

Mechanical Properties of Cellulose Acetate Propionate/Aliphatic Polyester Blends

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SYNOPSIS

Useful blends of cellulose esters with other high molecular weight polymers are generally unknown. Two aliphatic polyesters, poly(tetramethylene glutarate) (PTG) and poly(tetramethylene succinate) (PTS), have been thermally compounded with cellulose acetate propionate (CAP) in the range of 10–40 wt % polyester. These blends have been injection molded, and the mechanical properties of the molded bars were compared to bars molded from CAP plasticized with a low molecular weight diester, dioctyl adipate (DOA). The CAP/aliphatic polyester blends have significantly higher tensile strengths, flexural moduli, heat deflection temperatures, and greater hardness values than the corresponding CAP/DOA blends. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Cellulose esters are important thermoplastic polymers used in film, molding, and fiber applications. In general, cellulose esters have been used in applications requiring a combination of high melting and glass-transition temperatures as well as high modulus and good tensile strength. Because of their relatively high melting temperatures and relatively low decomposition temperatures, cellulose esters are normally processed in solution or in combination with low molecular weight plasticizers.

Miscible blends of cellulose esters and other high molecular weight polymers are generally unknown. Koleske et al.¹ originally reported in 1975 that polycaprolactone and cellulose esters form miscible blends. However, more recent work² demonstrated that cellulose acetate butyrate/polycaprolactone blends are, in fact, only partially miscible. Polyester carbonates and polyether carbonate blends with many cellulose esters have been reported to be miscible.³ In late 1991, it was reported that poly(hydroxybutyrate) forms miscible blends with cellulose esters⁴; and in 1992, we described the thermal and mechanical properties of some blends of cellulose

acetate butyrate and poly(hydroxybutyrate-co-valerate).⁵ More recently we have reported on the thermal properties of cellulose acetate propionate/poly(tetramethylene glutarate) (CAP/PTG) blends and showed these polymers to be miscible throughout the composition range of 0–50 wt % polyester.⁶ In addition to PTG, we have investigated other glutarate polyesters, such as poly(ethylene glutarate), poly(hexamethylene glutarate), poly(diethylene glutarate), and poly(octamethylene glutarate). These glutarate polyesters were also miscible with CAP in the composition range studied (up to 40 wt % polyester) with the exception of poly(octamethylene glutarate) which was only partially miscible.⁷ In this article we report the mechanical properties of blends of CAP with two high molecular weight aliphatic polyesters, PTG and poly(tetramethylene succinate) (PTS).

EXPERIMENTAL

The inherent viscosity (IV) measurements of the polyesters and the blends were made at a concentration of 0.5 wt % in tetrachloroethane : phenol (40 : 60). The CAP used for these experiments was CAP482-20, commercially available from Eastman Chemical Company (Kingsport, TN). The IV of PTG used for blending was 0.90, and the IV for PTS

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was 0.74. Melt blending was conducted on a Werner-Pfleiderer 30-mm twin-screw extruder. The compositions of the blends were determined by ^1H NMR. We found no evidence of reaction between the polyesters and CAP upon thermal compounding.⁶

General Procedure for Blending of CAP482-20 and Polyesters

The polymers were dry blended and fed as a mixture to zone 1 of the twin-screw extruder. The extruded blend was cooled in a water bath and cut into pellets with a Conair-Jetro pelletizer. The pellets were dried in a desiccant air system before molding. Total output from extruder = 43 lb/h; rpm of the screw = 207; torque = 30%; extruder zone temperatures: zone 1 = 180°C; zones 2–7 = 215–230°C.

Injection Molding of Blends

Blends were molded on a Toyo 90 injection molding machine under the following conditions: nozzle temperature = 200°C; zone 1 temperature = 210°C; zone 2 temperature = 210°C; zone 3 temperature = 190°C; zone 4 temperature = 180°C; melt temperature = 215°C; injection and hold pressures = 750 psig; mold temperature = 14°C; screw speed = 75 rpm. The tensile properties were measured according to ASTM D638 (crosshead speed of 2.0 in/min), and the flexural properties were measured according to ASTM D790.

