

Thermotropic Polyester Carbonates. III. Thermotropic Polyester Carbonates as Self-Reinforced Plastics

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Synopsis

Thermotropic polyester carbonates derived from *t*-butylhydroquinone, methylhydroquinone, diphenyl terephthalate, and diphenyl carbonate in the molar ratio of 50 : 50 : 55 : 45; 50 : 50 : 57.5 : 5 : 42.5 and 50 : 50 : 60 : 40 can be injection molded successfully from temperatures 10°C below melting to 30–40°C above melting. Normally the best molding temperatures are 10–20°C above melting. If the molding conditions are controlled properly, tensile strengths as high as 1.8×10^4 psi, tensile moduli as high as 7.4×10^5 psi, and flex moduli as high as 1.1×10^6 psi can be obtained.

INTRODUCTION

Because of their potential for orientation, it is generally believed that liquid crystalline polymers can be processed in the melt into high-performance self-reinforced plastics. One way to conduct the processing is by injection molding because the liquid crystalline behavior can be at least partially exploited during injection.

Following our extensive work on fiber spinning/heat treatment,¹ studies on thermotropic polyester-carbonates as self-reinforced plastics were initiated. Since no information on mechanical properties of molded thermotropic polyesters was generally available at the time we initiated this study, our interest was completely based on (1) our success in obtaining good fiber properties from our thermotropic compositions, and (2) trying to evaluate the properties of thermotropic polyester-carbonate as plastics which can be processed in the same temperature range (250–300°C) as those of high performance engineering plastics.² Initially, compression molding was conducted to narrow down processing variables. Injection molding studies then proceeded.

RESULTS AND DISCUSSION

Compression Molding of Thermotropic Polyester Carbonates

Samples of thermotropic polymers derived from *t*-butylhydroquinone (tBuHQ), methylhydroquinone (MHQ), diphenyl terephthalate (DPT) and diphenyl carbonate (DPC) in the molar ratios of 50 : 50 : 55 : 45; 50 : 50 : 57.5 : 42.5 and 50 : 50 : 60 : 40 were compression molded at tempera-

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TABLE I
 Compression Molding of Thermotropic Polyester Carbonates

Composition tBuHQ/MHQ/DPT/DPC	RV	T_m (°C)	Molded at (°C)	Tensile strength ($\times 10^3$ psi) max/mean	Tensile modulus ($\times 10^5$ psi) max/mean	Elongation (%) ave
50/50/55/45	1.97	240	280	7.45/5.46	3.34/3.17	2.3
	3.38	278	280	5.00/4.39	2.72/2.65	1.9
	6.95	294	300	11.4/10.5	3.26/3.02	4.9
	9.45	299	310	10.7/9.93	3.19/3.12	4.4
	12.7	303	310	15.4/13.4	3.57/3.47	6.2
50/50/57.5/42.5	2.07	250	270	3.92/3.72	3.45/3.30	1.2
	3.19	288	280	5.20/4.77	3.31/3.18	1.6
	6.63	297	310	13.4/11.9	4.68/3.77	4.3
	10.9	304	310	15.0/13.6	4.25/3.79	5.3
	16.3	307	310	10.8/9.50	4.04/3.79	3.4
50/50/60/40	3.10	289	310	9.56/8.12	4.41/4.05	2.2
	6.70	299	310	6.84/6.41	3.68/3.35	2.1
	9.59	299	310	9.20/8.56	3.78/3.63	2.8
Nylon-6				7.4/12.0	3.80	30-100
Polycarbonate				9.5	3.45	110

tures near or above their melting temperatures.² Table I lists the complete data for the studies. Some findings and conclusions from this study are as follows:

