

# Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. VIII. Mechanical Properties of Copolymer

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## Synopsis

Copolymers obtained by the solid-state copolymerization of tetraoxane with 1,3-dioxolane were pelletized using a vent-type extruder and the mechanical properties were measured. The mechanical properties were found to be largely influenced by the distributions of molecular weight and ethylene oxide, which were controlled by the addition method of the 1,3-dioxolane–methylal solution into polymeric system. The mechanical properties of the copolymers were also found to be intermediate between those of Duracon M90 and Delrin 500.

## INTRODUCTION

Poly(oxymethylene) is one of the most useful engineering plastics because of its excellent mechanical properties. Both homopolymers (Delrin, DuPont) and copolymers (Celcon, Celanese; Hostaform, Hoechst; Duracon, Polyplastics; Ultraform, BASF) are commercially available.

In order to develop a simple process for polyoxymethylene production, the authors have studied the solid-state copolymerization of tetraoxane with 1,3-dioxolane and clarified various characteristics as reported previously.<sup>1-7</sup> This copolymerization can be characterized by the process in which one can easily obtain oxymethylene copolymer with an excellent thermal stability and a well-controlled molecular weight by using a very compact reactor without solvent. The process developed has the advantage over the conventional processes of being extremely simple.<sup>7</sup>

In the present paper the mechanical properties of the copolymer obtained in the solid-state copolymerization were determined and are discussed in comparison with those of Duracon (which seems to be a trioxane–ethylene oxide copolymer) and Delrin (acetylated polyformaldehyde). It was found that the mechanical properties of the copolymer are greatly influenced by the composition and the molecular weight distribution which can be controlled by the amount and the addition method of the 1,3-dioxolane–methylal solution. It was also found that the mechanical properties of the copolymer obtained by this process were intermediate between those of Delrin and Duracon.

## EXPERIMENTAL

### Polymer Samples

The polymer samples used in the present work were five kinds of polyoxymethylene: copolymer 1, copolymer 2, copolymer C, Delrin 500, and Duracon M90. Delrin 500 and Duracon M90 were obtained commercially in pellet form. Copolymers 1, 2, and C were obtained by the solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal; 1, 2, and C are symbols for the addition method of the 1,3-dioxolane-methylal solution into the copolymerization system, i.e., one addition, two additions, and continuous addition, respectively. The detailed procedures were described in a previous paper.<sup>3</sup>

Since copolymer 1 as polymerized cannot be pelletized due to its slightly lower thermal stability, it was pretreated according to a patent<sup>8</sup> as follows. Copolymer 1 was heated at 150°C for 5 min in a water-isopropyl alcohol solution containing 1.0 wt. % sodium thiosulfate. The pelletization of the copolymers was carried out as follows. The powdery copolymer was mixed with 0.6 part Yoshinox BB (Yoshitomi Pharmaceutical Co. Ltd.) as an antioxidant and 1.0 part Amilan CM-4000 (Toray Co. Ltd.) as a formaldehyde scavenger in a Henshell Mixer (Mitsui Miike Seisakusho, Model FM-20B) and then pelletized by using a vent-type extruder (Tanabe Plastics, Model UE-4D-26). The operating conditions of the extruder were mentioned in detail before.<sup>7</sup>

### Molding of Test Pieces

The test pieces for the measurement of mechanical properties were made by injection molding. Polymer in pellet form was molded into the test piece by using a 4-ounce injection molding machine (Nikko-Ankerberg, Model V15-75). The operating conditions of the machine are as follows. (a) Feed system of the molten polymer: temperature at the cylinder head, 190°C; at the cylinder center, 180°C; at the cylinder nozzle (die), 190°C; injection pressure, 740 kg/cm<sup>2</sup>. (b) Test piece channel: temperature, 190°C. (c) Cycle of injection: injection, 18 sec; cooling, 20 sec.

### Measurements of Mechanical and Physical Properties

Measurements of mechanical properties of the copolymer samples were mainly carried out according to ASTM. The melt viscosity of the polymer was determined at 190°C ± 0.4°C using a Shimazu Koka Flow Tester (Shimazu Seisakusho, Model 301).

The physical properties, such as thermal stability, solution viscosity, and molecular weight distribution, were measured by the same method as mentioned before.<sup>1,2</sup> The content of ethylene oxide units in copolymer was determined at 140–150°C in *o*-dichlorobenzene (5 wt. % solution) with a high-resolution NMR spectrometer (JEOL, Model 4H-100) working at 100 MHz.

