.

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