Mechanical Properties of Polypivalolactone: Effects of Thermal History and Solvent Exposure

CHARLES W. PAUL,* *Allied-Signal, Corporate Research, Polymer Laboratory, Columbia Road and Park Avenue, Morristown, New Jersey 07960*

Synopsis

The mechanical properties and solvent resistance of polypivalolactone (PPL) were determined as part of our study of PPL composites. High elongation (30%) films were obtained when moldings were cooled slowly and annealed for 15 min at 200°C prior to testing. The ductility fell when samples were held at 71°C for 2 weeks either dry or more so when exposed to water. Molecular weight degradation is believed to be responsible. This conditioning, however, raised the modulus of the sample by up to 32% in the vicinity of the conditioning temperature. It is speculated that this is due to densification in some of the stressed amorphous regions. The high crystallinity of PPL makes it insoluble in all common organic solvents. However, it swells and softens considerably when immersed in methylene chloride or methyl ethyl ketone.

INTRODUCTION

Polypivalolactone (PPL) has an exceptionally high degree of crystallinity, up to 80%. It is primarily this feature which has attracted interest in this material as a candidate for applications such as apparel fiber,[1] modification of rubbers,[2] and most recently as a matrix for continuous fiber composites.[3,4] In the latter application, composite prepregs were formed via *in situ* polymerization. It was during the course of investigating PPL composites that we discovered the unusual dependence of PPL's mechanical properties on prior thermal and solvent history. This paper describes these results.

EXPERIMENTAL

Pivalolactone monomer obtained from Polysciences was vacuum-distilled at ~ 30°C, inhibited with ~ 0.03 wt % 4-chlorobenzene diazonium hexafluorophosphate, and stored in a freezer at −15°C. Prior to use, 0.1 wt % of the antioxidant *N*-phenyl-2-napthylamine was dissolved in the monomer, and then 0.1 vol % of the initiator tri(*n*-butyl) phosphine was added. This polymerization mixture was injected through a port into an aluminum mold preheated to 130°C. The two halves of the mold were clamped vertically between electrically heated aluminum platens. Polymerization was completed in about 1 min. The intrinsic viscosity and weight average molecular weight ($\bar{M}_w$) of the polymer were measured in trifluoroacetic acid. $\bar{M}_w$ was determined by low angle light scattering using a Chromatix KMX-6. The molecular weight distribution was measured by gel permeation chromatogra-

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*Present address: National Starch and Chemical Corp., Corporate Research, Finderne Avenue, Bridgewater, NJ 08807.
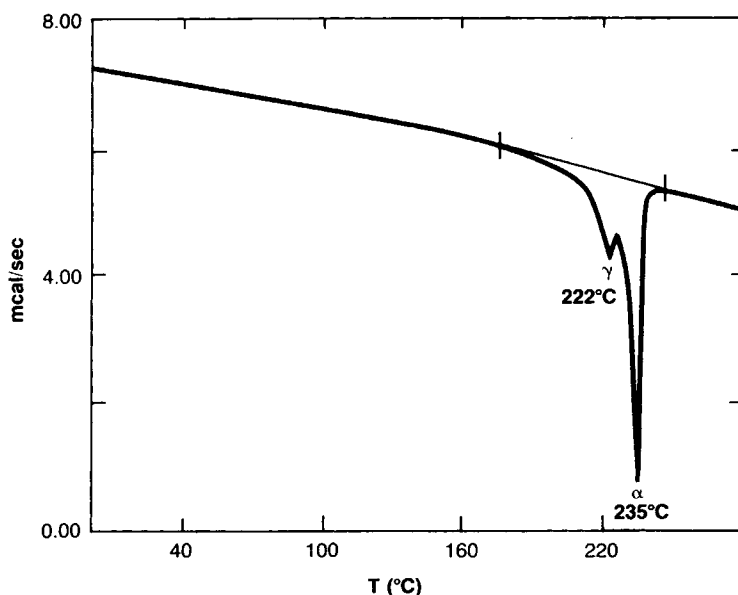
Fig. 1.   DSC scan of PPL (10°C/min) after melting and then cooling at 80°C/min.

phy in *m*-cresol at 110°C using a Waters 150C GPC with refractive index detection under the following operating conditions: 0.5% solution, 150 μL injection, 1 mL/min flow rate, 10^5, 10^4, and 10^3 Å μStyragel columns in series. Molded polymer samples were analyzed by dynamic mechanical analysis (DMA) using a Polymer Labs DMTA operated at 1 Hz and a heating rate of 3°C/min, by thermogravimetric analysis (TGA) using a DuPont 951 TGA at a heating rate of 3°C/min, and by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2. An argon blanket was maintained over the sample in each of the above experiments. Tensile strength and elongation were determined on microtensile dogbone specimens (3/16 × 0.9 in. gage section, 1.5 in. overall length) in an Instron using a crosshead speed of 0.050 in./min.