1. In general, the higher the reduced viscosity (RV) value and the larger the difference between molding temperatures and melting temperatures, the better the tensile properties. For example, samples of RV 3.38 with melting temperature of 278°C which were molded at 280°C gave lower tensile values than those of samples with RV = 1.97 (mp 250°C) but molded at 280°C.
2. In general, increasing the stiffness of the chain would increase the tensile modulus, as can be seen by comparing the samples with 57.5% aromatic ester content to samples with 55% ester content. If the chain is stiff enough to retard the flow in the melt, it depresses the tensile modulus, particularly when the molding temperatures are close to the melting temperatures of the sample.
3. Samples of compositions containing 55% and 57.5% of (aromatic) ester content of RV higher than 6.5 gave tensile strengths as high as 15×10^3 psi and modulus as high as 468×10^3 psi which are very high for isotropic thermoplastics. Samples of even higher (aromatic) ester content (60%) may give higher tensile strength/modulus if they could be molded at the required higher temperatures without degradation.
4. Thermotropic polyester carbonates listed here in some cases have better properties than those of polycarbonate and Nylon-6, two well established engineering polymers. Because we believed that little orientation developed during the compression molding, the tensile properties of the thermotropic polyester carbonates were probably not maximized. These data, however, served as a reference for the injection molding work.

Injection Molding the Thermotropic Polyester Carbonates

Although properties of injection-molded PET modified with HBA had been reported previously,³ no results on injection molding of thermotropic polyesters had been reported in the patent literature before we started our work.

In our injection molding studies, samples of various RV's of these above three selected compositions were injection molded at temperatures from 10°C below to 50°C above the melting temperatures of samples at 11°C intervals, and the temperatures were well controlled. The mold was warmed in order to retain good flow characteristics.

Table II gives the details of injection molding studies of thermotropic polyester carbonates derived from tBuHQ/MHQ/DPT/DPC (50/50/55/45). Some conclusions are as follows:

1. Normally the viscosity of the sample drops after molding. The higher the viscosity and processing temperature, the larger the drop in RV. Low viscosity material did not register a severe drop.
2. Heat-deflection temperatures (HDT's), as measured by ASTM methods, within experimental error, are close to the glass transition temperatures.
3. Izod impact strengths (notched) of these samples are within the range expected for high performance engineering plastics (1–3 ft-lb/in.).
4. By comparing the data on Table II and Table I, for samples of the same viscosity, tensile properties are better from injection molding than from compression molding, apparently because the liquid crystalline nature is better employed in injection molding than in compression molding. Usually a given isotropic thermoplastic gives similar tensile properties regardless of the processing methods.
5. Even when they are of medium viscosity, the tensile and flex properties of thermotropic polymers are much higher than those of conventional engineering plastics such as nylon and polycarbonate.
6. Among the samples of the same composition, samples with lower melting temperatures give better properties. This is because of higher flow and ease of developing orientation during flow. Samples with higher viscosity can also yield high strength materials if they can be processed at higher temperature without degradation.
7. The results of injection molding and tensile measurements were consistent as long as viscosities were about the same. For example, comparing the results of samples with RV 6.01 and 6.44 respectively, both gave the best tensile properties when they were molded at temperatures in the 310–320°C range.

In addition, it is clear that samples injection molded at temperatures 10–20°C above the melting temperatures gave specimens with higher tensile properties than those of specimens molded either at lower or at higher temperatures. The ease of flow and ease of developing orientation as the temperature increases accounts for the improvements in properties as molding temperatures move from near the melting temperature to 10–20°C above the melting temperature. However, it is difficult to explain why the tensile properties drop after molding at temperatures 20°C above the melting tem-

TABLE IV
Injection Molding and Mechanical Testing of Thermotropic Polymers Derived
from tBuHQ/MHQ/DPT/PDC (50/50/60/40)