RESULTS AND DISCUSSION

A number of high molecular weight aliphatic polyesters give optically clear blends with CAP, which

are miscible as determined by DSC/DMTA measurements.^{6,7} Two aliphatic polyesters that yield optically clear, miscible blends, PTG and PTS, were chosen for this investigation. Blends of CAP with PTG and PTS were prepared in the range of 10–40 wt % of the polyester, and these blends were compared to blends of CAP with a common plasticizer, dioctyl adipate (DOA). Each of the high molecular weight aliphatic polyesters was compounded with CAP at four different levels, and DOA was compounded with CAP at two levels. All of the blends were then injection molded, and the mechanical properties were measured.

The tensile properties of the molded bars are listed in Table I. There are significant differences between the tensile strengths of the CAP/DOA blends and the CAP/aliphatic polyester blends. When compared at the same level of modification, the tensile strengths for the CAP/polyester blends are significantly higher. For example, at 12 wt % DOA, the tensile strength of the CAP blend is 4,760 psi, whereas the tensile strength of CAP blended with 12 wt % PTG is 7,940 psi. Figure 1 illustrates that there is only a minor difference between tensile strengths of the two CAP/polyester blends and that there is a rapid linear decline in tensile strength for CAP/DOA blends. In fact, approximately 30 wt % of a polyester is required to lower the tensile strength of the blend to the level seen for the CAP/DOA blend with 12 wt % DOA. There are also major differences in the elongations for the two types of blends. The DOA dramatically increases the elongation of CAP even at the lowest level studied (6.5 wt %); however the polyesters have no significant effect on the elongation of the blends until the weight percent of the polyester exceeds approximately 20–

Table I Tensile Properties of Blends of CAP

Blend Component		Elongation at Yield (%)	Elongation at Break (%)	Tensile Strength (10^3 psi)
Name	Wt %			
PTG	12	6	9	7.94
	25	6	20	6.02
	35	6	72	2.82
	40	10	92	2.28
PTS	8.7	6	9	8.36
	18	6	15	7.76
	27	6	29	5.93
	42	7	53	3.32
DOA	0.0	n/a	11	8.70
	6.5	5	25	6.86
	12	5	27	4.76

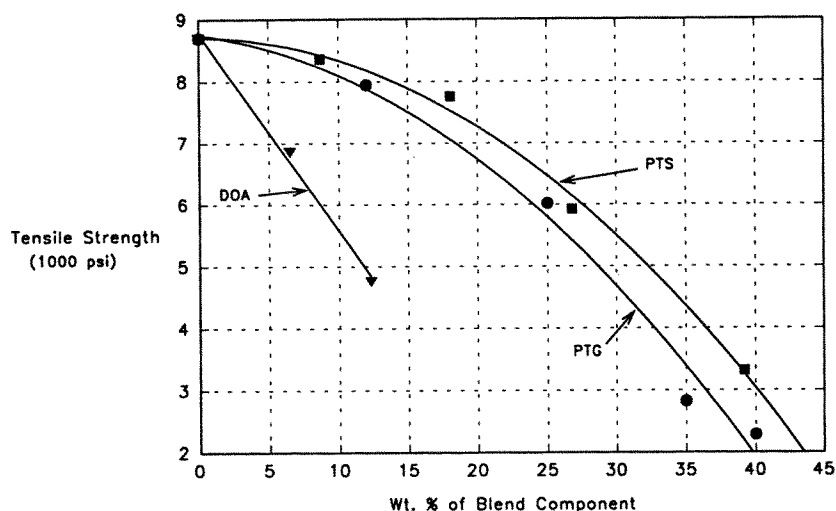


Figure 1 Tensile strength of CAP blends.