RESULTS AND DISCUSSION

Crystalline Phases

PPL has three crystalline forms. The α and γ are 2/1 helices with anti-parallel chain packing.[5] The β-phase is only induced by stretching α-phase PPL[6,7] and was therefore not present initially in any of our samples. A typical DSC scan for PPL containing both α- and γ-phases is shown in Figure 1. The γ-phase can be distinguished from the α-phase under cross-polarized light. While the α-phase spherulites have a smooth radial texture, the γ-phase spherulites have a rougher ringed or angular texture[5] and are generally smaller in size. The amount of γ-phase increased with cooling rate, and at 80°C/min 25–30% of the sample is γ-phase. However, extremely rapid quenching, such as by liquid nitrogen cooling in the DSC unit, produced only the α-phase. The quenching of molded films (0.015 in. thick) by rapid transfer

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*In Oosterhof's paper the γ-phase discussed here is denoted as the β-phase.

from a press to an ice bucket also produced only α-phase PPL. The latter result may account for Oosterhof's[6] claim that the γ-phase* only arises upon slow cooling if what he calls "slow" cooling is still relatively fast. All other reports[5,7-9] indicated that the γ-phase only appeared upon rapid cooling. The disappearance of the γ-phase at extremely rapid cooling rates that we observed was not reported in any of these works. When samples containing both α- and γ-phase were annealed near T_γ, the γ-phase was eliminated, the melting point of the α-phase rose, and the degree of crystallinity increased. For example, when a sample which was cooled by transfer of the mold to a cold press was subsequently annealed at 225°C for 5 h, the α-phase melting point rose from 239° to 244°C and the crystallinity rose about 8%. Annealing at 225°C always eliminated any γ-phase (as determined by DSC), even though this is slightly below the temperature of the maximum in the γ-phase endotherm (228°C). In contrast, Oosterhof[6] observed the elimination of the γ-phase upon annealing between T_γ and T_α. A similar increase in crystallinity was achieved simply by annealing for 15 min at 200°C (below T_γ). This short annealing raised the α melting point by only about 1°C but raised T_γ by 5°C. X-ray data[5] showed indications of γ crystals eliminating defects upon annealing, which is consistent with an increase in T_γ. The relative amounts of γ- and α-phase are difficult to determine due to peak overlap, but appear to be unchanged in our samples by annealing at 200°C for 15 min. This brief annealing below T_γ dramatically increased the elongation to break of PPL as discussed below.

Tensile Properties

The tensile properties of PPL were extremely sensitive to the method of molding and subsequent annealing. Initially, films were prepared by molding
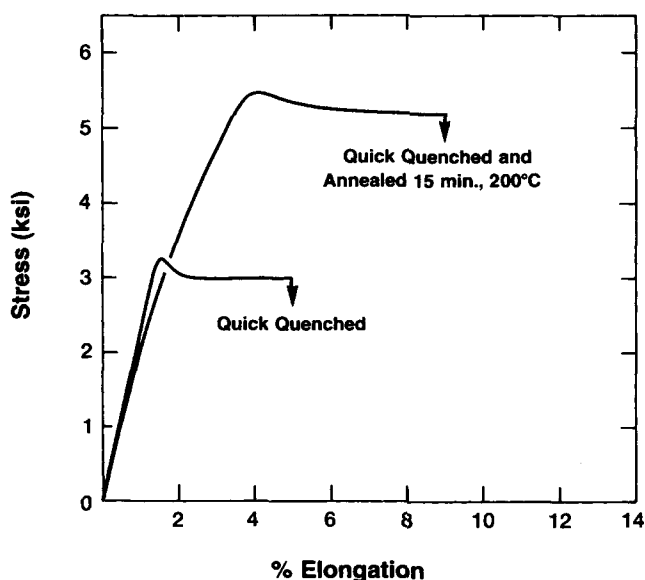

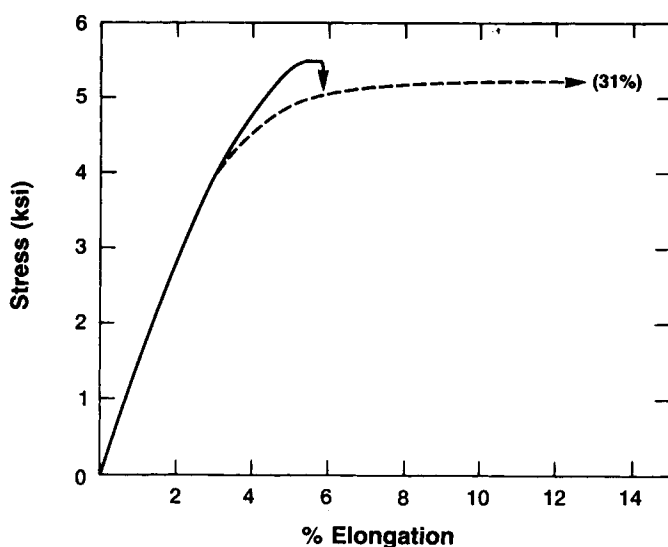Fig. 2(a). Tensile stress–strain curves for quenched PPL.

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Fig. 2(b). Tensile stress–strain curves for PPL cooled at moderate rates in a press: (——) cooled in press; (---) cooled in press and annealed 15 min at 200°C.

in a window frame and quenching the film in an ice bucket. We found, however, that these films were both weak and brittle, with tensile strengths ~ 3.5 ksi and elongations to break of about 5%. The strength of these samples could be raised to the value of 5.5 ksi reported by Oosterhof[6] by annealing for 15 min at 225 or 200°C, or by cooling the sample more slowly in the press. Typical stress-strain diagrams are shown in Figure 2. The tensile data after various thermal histories are summarized in Table I. Annealing at 200°C improved the elongation of quick-quenched samples, while annealing at 225°C slightly decreased the ultimate elongation. However, neither procedure raised the elongation of the films to the reported 10–70%.[6] Noah and Prud'homme[10] were also unable to obtain ductile PPL samples from quenched films even after annealing for 6 h at 195°C. We found that we could obtain high elongation PPL films by altering their thermal history. Films prepared in a closed mold cooled by transfer to a cold press achieved elongations of 31 ± 10% when annealed at 200°C for 15 min. Without annealing the elongation to break was 5.8% (see Table I).