RV	1.64			2.55			4.77	6.52
T_m (°C)	2.86			290			300	303
T_g (°C)	135			136			138	138
Molding temp. (°C)	282	293	304	282	293	304	299	299
RV after molding		1.55		1.75		1.70	2.04	4.86
HDT °C							136	
Izod ft-lb/in.								
Max.	0.7						2.6	3.1
Ave.	0.6			0.4		0.6	2.0	2.4
Tensile properties								
Strength ($\times 10^3$ psi)								
Max.	14.3	11.8	10.7	16.1	17.2	15.5	14.6	12.6
Mean	11.3	10.5	10.6	14.7	13.5	13.6	13.2	10.5
Modulus ($\times 10^5$ psi)								
Max.	7.36	6.96	5.34	5.50	6.06	6.53	3.95	4.03
Mean	6.42	6.18	5.32	5.00	5.60	5.44	3.63	3.71
Elongation	2.0	1.9	2.2	3.7	3.0	3.1	5.7	3.5
Flex properties								
Modulus ($\times 10^5$ psi)								
Max.	10.4			10.0		8.33	10.1	10.3
Mean	8.4			8.60		7.41	10.1	9.84

peratures. Two possible reasons for this phenomenon are: (1) the drop of thermotropicity with temperatures. In other words, thermotropicity for these compositions may reach its peak at 10–20°C above the melting temperature; (2) degradation of sample becomes more pronounced at temperatures 20°C above the molding temperature particularly when these temperatures are over 310°C.

Table III gives the details of injection molding studies of thermotropic polyester-carbonates derived from tBuHQ/MHQ/DPT/DPC (50/50/57.5/42.5). As before, similar results were obtained for samples of RV 3.29 and 3.50. Slight differences in tensile properties were due to the slight variations in molding conditions and homogeneity. It is interesting to note here that tensile modulus as high as 6.8×10^5 psi was obtained for a sample with viscosity of 3.5 while lower moduli were obtained for samples with lower RV (2.98) and higher RV (15.9). The other conclusions for the results were the same as described in previous sections except that the moduli obtained for this composition were generally higher than those with lower (aromatic) ester content.

Because of the high melting temperature ($\geq 290^\circ\text{C}$) of thermotropic polyester carbonate derived from tBuHQ/MHQ/DPT/DPC (50/50/60/40), and the severe degradation of samples in the barrel at temperatures above 310°C during the injection molding process, samples of this composition were not subjected to injection molding study except for those of low RV's. Table IV lists the results from these injection molding studies. As expected, from the low molding temperatures (304°C) relative to melting temperatures ($\geq 290^\circ\text{C}$)

and from the severe degradation of sample in the barrel, low tensile strength and Izod impact properties were obtained. However, the values of tensile and flex moduli remain relatively high as a result of chain rigidity. Tensile modulus as high as 7.4×10^5 psi was obtained.

SUMMARY

After intensive studies of compression molding and injection molding processes at the same temperature range as those of most high performance engineering plastics (250–300°C), we demonstrated that thermotropic polyester carbonates derived from tBuHQ/MHQ/DPT/DPC can be processed into high performance plastics. Tensile strengths as high as 1.8×10^4 psi, tensile modulus as high as 7.4×10^5 psi, and flex modulus as high as 1.1×10^6 psi can be obtained. These properties are exceptionally high among most available engineering plastics and we believe there is still room for improvement. Notched Izod impact strength values were in the medium to high range among the available plastics and they can also be improved. What is most encouraging is that the Izod properties obtained are far better than we expected for thermotropic polymers of this type of comparable molecular weight. Among the composition, RV range and processing conditions studied, composition tBuHQ/MHQ/DPT/DPC (50/50/57.5/42.5), RV 3–4, processed at 10–20°C above melting temperatures gave the best combination of mechanical properties.

It is noteworthy that the same composition gave the best overall properties in the fiber-spinning studies, except that a slightly lower RV (2.0–3.5) performed best in this case. The reasons offered previously for why processing at 10–20°C above the melting temperature gave the best properties seem quite logical here as well.

One problem remaining in injection molding and fiber spinning is the degradation of samples at temperatures above 300°C. We believe that this problem can be overcome by fine tuning the process conditions, such as better temperature control, precise residence time, delicate machining, improved material quality, among others. In our practice, a standard, commercially available injection molding machine was used without further modification.