25%. Beyond that point, however, the elongation of the CAP/polyester blends increase significantly, exceeding that of the CAP/DOA blends studied. Again, the two CAP/polyester blends show similar trends in their effect on elongation.

Table II contains the impact and flexural properties of the CAP blends. As before there are significant differences between the CAP plasticized with DOA and the CAP blends with the aliphatic polyesters. When the blend components are compared at the same weight percentages, the flexural moduli for CAP/polyester blends are significantly higher. For example, at 12 wt % DOA, the flexural modulus of the blend is 216,000 psi, whereas the

flexural modulus of CAP with 12 wt % PTG is 307,000 psi. Viewed in a different light, it requires a significantly higher weight percent of polyester compared to DOA to reduce the flexural modulus by an equivalent amount. In order to achieve a flexural modulus of 216,000 psi, approximately 26 wt % PTG should be blended with CAP as compared with 12 wt % DOA (Fig. 2). The manner in which the flexural moduli decrease in CAP blends with added polyester is very similar to the manner in which the tensile strengths decrease. In both cases the CAP/PTS blends show consistently higher values than the CAP/PTG blends (Figs. 1, 2). These aliphatic polyesters are generally less effective than DOA at

Table II Impact and Flexural Properties of Blends of CAP

Blend Component		Notched Izod 23°C (ft lb/in)	Unnotched Izod 23°C (ft lb/in)	Notched Izod -40°C (ft lb/in)	Unnotched Izod -40°C (ft lb/in)	Flexural Strength (10 ³ psi)	Flexural Modulus (10 ⁵ psi)
Name	Wt %						
PTG	12	2.96	49.6	1.71	52.9	9.06	3.07
	25	4.56	55.6	1.76	52.5	6.04	2.13
	35	15.4 (P)	32.0	n/a	n/a	1.86	0.78
	40	10.8 (N)	22.5	2.05	12.6	0.48	0.15
PTS	8.7	2.26	55.8	1.00	39.9	10.33	3.44
	18	2.74	61.9 (N)	1.26	32.8	8.83	2.94
	27	5.69	48.4 (N)	1.19	17.9	6.19	2.21
	42	13.9 (P)	40.2 (N)	0.21	25.1	1.59	0.56
DOA	0.0	1.80	n/a	1.00	n/a	n/a	3.50
	6.5	3.82	39.8 (N)	2.06	51.8	7.87	2.75
	12	7.43 (H)	31.2 (N)	2.94	64.6	5.67	2.16

N, no break; P, partial break; H, hinge break.

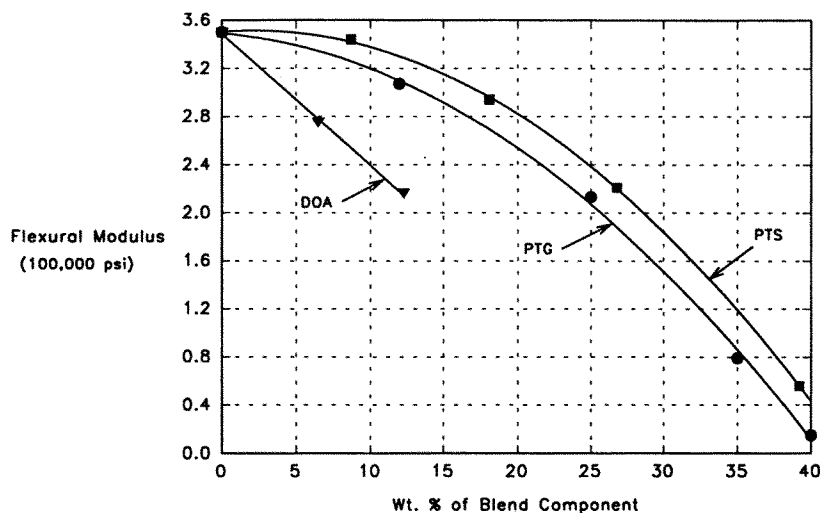


Figure 2 Flexural modulus of CAP blends.