TABLE I
Tensile Properties of PPL Films

| Thermal history	Yield stress (ksi)	Yield strain (%)	Elongation at break (%)
Quick quenched	3.4 ± 0.1	1.5 ± 0.4	5.3 ± 2.2
Annealed 15 min, 225°C	5.6 ± 0.3	3.3 ± 0.4	3.7 ± 0.9
Annealed 15 min, 200°C	5.5 ± 0.7	4.0 ± 0.1	9.3 ± 2.2
Cooled in press	5.6 ± 0.1	5.2 ± 0.4	5.8 ± 0.7
Annealed 15 min, 200°C	5.2 ± 0.1	—	31.0 ± 10

(a)
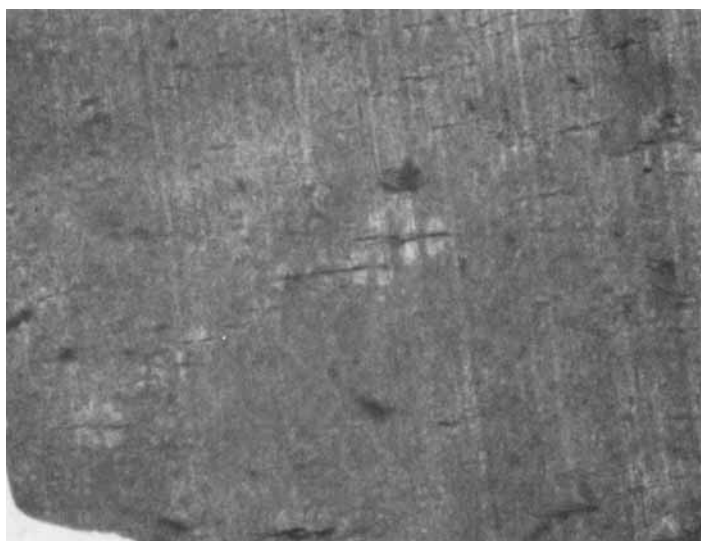
(b)

Fig. 3. PPL microtensile specimens observed under crossed polarizers: (a) quick-quenched sample at 1300×; (b) quick-quenched and then annealed at 200°C for 15 min; 320×; (c) cooled-in-press sample at 90×; (d) cooled in press and then annealed at 200°C for 15 min, 90×.

Failed tensile specimens with various thermal histories were analyzed under an optical microscope using crossed polarizers. Quick-quenched samples contained small spherulites (~ 10 μm) unevenly distributed throughout the sample [see Fig. 3(a)]. These samples were roughly 70% crystalline. None of the ringed γ-phase spherulites were evident. A few straight horizontal cracks away from the fracture surface were visible. Quenched samples which were
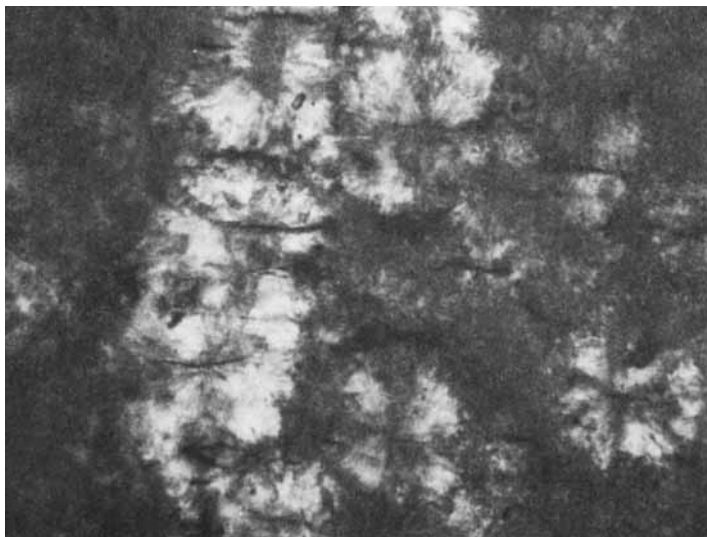
(c)

(d)

Fig. 3.   *(Continued from the previous page.)*

annealed for 15 min at 200°C had spherulites about twice as large but still nonimpinging. These samples exhibited multiple small horizontal cracks virtually all of which went through the center of a spherulite and stopped near its edges [see Fig. 3(b)]. The region adjacent to the fracture zone was cloudy. It may be that the annealing process removes the internal stresses generated by quick quenching, and consequently the annealed samples did not begin to fail until higher mechanical stresses were reached. Apparently fracture of spherulites occurs first, prior to catastrophic fracture. The samples cooled more

slowly, by transfer of the mold to a cold press, had a very different morphology. Spherulites impinged severly and grew as large as the sample width (~ 400 μm). They were visible to the naked eye and made the sample rough on one side. Like the quenched and annealed samples, many small cracks developed prior to fracture. Some of these went through spherulites and others followed their boundaries [see Fig. 3(c)]. While they run horizontally, they are not straight. Annealing leads to very extensive cracking. On the rough side of the sample, cracks occurred at virtually every spherulite boundary in the vicinity of the final fracture [see Fig. 3(d)]. On the smooth side of the sample, cracks appeared predominantly through spherulites rather than around them. Away from the break, the extent of cracking decreased, but there were still cracks throughout the gage section. The cracks look like waves running horizontally across the sample. Annealing did not increase the spherulite size, but did lower the yield stress [see Fig. 2(b)]. The latter observation and the shape of the stress–strain diagrams displayed in Figure 2(b) are in agreement with Oosterhof's findings.[6] In the press-cooled samples, stresses are concentrated in the valleys between spherulites on the rough side of the sample. Cracks most likely initiate here and travel through spherulites on their way to the smooth side.

