Mechanical Behavior of Poly(ε-Caprolactone)/ Poly(styrene-Co-Acrylonitrile) Blends

P. B. RIM* and J. RUNT,† *The Pennsylvania State University, Department of Materials Science and Engineering, Polymer Science Program, University Park, Pennsylvania 16802*

Synopsis

The mechanical properties of compatible poly (ε-caprolactone)/poly (styrene-co-acrylonitrile) blends were studied for samples prepared from both the melt and solution. The mechanical response was observed to be primarily dependent upon the variation of the glass transition temperature with blend composition. For certain compositions, varying the sample preparation scheme resulted in specimens of different modulus. This behavior was associated with differences in the degree of crystallinity.

INTRODUCTION

A compatible polymer blend is conventionally defined as one which exhibits a single glass transition temperature (T_g) between those of the pure component polymers. For amorphous compatible blends it might be expected that the mechanical properties would be a linear combination of the individual component properties. This idea was first tested by Yee for blends of poly(phenylene oxide) (PPO) and polystyrene (PS).[1] Certain tensile properties were found to be significantly greater than what a linear combination of component properties would predict. The basis for explaining this effect was provided by density measurements, which indicated a small negative excess volume of mixing. Yee postulated that relatively strong intermolecular interactions were responsible for the densification and stiffening of these materials. Other evidence supporting this idea in other amorphous, compatible blends has since been presented.[2-6]

The mechanical properties of compatible blends which contain one or more crystalline polymers (crystalline/compatible blends) have been studied in only a few cases.[7-9] In two previous publications we presented the thermal behavior and degrees of crystallinity for the crystalline/compatible poly(ε-caprolactone)/poly(styrene-co-acrylonitrile) (PCL/SAN) blend system.[10,11] We felt that it would be of interest to determine the extent to which the mechanical properties of this system could be related to the variation of T_g and crystallinity with blend composition and if any measurable synergism characteristic of totally amorphous compatible blends could be detected.

EXPERIMENTAL

The polymers employed in this study were a random copolymer of styrene and acrylonitrile and poly(ε-caprolactone) (Union Carbide Corp., PCL-700)

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* Present address: Johnson Wax, Racine, WI 53403.
† To whom correspondence should be sent.

and are identical to those used previously.[10,11] PCL ($T_g \approx 213$ K) is semi-crystalline whereas SAN ($T_g \approx 373$ K) is an amorphous polymer which was found by elemental nitrogen analysis to be 76% styrene by weight. In order to make comparisons between the samples in this study and those prepared previously, blends were again allowed to crystallize in both the presence and absence of solvent.

Solution-crystallized samples were prepared by initially making individual 1% solutions of the respective polymers in tetrahydrofuran followed by stirring for approximately 4 h. The solutions were subsequently blended in the proper proportions and stirred overnight. Twenty milliliters of the resulting solutions were then cast at room temperature into aluminum pans of 57 mm diameter. The resulting films were removed from the pans, placed under vacuum (6×10^{-5} torr) to remove residual solvent, and then aged at room temperature for approximately 2 months to insure "complete" crystallization. For blends having a T_g in excess of room temperature, physical aging (densification) of the glasses will occur during storage. The aging will take place at different rates for different blend compositions because of the temperature difference between T_g and room temperature. Melt-crystallized specimens were prepared by first melting the solution-cast films at 360 K for 2 min. The samples were subsequently quenched into liquid nitrogen, rapidly warmed to room temperature then aged for two months.

"Dogbone" tensile specimens were cut from the solution and melt-crystallized films. The overall length of the dogbone was 1.5 in. and the widths of the narrow and wide sections were 0.1875 and 0.625 in., respectively. Film thicknesses were on the order of 30–40 μm. Mechanical testing was performed at 23°C in tension on an Instron Table Model Universal Testing Instrument (TM-S) at a crosshead speed of 0.5 cm/min. A measure of the Young's modulus (E) was obtained from the initial linear portion of the load/elongation curves using the initial cross-sectional area of the test specimen. Elongation to break (ϵ_B), elongation at yield (ϵ_y), tensile strength (σ_B), and yield strength (σ_y) were determined by the usual methods. All data cited are the average of 5–8 runs.

RESULTS AND DISCUSSION

Solution-Crystallized Samples

Typical load/elongation curves for the solution-cast samples are depicted in Figure 1. In general, as expected, ϵ_B decreases with increasing SAN content whereas σ_B and E increase (Table I). The variation of E with blend composition is plotted in Figure 2. The modulus data will be highlighted in this and subsequent discussions because the good reproducibility of this data allows subtle differences between samples to be resolved.