increasing the Izod impact strength of CAP when compared on an equal weight basis (Table II). Roughly equivalent impact strengths at room temperature are seen when CAP modified with 9% DOA is compared with CAP modified with a polyester at 27%. Impact strengths of the CAP/polyester blends at room temperature show similar trends for both polyesters; however, this is not the case for low temperature impact strength. Overall, these low temperature impact strengths for the CAP/polyester blends were lower than expected. At -40°C the impact strengths for CAP/PTG blends are significantly higher than those for CAP/PTS blends; however, both are low in comparison with the CAP/

DOA blends. There is a good correlation between the low temperature impact strengths and the glass-transition temperatures of the blend components (T_g of PTG = -55°C , PTS = -28°C , and DOA = -84°C) where the blend component with the lowest T_g provides the greatest low temperature impact strength and vice versa. These differences in impact strengths at low temperature and ambient temperature can be more clearly seen in cross-plots of flexural modulus versus impact strength. Figure 3 shows a good correlation between flexural modulus and ambient temperature impact strength for the CAP/DOA blends and the CAP/polyester blends. However, the significant differences between the different

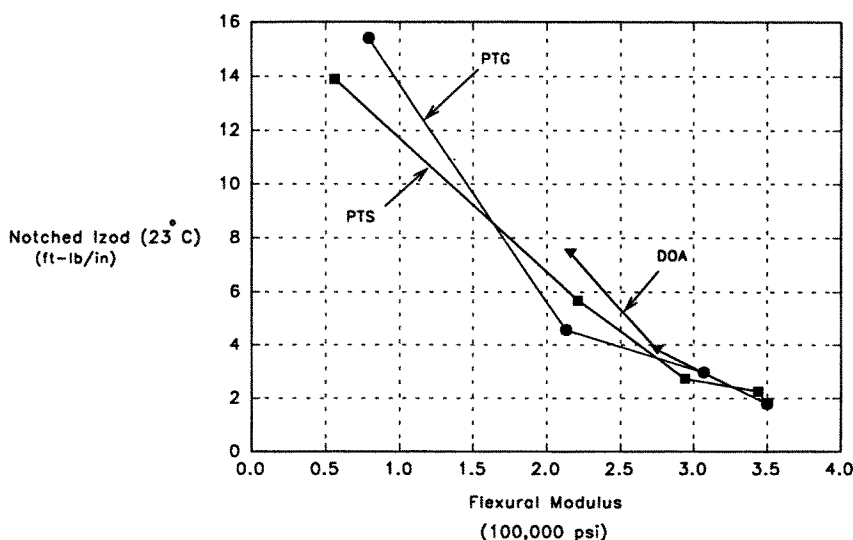


Figure 3 Flexural modulus versus impact strength at 23°C .