## RESULTS AND DISCUSSION

Mechanical properties and melt characteristics of the copolymers obtained by the various addition methods of 1,3-dioxolane-methylal solution were measured and discussed in comparison with those of commercially available polyacetals.

As mentioned above, copolymer 1 was pelletized after the pretreatment. Its thermal stability  $R_{222}^{60}$  and intrinsic viscosity  $[\eta]$  changed by the pretreatment from 93.2% to 99.5% and from 1.6 to 1.65 dl/g, respectively. However, the intrinsic viscosities of the copolymers were found to be unchanged by the pelletization as shown in Table I. It was also found that the thermal stabilities of copolymers 2 and C were improved by ca. 1% by the pelletization and reached more than 99%. This indicates that the thermally unstable parts of the copolymer were removed by heating in the vent-type extruder. The ethylene oxide unit contents of the copolymers were lower than that of Duracon M90, which presumably is synthesized by the copolymerization of trioxane with ethylene oxide in the liquid state.<sup>9</sup>

Figure 1 shows the pressure dependences of melt viscosities of copolymers 1,

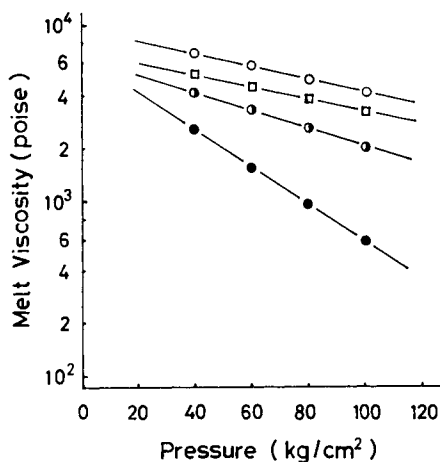


Fig. 1. Pressure dependencies of melt viscosity of copolymers: (●) copolymer 1; (●) copolymer 2; (○) copolymer C; (□) Duracon M90.

TABLE I  
Physical Properties

	Copolymer 1 <sup>a</sup>	Copolymer 2	Copolymer C	Duracon M90
		Before Pelletization		
Intrinsic viscosity $[\eta]$ , dl/g	1.6	1.5	1.5	—
Thermal stability $R_{222}^{60}$ , %	93.2	98.4	98.3	—
		After Pelletization		
Melting point °C	170	170	173	165
Intrinsic viscosity $[\eta]$ , dl/g	1.65	1.5	1.45	1.4
Thermal stability $R_{222}^{60}$ , %	99.8	99.3	99.2	99.4
Ethylene oxide content mole-%	1.6	1.4	1.0	2.0
$\bar{M}_w/\bar{M}_n$	— <sup>b</sup>	3.10	1.75	2.23
Halfwidth of DSC spectrum	10.0	6.9	4.9	5.1

<sup>a</sup> Copolymer 1 was pretreated before pelletization to  $[\eta] = 1.65$  dl/g and  $R_{222}^{60} = 99.5\%$ .

<sup>b</sup> This value was not determined because the GPC curve was bimodal.

2, and C in comparison with that of Duracon M90. It can be seen that at a given pressure the melt viscosity of copolymer 1 is considerably low and its pressure dependence is the largest, although the melting point of copolymer 1 is higher than that of Duracon M90. As reported previously<sup>5,6</sup> and as understood from the values of  $\overline{M}_w/\overline{M}_n$  and halfwidth of DSC thermogram listed in Table I, copolymer 1 is characterized by the broad distribution of molecular weight and the heterogeneous distribution of ethylene oxide units in the polymer chain. Copolymer 1 consists of the copolymer with lower molecular weight and higher ethylene oxide unit content, which forms in the early stage of copolymerization, and of the copolymer with larger molecular weight and lower ethylene oxide unit content, which forms in the later stage of copolymerization. Consequently, the lower molecular weight copolymer containing a larger amount of ethylene oxide units might act as a lubricant when copolymer 1 is molten under a high pressure.