Two important factors which need to be considered when rationalizing the mechanical behavior of this system are the blend T_g and degree of crystallinity (X_c). The T_g of interest is that which results after PCL has completed crystallization and not the T_g of the original blend composition. In a previous paper we found that we could rationalize the variation in
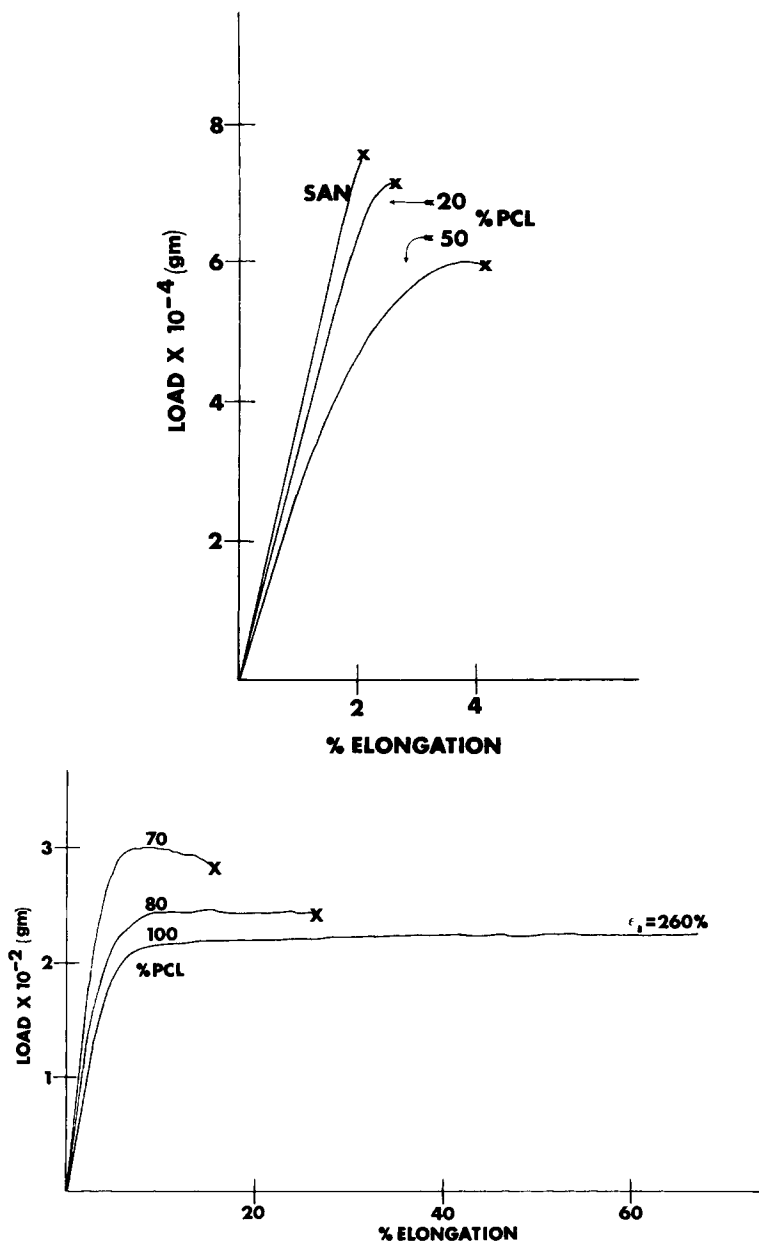
Fig. 1. Typical load elongation curves for solution-cast SAN/PCL blends.

blend crystallinity with composition by assuming a simple two phase (crystalline/amorphous) morphology.[10] The major assumption in this model is that, as PCL crystallizes, the amorphous regions increase in SAN concentration yet still remain homogeneous. By employing this model and the previously determined X_c's for the solution-crystallized samples, the blend T_g's, which would be expected at the cessation of crystallization, were approximated using the Fox equation[12] (Table II). In general, matrix T_g in-

TABLE I
Variation of Young's Modulus, Elongation to Break, and Tensile Strength with Composition
for Solution-Cast SAN/PCL Blends[a]

% PCL	E (psi)	ϵ_B	σ_B (psi)
100	33,000	2.2	1900
	±3,200	±1.3	±170
90	31,700	0.63	1600
	±3,600	±0.38	±70
80	54,700	0.91	2100
	±2,900	±1.3	±180
70	79,800	0.13	2500
	±8,600	±0.05	±290
60	114,000	0.076	3800
	±16,300	±0.009	±300
50	200,000	0.042	4400
	±13,800	±0.005	±490
40	232,000	0.024	4500
	±25,400	±0.003	±390
30	210,000	0.030	4600
	±27,700	±0.006	±640
20	243,000	0.032	5200
	±9,700	±0.003	±740
10	292,000	0.027	5800
	±13,500	±0.007	±540
0	294,000	0.030	6200
	±25,300	±0.009	±740