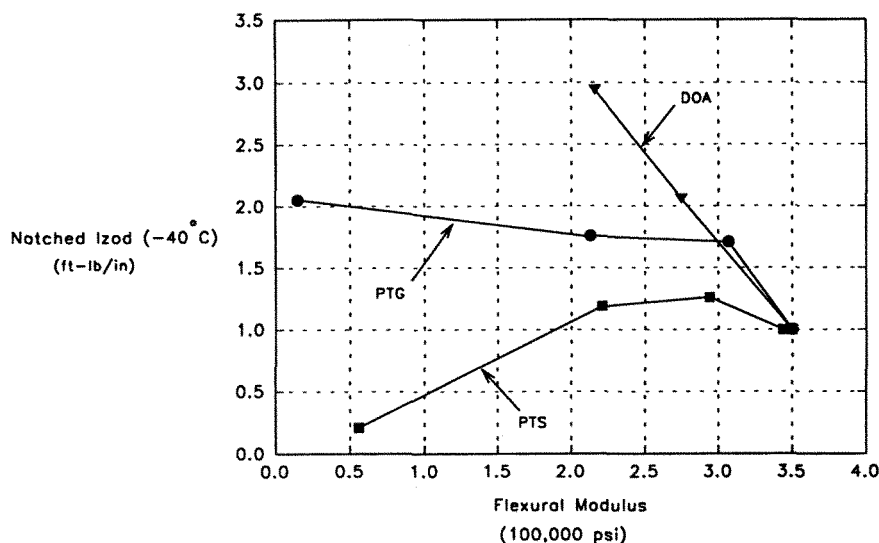


Figure 4 Flexural modulus versus impact strength at -40°C .

types of blends is evident in the cross-plot of flexural modulus versus low temperature impact strength (Fig. 4).

Table III shows the heat deflection temperatures and Rockwell hardness data for the blends. At a given level of modification, the CAP/aliphatic polyester blends give significantly higher heat deflection temperatures and higher hardness values compared with the corresponding CAP/DOA blends. The heat deflection temperatures of the CAP/polyester blends would be expected to be higher than the CAP/DOA blends because the T_g 's for the corresponding CAP/polyester blends are higher. Likewise, the hardness values are consistent with other

observations, which indicate that the hardness values of blends of this type are higher when the molecular weight of the minor component is higher.⁸

A number of research groups have demonstrated that the physical properties of plasticized polymers are related to the polymer-plasticizer dual mobilization process and to the ability of the plasticizer to disrupt polymer-polymer interactions.^{4,8,9} We have shown previously that these CAP/polyester blends are miscible, and hence we believe that these observed differences in physical properties are probably related to the differences in the molecular mobility of the blends. Due to the higher molecular weight of the aliphatic polyesters, the mobilities of the CAP/polyester blends are lower relative to the CAP/DOA blends. It is also clear from the mechanical properties that both the aliphatic polyester and DOA blends with CAP have increased molecular mobility over that of CAP. At very low levels the DOA causes a decrease in the tensile strength and flexural modulus relative to CAP and an increase in the elongation and impact strength. On the other hand, the mechanical properties of the CAP/polyester blends are not dramatically different from CAP until the weight percent reaches approximately 20–25%. Once the level of the polyester exceeds 25 wt %, similar effects to those of DOA on tensile strength, flexural modulus, elongation, and impact strengths are observed. The differences in mechanical properties between the two CAP/polyester blends are small but noticeable. The CAP/PTG blends consistently show lower tensile strengths and flexural moduli and higher elongations and impact

Table III Heat Deflection and Hardness Values for Blends of CAP

Blend Component		HDT	HDT	Rockwell Hardness (R Scale)
Name	Wt %	66 psi (°C)	264 psi (°C)	
PTG	12	79	60	112
	25	59	43	99
	35	51	33	n/a
	40	n/a	n/a	n/a
PTS	8.7	84	82	114
	18	64	60	112
	27	51	52	97
	42	32	41	n/a
DOA	6.5	84	62	104
	12	67	53	84

strengths than those exhibited by the CAP/PTS blends, indicating a greater mobility in the CAP/PTG blends relative to the corresponding CAP/PTS blends. These trends are similar to those seen when other high molecular weight polymers, such as PVC, are blended with low and high molecular weight plasticizers.^{8,10}

CONCLUSION

At relatively low levels, the polyesters offer the advantage of significantly higher tensile strengths, flexural moduli, heat deflection temperatures, and hardness values compared to the CAP/dioctyl adipate blends at the same weight percent. However, the levels of the aliphatic polyesters must exceed 20% before significant increases in elongation and impact strength are realized. The low temperature impact strengths of the CAP/polyester blends were lower than expected and inversely correlated with the glass transition temperatures of the polyesters. Due to their high molecular weight, these polyesters are expected to exhibit much better long-term stability and much lower susceptibility to solvent extraction than CAP modified with low molecular weight plasticizers. Work in this area continues and will be disclosed in due course.

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