Since the completion of this study, two thermotropic polyesters have been introduced commercially, namely Dartco's Xydar® and Celanese's Vectra®. These samples maintain thermal stability at their respective processing temperatures, possible because delicate processing conditions, particularly for Xydar® ($T_m = 421^\circ\text{C}$), have been applied.

It is appropriate to stress here that our intention in working on this class of thermotropic polymers was not to make yet another high melting thermotropic polyester, but rather to create thermotropic polymeric systems which can be processed at the usual conditions as those of other engineering polymers yet with far better overall mechanical properties close to those of all aromatic polyesters. Although some thermotropic polyesters may show better properties after processing under very delicate conditions when compared to those of thermotropic polyester carbonates as reported here, they may behave similarly if exactly the same processing conditions are applied.

EXPERIMENTAL

Compression Molding

Dried powder samples of thermotropic polyester carbonates were compression molded by using an Industrial Hydraulic Machine Co. Press. About 30 g of sample were placed into a 6" × 6" mold preheated to 280–310°C, as desired. Initial 1/2 ton pressure was then applied which was gradually increased to 2–7 tons. The press was then opened. The 6" × 6" 1/16" sheet was released from the mold, and it was cut into ASTM Type IV (C) specimens for tensile testing.

Injection Molding

A ram extruder (Simplomatic Manufacturing Co. Model: PR063) with barrel capacity of 80 g was used for injection molding studies.

The extruder was first heated to the desired temperature (normally 249–327°C) with the mold (either tensile mold or bar mold used one at a time) attached. Dried sample was then charged into the barrel and injected into the mold. Enough specimens were molded for tensile, flex, Izod, and HDT testing. The molds used were: Tensile mold for Type V tensile specimen; Bar mold: to mold 5" × 1/2" × 1/8" bars suitable for Izod, flex, HDT testing. The mold was changed from one to the other while hot in order to maintain polymer orientation and flow while molding. Normally molding was started at temperatures about 10°C below melting, increasing at 11°C intervals until 30–40°C above melting was reached. While the tensile mold was used at every molding temperature, the bar mold was usually used at three distinct temperatures (lowest, medium, and highest). Extruded waste sometimes was recharged into the barrel when needed and when no degradation occurred. Usually 200–300 g were needed to complete one run.

Tensile Measurements

All tensile measurements were obtained using ASTM Type V (1/32" thickness) or Type IV (1/16" thickness) specimens. In most cases the evaluation included measurement of tensile strength, tensile modulus, ultimate (total) elongation, all expressed in psi or %. Test method ASTM-D638 was employed with a constant rate of extension instrument (Instron) under a load of 500 lb at a crosshead velocity of 0.20 in/min for 1.31" gauge length under a controlled environment (23°C, 50% relative humidity, RH). The results of tensile testing are averages of at least 5 runs for all materials.

Izod Impact Strength

All Izod impact measurements were obtained on 1/8" thick specimens having standard notch geometry under conditions specified in ASTM-D256 (method A). A Baldwin Impact Tester was employed at 23°C and 50% RH. For most materials, the average of seven or more runs is reported. Specimens were obtained from injection molded bars. For all polymeric materials covered in this report the mode of failure during the Izod test was complete break.

Flexure Measurement

All flexure measurements were obtained using the ASTM D790 standard method on 1/8" depth, 1/2" width, 2.5" length specimens. The test was conducted at 23°C, 50% RH on a specimen span of 2.0 in. with crosshead velocity of 0.05 in./min until 5.0% strain was reached. The results of flexure strength, and modulus were averaged from at least 4 runs for all materials.

Heat Deflection Temperature Measurement (HDT)

HDT measurements were conducted on 1/8" thick test specimens according to ASTM-D648. A Custom Scientific Co. apparatus was employed at 264 psi fiber stress at a heating rate of 2°C/min. In all cases the reported values are for a deflection of 0.01 in. (0.25 mm). All samples were injection-molded bars. The samples were conditioned to 23°C and 50% RH before measurement.

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