Effects of Solvent Exposure and Thermal Aging

A crucial test for any potential composite matrix is solvent resistance. Bars of PPL suitable for dynamic mechanical analysis (DMA) (1.6 × 0.4 × 0.06 in.) were cut from a plaque molded in a closed mold and cooled by transfer to a cold press. The DMA scan of an as-molded PPL bar is shown in Figure 4. The T_g would appear to be at about 6°C, but it is very broad and may extend up to 100°C. Broad tan δ peaks are typical with highly crystalline polymers. The true T_g of unstressed amorphous PPL is probably close to 6°C, but, owing to internal stresses generated upon crystallization, a considerable portion of the
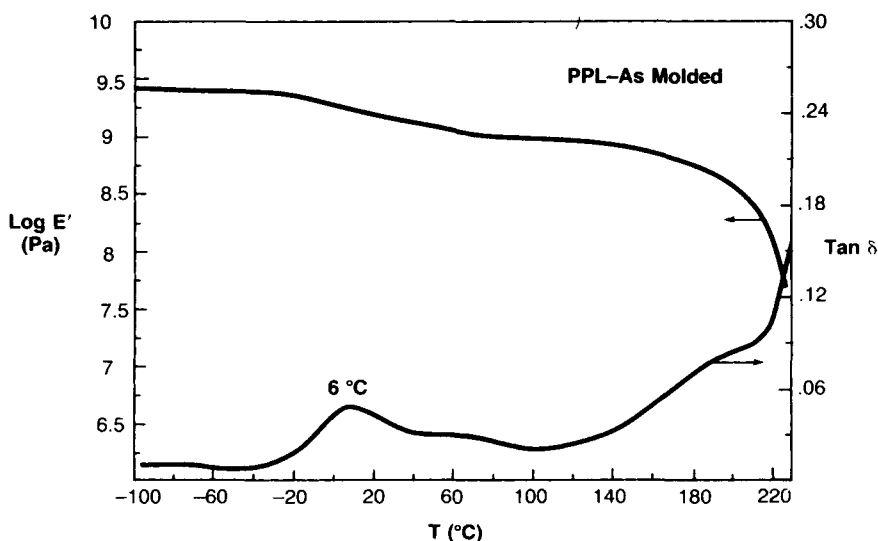

Fig. 4. DMA of PPL as molded.

amorphous fraction has a range of higher T_g's. It should be noted that the true T_g of PPL is a subject of debate.

Malik and Prud'homme[11] reported dielectric and dynamic mechanical data which showed transitions centered at 2 and 137°C. The mechanical relaxation at 2°C increased in intensity as the percent crystallinity increased, and therefore was ascribed to a crystal transition. The relaxation at 137°C was barely observable in the dynamic mechanical spectrum, but showed up strongly in the dielectric data. The opposite was true of the relaxation at 2°C. It is the author's opinion that the low temperature transition is most likely the T_g. The strongest evidence for this is Pratt and Geil's work,[9] which showed that ultra-quenched completely amorphous PPL crystallizes when warmed to room temperature. Thus, the T_g of PPL must be below room temperature. Further, less conclusive evidence for this is that the room temperature stiffness (250 ksi) and strength (5.5 ksi) of PPL are below that one would expect for a highly crystalline polymer below its T_g. At -50°C, these mechanical properties increase to 413 ksi-modulus and 9.5 ksi-tensile yield stress, which are reasonable for a glassy polymer. PPL shows good percent retention of its room temperature modulus up to very high temperatures due to its high crystallinity. Figure 5 illustrates this point and compares the modulus retention of as-molded PPL with that of PPL which was annealed for 5 h at 225°C. Annealing raised the crystallinity from 74 to 80% as determined by DSC using 146.8 J/g as the heat of fusion for 100% crystalline PPL.[8] As a result, annealed PPL shows a better retention of modulus with temperature. Annealing reduced the molecular weight of the sample by about 7% based on the 5.5% drop in intrinsic viscosity and the relationship

$$[\eta] = 1.89 \times 10^{-4}(\text{dl/g})(\text{mol/g})^{0.74}\overline{M}_w^{0.74} \tag{1}$$
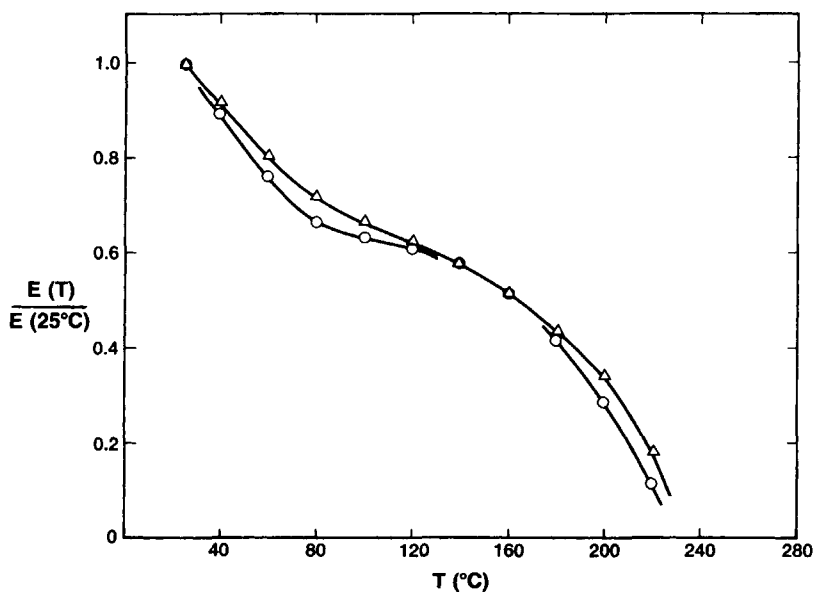

Fig. 5. Modulus retention versus temperature for PPL as molded (○) and after annealing for 5 h at 225°C (△).