[a] The reported errors are ±1 standard deviation.
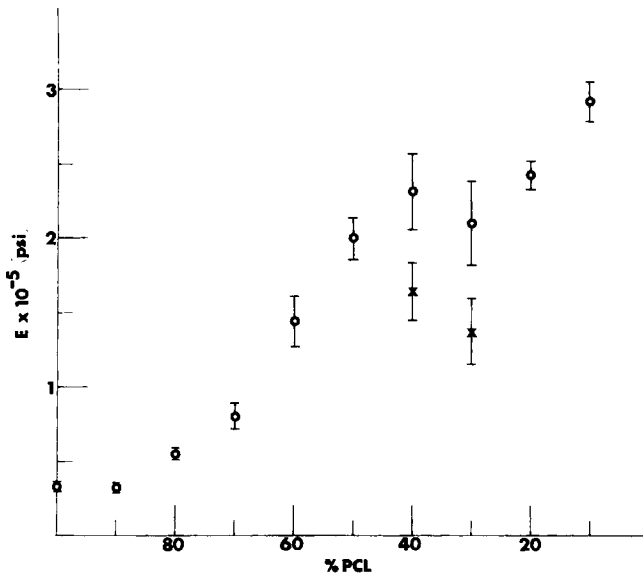

Fig. 2. Plot of E vs composition for SAN/PCL blends: (O) solution-cast samples; (X) melt crystallized samples (the error bars correspond to ±σ).

creases with increasing SAN content, and this is consistent with the increase in modulus observed upon adding more SAN to the blend. Closer examination of the calculated T_g's shows that a drop in T_g might be expected for blends containing 30% PCL. This arises as a consequence of solvent-induced crystallization and has been discussed previously.[10,11]

For semicrystalline materials with T_g's below the test temperature (i.e., blends containing from 100% to 60% PCL), the degree of crystallinity would be expected to strongly influence E, with E decreasing with decreasing X_c at constant T_g. However, for our samples, it appears that the influence of X_c has been overwhelmed to a large degree by the significant T_g variation.

As discussed in the Introduction, compatible blends of two amorphous polymers often exhibit moduli and tensile strengths, which are superior to those expected from a linear combination of the properties of the components. Synergistic behavior is found for solution-crystallized blends containing 50% and 40% PCL; however, this is not necessarily a consequence of blend densification resulting from intermolecular interactions but is more likely a result of the combined influence of matrix T_g, X_c, and, perhaps, the more rapid physical aging of these relatively low T_g, glassy blends. For blends of 70% to 90% PCL the moduli are significantly less than those expected on the basis of property averaging, contrary to what would be anticipated for an amorphous compatible mixture.

Melt-Crystallized Samples

Figure 3 depicts typical load/elongation curves for samples crystallized from the melt. In general, the behavior is similar to that observed for the solution-crystallized specimens. Although it is difficult to make an absolute judgement because of experimental error, the moduli appear to be somewhat higher than those of the solution-cast specimens except for compositions containing 40 and 30% PCL (Table III). In addition, the melt-crystallized specimens have greater ϵ_B's and exhibit more distinct yield points than the solution-crystallized samples. The explanation for these differences is not clear at this time but may be a consequence of inhomogeneities (e.g., voids) in the solution-cast films.

TABLE II
Variation of Overall Blend Crystallinity and T_g (at the Cessation of Crystallization) with Composition for Solution-Cast SAN/PCL Blends