TABLE II
Effects of Solvent Exposure at Room Temperature

Sample	Annealed	Solvent	Wt % pickup vs. time						% Retention RT modulus	ΔT_g (°C)
			3	7	9	11	14	days		
PPL	x	MEK	5.7	6.7	6.7	6.7	6.7		54	−27
	—		3.9	8.4	8.7	8.7	8.8		50	−25
			2	6	8	11	13	days		
PPL	x	Hydraulic	−0.01	−0.01	0	0.04	0.01		—	—
	—	fluid[a]	0.01	−0.01	0	0.03	0.01		—	—
			1	5	7	9	13	days		
PPL	x	JP-4[b]	0.06	0.12	0.16	0.19	0.22		99	0
	—		0.05	0.14	0.15	0.19	0.20		106	—
			4	6	8	11	13	days		
PPL	x	CH_2Cl_2	21.3	22.5	22.7	22.7	22.4			−37
	—		26.4	26.9	27.3	27.0	27.3		33	−38
			4	6	8	11		days		
PPL	x	Water	0.13	0.13	0.14	0.14			—	—
	—		0.15	0.19	0.22	0.22			—	—

[a] Hydraulic fluid = Skydrol 500 B-4 from Monsanto.
[b] JP-4 = jet fuel for Air Force planes. Obtained from Maguire AFB.

determined experimently in trifluoracetic acid at 25°C on polydisperse samples with $\overline{M}_w/\overline{M}_n \approx 2.5$ (by gel permeation chromatography). Our polymerization conditions produced PPL with $\overline{M}_w \sim 300{,}000$.

DMA bars of as-molded and annealed (5 hr, 225°C) PPL were immersed in various solvents considered important in aerospace composite applications. The weight pickup was recorded as a function of time for about 2 weeks. The final data are tabulated for room temperature exposure in Table II and for 71°C exposure in Table III. Included in these tables are the change in T_g due to solvent exposure and the percent retention of the initial modulus at room temperature; both were determined by DMA. Skydrol is a hydraulic fluid from Monsanto which contains phosphate esters, primarily tributyl phosphate and dibutyl phenyl phosphate. Jet fuel consists of primarily aliphatic hydrocarbons. Alkaline cleaner probably contains phosphates. While PPL did not dissolve in any of these solvents due to its high crystallinity, it did soften badly in methylene chloride, methyl ethyl ketone (MEK), and 71°C alkaline cleaner. The latter solvent probably hydrolyzed PPL as evidenced by the weight pickup which increased with time up to 8 days and then decreased. The results in Tables II and III while not damning are considered somewhat disappointing with regard to the potential of PPL as an aerospace composite matrix.

The modulus as a function of temperature after solvent conditioning was determined by DMA. These data $E^c(T)$ were normalized by the modulus at −95°C [$E^c(-95°C)$], and the results were divided by the same ratio obtained on the unconditioned PPL [$E(T)/E(-95°C)$]. The resulting plots are displayed in Figures 6–9. The ordinate is the relative modulus of conditioned (solvent exposed) vs. unconditioned PPL if it is assumed the modulus at

TABLE III
Effects of Solvent Exposure at 71°C

Sample	Annealed	Solvent	Wt % pickup vs. time						% Retention RT modulus	ΔT_g (°C)
			1	3	7	11	15	days		
PPL	x	Water	0.28	0.29	0.30	0.34	0.34		97	−6
	—		0.40	0.48	0.55	0.60	0.62		99	−4
			1	3	6	10	15	days		
PPL	x	Hydraulic fluid[a]	0.39	0.72	1.00	2.0	2.7		84	−1
	—		0.26	0.48	0.65	1.30	1.53		91	+1
			1	4	8	12	15	days		
PPL	x	Alkaline cleaner[b]	2.6	6.6	8.5	7.5	6.5		65	−11
	—		2.4	7.2	9.2	8.9	8.6		57	−13
			1	3	7	11	15	days		
PPL	x	Jet fuel A[c]	0.27	0.54	1.43	2.19	2.78		81	0
	—		0.22	0.43	1.01	1.33	1.51		95	0

[a] Hydraulic fluid, see Table I.
[b] Alkaline cleaner, obtained from Morristown Airport, pH = 11.
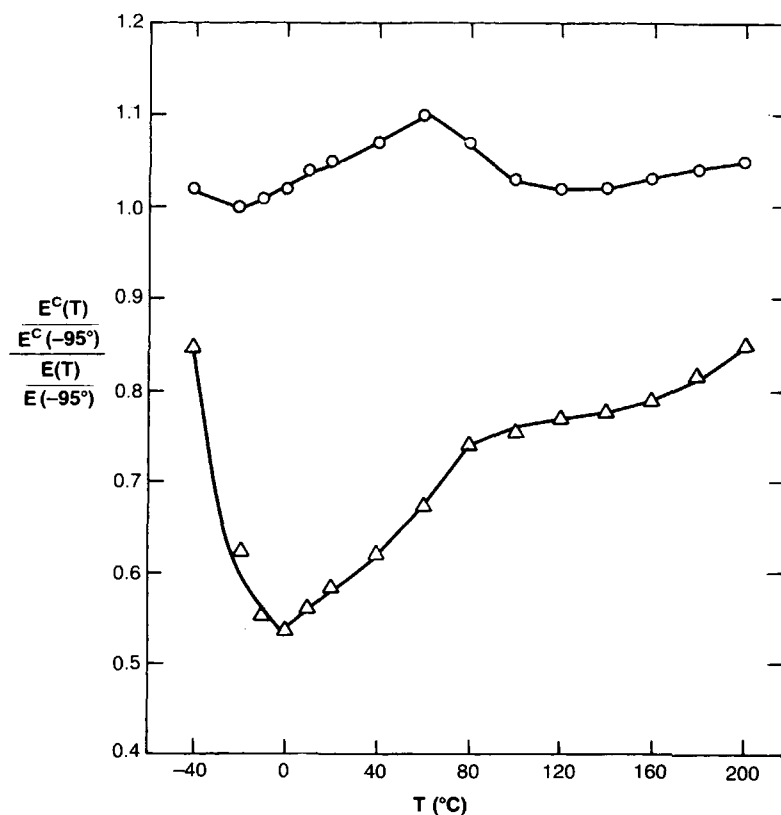[c] Jet fuel A = commercial jet fuel obtained from Morristown Airport.

Fig. 6. Relative modulus retention vs. temperature after immersion in solvent for 2 weeks at room temperature, PPL as molded: (○) JP-4 (0.2% pickup); (△) MEK (8.8%).
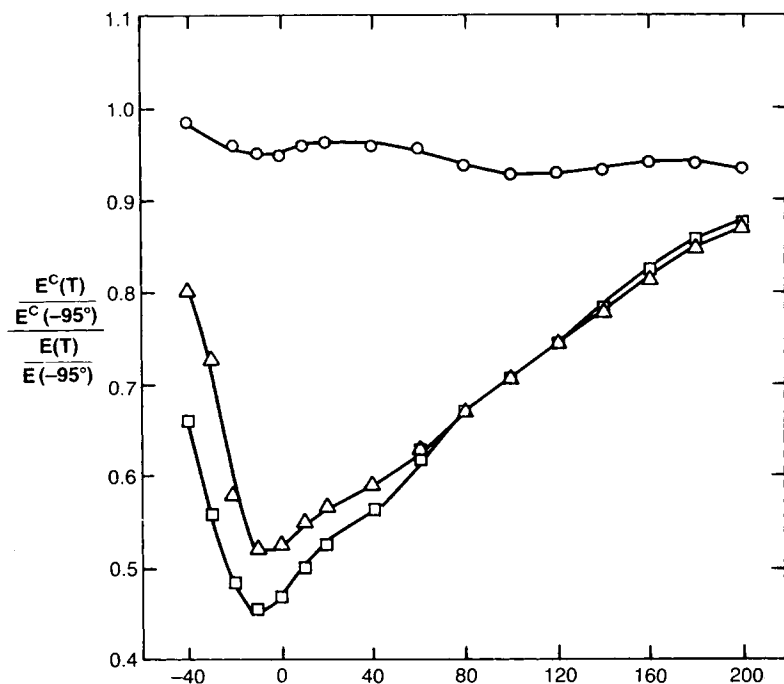
Fig. 7. Relative modulus retention vs. temperature after immersion in solvent for 2 weeks at room temperature, PPL annealed 5 h at 225°C: (○) JP-4 (0.20% pickup); (△) MEK (6.7%); (□) CH_2Cl_2 (22.4%).

−95°C is essentially unaffected by the presence of solvent. By comparing the room temperature modulus drop on conditioning so calculated vs. that determined experimentally, the validity of this assumption was tested. It was valid except for the PPL samples which picked up more than 7% solvent. Above 7% pickup, the −95°C modulus of PPL was somewhat lower, and therefore the relative modulus retention after solvent exposure was actually worse than indicated in Figures 6–9.

The data in these figures are also complicated by solvent loss during DMA testing. Thermogravimetric analyses conducted at the same heating rate as the DMA (3°C/min) showed that weight loss began immediately (starting at room temperature) and continued throughout the experiment, being essentially complete by 200°C. Figures 6–9 indicate that higher solvent pickup leads to poorer relative modulus retention and that the poorest retention for a given sample generally occurs in the vicinity of T_g as expected. Lower modulus retention near T_m was also observed, especially after exposure to alkaline cleaner. Degradation of PPL by this solvent probably lowered the melting point.