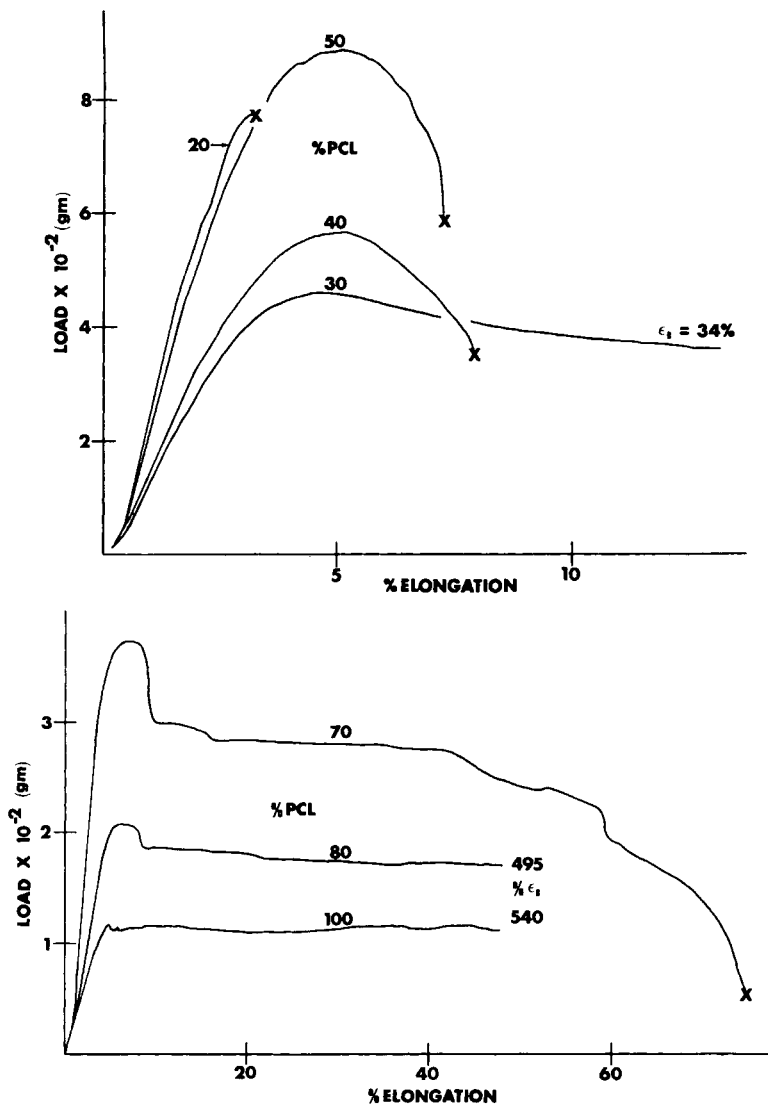| % PCL	T_g (°C)	X_c
100	−71	71
90	−41	65
80	−21	54
70	−5	44
60	16	39
50	31	32
40	46	25
30	37	8
20	46	—
10	71	—
0	100	—

Fig. 3. Typical load/elongation curves for melt-crystallized SAN/PCL blends.

Sample preparation technique appears to have the most profound effect on the behavior of blends possessing 30% and 40% PCL. For these compositions, crystallizing from solution yields higher moduli (Fig. 2) and much lower ϵ_B's than crystallizing from the melt. We observed previously that solution-casting induced higher levels of crystallinity than melt-crystallizing for the two compositions of interest.[10] One would therefore intuitively expect the solution-cast blends to exhibit higher moduli. In addition, the amorphous phase of the solution-cast materials will contain less PCL than the corresponding melt-crystallized blends. This would result in an increase in the blend T_g and could be partially responsible for the observed increase in modulus.

TABLE III

Tensile Mechanical Properties of Melt-Crystallized SAN/PCL Blends[a]

% PCL	E (psi)	ϵ_y	ϵ_B	σ_y (psi)	σ_B (psi)
100	38,900	0.054	2.5	1400	2000
	± 7,300	±0.025	± 2.4	± 370	± 200
90	52,400	0.063	4.9	1800	2200
	± 8,100	±0.017	± 1.9	± 380	± 600
80	80,500	0.066	5.8	2300	2800
	±18,600	±0.009	± 1.6	± 530	± 900
70	104,000	0.072	1.2	3100	3200
	±34,800	±0.025	± 1.6	± 930	± 590
60	154,000	0.056	0.35	4000	2400
	±11,100	±0.009	± 0.31	± 300	± 220
50	221,000		0.62		5500
	±43,900		±0.05		±1500
40	165,000		0.13		4400
	±19,400		± 0.10		± 140
30	138,000	0.050	0.32	3600	2500
	±22,000	±0.005	± 0.05	± 320	± 280
20	263,000		0.34		5000
	±22,500		± 0.01		± 630
10	295,000		0.33		6000
	±39,200		± 0.01		± 160
0	335,000		0.029		6100
	±27,000		±0.009		±1500

[a] The reported errors or ±1 standard deviation.

CONCLUSIONS

The mechanical properties of the compatible SAN/PCL system were observed to be dependent on the blend T_g and the degree of blend crystallinity. In general, moduli increased with increasing T_g for samples prepared from both solution and the melt. The influence of crystallinity was exemplified by blends of 40% and 30% PCL. The higher modulus of the solution-cast samples at these compositions was attributed to the higher levels of crystallinity which resulted when preparing these blends from solution.

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