An intriguing feature appears in Figures 8 and 9: The relative modulus retention curves after 71°C solvent exposure show a broad maximum between 40 and 120°C. After discovering these maxima, PPL samples were conditioned at 71°C in air and DMA data taken. These results, also displayed in Figures 8 and 9, show that the thermal conditioning, not solvent conditioning, are responsible for these peaks. DSC data showed that the degree of crystallinity,
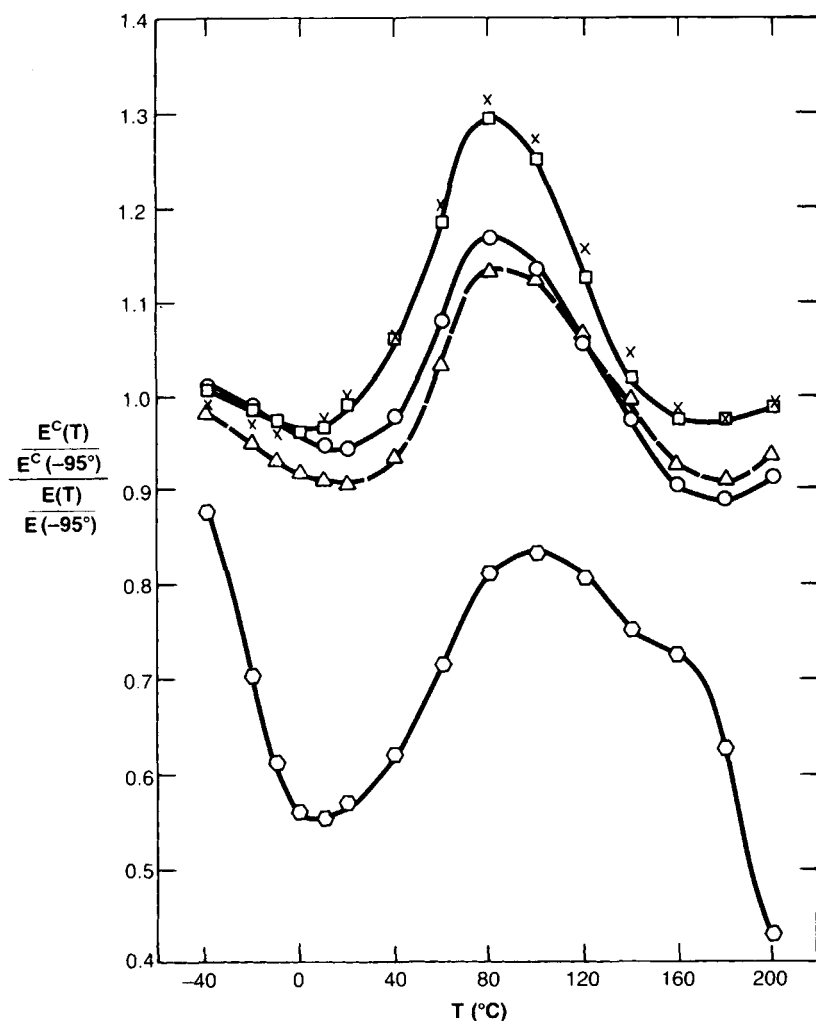
Fig. 8. Relative modulus retention vs. temperature after immersion in solvent for 2 weeks at 71°C, PPL as molded: (×) no solvent; (□) water (0.62% pickup); (△) hydraulic fluid (1.5%); (○) jet fuel A (1.5%); (○) alkaline cleaner (8.6%).

and the melting points of the crystalline phases as well as their relative proportions were unchanged by thermal conditioning. Optical microscopy also showed no change in average spherulite size. Comparing the DMA curves of unconditioned PPL (Fig. 4) with PPL after 2 weeks at 71°C in water (Fig. 10) reveals that the broad tan δ peak in the vicinity of 60°C has been very much reduced. This fact prompts the following speculation on the cause of the maxima seen in Figures 8 and 9.

First, it should be noted that while the relative modulus retention at 80°C is up to 32% higher after 71°C conditioning, the absolute modulus is still only 86% of its 25°C value, i.e., the modulus decreases monotonically with temperature, even though the relative modulus retention shows a maximum. The broad loss peak at about 60°C in the unconditioned PPL sample (Fig. 4)
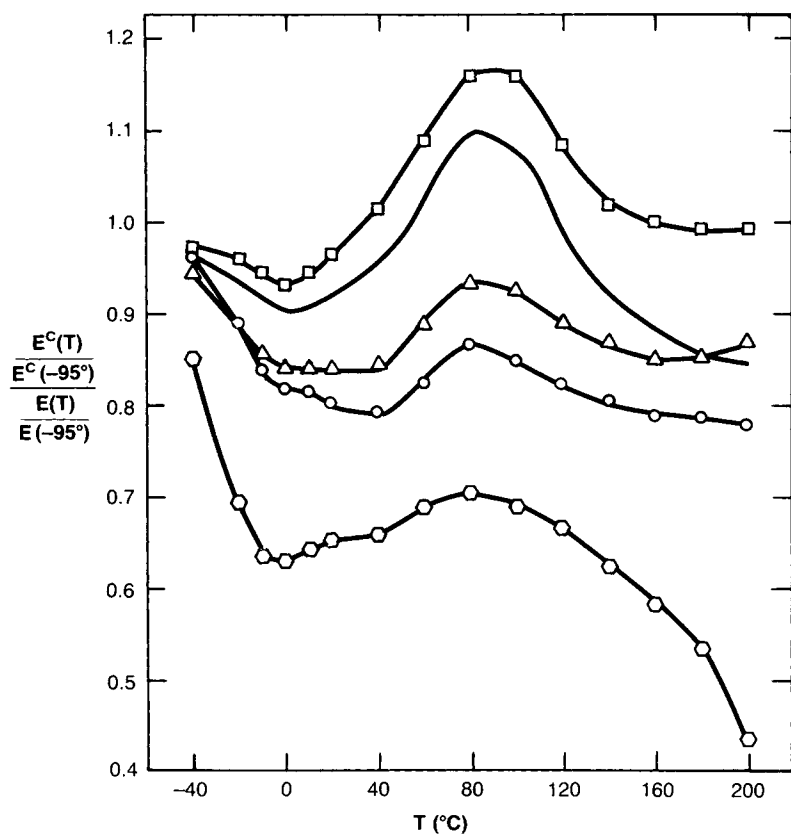
Fig. 9. Relative modulus retention vs. temperature after immersion in solvent for 2 weeks at 71°C, PPL annealed 5 h at 225°C: (□) water (0.34% pickup); (—) no solvent; (△) hydraulic fluid (2.7%); (○) jet fuel A (2.8%); (◯) alkaline cleaner (6.5%).
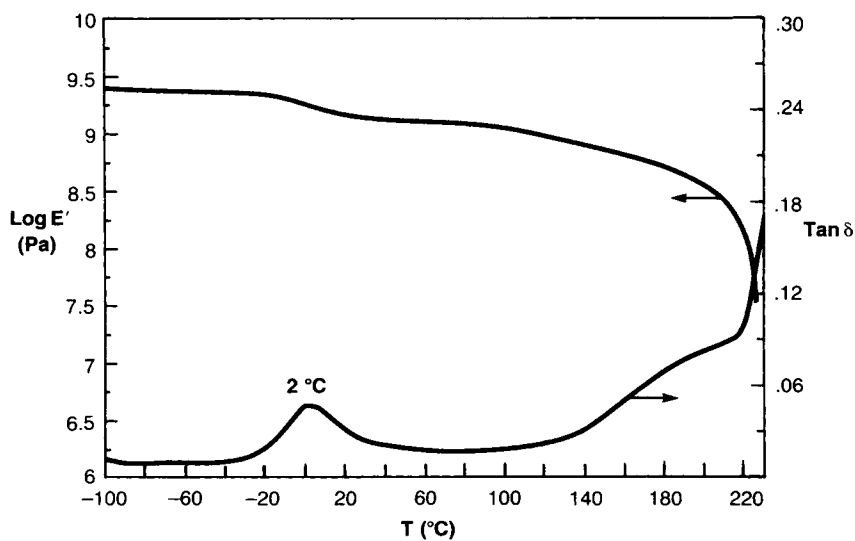

Fig. 10. DMA of PPL (as molded after 2 weeks in 71°C water).

TABLE IV
Thermal and Hygrothermal Effects on the Tensile Properties of PPL

	% Retention of RT properties	
Test conditions	Tensile strength	Elongation to break
82°C	72	134
82°C after 18 days at 71°C[a]	71	68
82°C after 18 days at 71°C and 100% RH[b]	73	28

[a] Lost 0.044% of its weight on conditioning.
[b] Picked up 0.46% water.

probably represents the glass transition of highly strained amorphous regions. These regions arise due to the extreme crystallinity of the sample. Annealing at 225°C for 5 h reduces, but does not eliminate these regions, as the subsequent cooling to room temperature causes a substantial volume contraction particularly in the amorphous regions. The constraints imposed by the crystallites do not allow the amorphous regions to contract to an equilibrium level. As the temperature is raised and these strained amorphous regions go through their T_g, the greater free volume causes them to be less stiff. By conditioning, or more properly annealing, at a temperature in the vicinity of the T_g of these strained regions, the stresses can partially relax and these amorphous regions densify. When an annealed sample is tested by DMA, the reduced content of high T_g regions causes slightly poorer modulus retention just above the main T_g peak (see Figs. 8 and 9), but better retention at temperatures in the vicinity of the annealing point, because of the greater density (lower free volume) in the rubbery amorphous regions. The stiffness of the amorphous regions is critical as they absorb most of the strain of deformation. Due to the reduced level of internal stresses in the samples annealed for 5 h at 225°C, they are less dramatically affected by subsequent annealing at 71°C (compare Figs. 8 and 9).

The tensile properties of PPL at 82°C were also measured after conditioning at 71°C for 18 days both dry and at 100% relative humidity (RH). These results are summarized in Table IV. The samples tested were microtensile bars prepared in a closed mold cooled by transfer to a cold press and then annealed at 200°C for 15 min prior to any subsequent conditioning. Unconditioned specimens were more ductile but slightly weaker at 82°C than at room temperature. Conditioned samples were as strong, but much less ductile. The loss in ductility may be associated with the slight degradation in molecular weight which occurs upon conditioning. A 7% drop in $\overline{M}_w$ occurs on dry conditioning while $\overline{M}_w$ falls 9% under wet conditioning at 71°C. This degradation while not severe probably occurs disproportionately in the strength-limiting amorphous regions, particularly at spherulite boundaries, thereby embrittling the sample. Nonetheless, even the least ductile sample yielded prior to breaking and had an elongation to break of 5.5%.

SUMMARY

The properties of polypivalolactone, due to its high crystallinity, are very sensitive to how it is molded and its subsequent thermal history. PPL films must be cooled slowly and briefly annealed to obtain high elongation to break. Longer term conditioning (2 weeks) at 71°C raises the modulus in the vicinity of this temperature by up to 32% without an increase in crystallinity. It is proposed that this is due to densification of some of the stressed amorphous regions. The above conditioning lowers the molecular weight of PPL, even when an antioxidant has been added. While the reduction is less than 10%, it is believed to be responsible for the lower elongation to break of the conditioned material, through preferential degradation of the amorphous regions which tie together the crystallites. The reduction in $\overline{M}_w$ and the drop in elongation are both larger when 71°C conditioning is done at 100% relative humidity.

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