Table II shows the mechanical properties of copolymers 1, 2, and C in comparison with those of commercially available Duracon M90 and Delrin 500. It was found that the mechanical properties are largely influenced by the addition method of 1,3-dioxolane-methylal solution. The tensile strength, shear modulus, compressive strength, and shear strength of the copolymers decreased in the order copolymer 1 > copolymer 2 > copolymer C. The tensile elongation and izod strength, on the contrary, increased in that order. The bending strength and Young's modulus in flexure of copolymer 1 are considerably low compared with those of copolymers 2 and C, and the melt index of copolymer 2 is larger than that of copolymer C. These results suggest that copolymer 1 is hard and brittle compared with copolymer C and that the mechanical properties of copolymer 2 are intermediate between those of copolymers 1 and C. It is reasonably concluded that the mechanical properties of oxymethylene copolymer are strongly dependent on the distribution of the ethylene oxide units and molecular weight as well as on the ethylene oxide unit content in the main chains. As listed in Table I, the ethylene oxide contents of copolymers 1 and 2 are higher than that of copolymer C. The crystal structure of oxymethylene polymer is distorted by incorporating ethylene oxide units into its main chain, i.e., the crystallinity decreases with increasing ethylene oxide content so that the melting point of the copolymer decreases as the ethylene oxide content increases. If the mechanical properties of the copolymer are dependent only on the amount of ethylene oxide unit in the main chain, the mechanical properties of copolymers 1 and C should be close to those of Duracon M90 and Delrin 500, respectively.

However, the bending strength and izod impact strength of copolymer 1 were found to be lower than those of Duracon M90 and Delrin 500, although the tensile strength and compressive strength were close to those of Delrin 500. As mentioned above, copolymer 1 is characterized by heterogeneities in the distributions of molecular weight and ethylene oxide unit content. Therefore, the finding that the mechanical properties of copolymer 1 are close to those of Delrin 500 rather than to Duracon M90 irrespective of the relatively larger content of ethylene oxide unit in the polymer chain may be attributable to its heterogeneity. On the other hand, the mechanical properties of copolymer C were found to be approximately intermediate between those of Duracon M90 and Delrin 500, although the compressive strength and Rockwell hardness were about the same as those of Duracon M90 and the bending strength and izod impact strength,

TABLE II  
Mechanical Properties<sup>a</sup>

Mechanical properties	ASTM no.	Copolymer 1	Copolymer 2	Copolymer C	Duracon M90	Delrin 500
Tensile test						
Yield strength, kg/cm <sup>2</sup>	D-638-61T	641( <sup>657</sup> / <sub>624</sub> )	637( <sup>651</sup> / <sub>621</sub> )	644( <sup>665</sup> / <sub>646</sub> )	600( <sup>619</sup> / <sub>587</sub> )	680
Tensile strength, kg/cm <sup>2</sup>	D-638-61T	627( <sup>637</sup> / <sub>625</sub> )	570( <sup>599</sup> / <sub>528</sub> )	554( <sup>573</sup> / <sub>533</sub> )	501( <sup>541</sup> / <sub>443</sub> )	629
Tensile breaking elongation, %	D-638-61T	21( <sup>23</sup> / <sub>15</sub> )	35( <sup>45</sup> / <sub>26</sub> )	48( <sup>59</sup> / <sub>33</sub> )	39( <sup>54</sup> / <sub>26</sub> )	39
Shear modulus, kg/cm <sup>2</sup>	D-638-61T	24,200( <sup>27,000</sup> / <sub>21,300</sub> )	23,600( <sup>24,200</sup> / <sub>22,800</sub> )	21,800( <sup>22,400</sup> / <sub>21,400</sub> )	20,800( <sup>21,300</sup> / <sub>20,100</sub> )	26,300
Bending test						
Yield strength, kg/cm <sup>2</sup>	D-790-49	619( <sup>628</sup> / <sub>609</sub> )	970( <sup>982</sup> / <sub>959</sub> )	946( <sup>967</sup> / <sub>916</sub> )	866( <sup>890</sup> / <sub>840</sub> )	942
Young's modulus, kg/cm <sup>2</sup>	D-790-49	24,070( <sup>32,100</sup> / <sub>22,700</sub> )	27,200( <sup>28,100</sup> / <sub>26,400</sub> )	26,700( <sup>27,800</sup> / <sub>25,600</sub> )	22,700( <sup>23,400</sup> / <sub>21,800</sub> )	24,700
Compressive strength, kg/cm <sup>2</sup> (1% def.)	D-695-54	136( <sup>152</sup> / <sub>123</sub> )	123( <sup>139</sup> / <sub>113</sub> )	121( <sup>132</sup> / <sub>112</sub> )	122( <sup>132</sup> / <sub>113</sub> )	141
Shear strength, kg/cm <sup>2</sup>	D-732-46	597( <sup>625</sup> / <sub>577</sub> )	580( <sup>595</sup> / <sub>559</sub> )	575( <sup>583</sup> / <sub>568</sub> )	542( <sup>574</sup> / <sub>517</sub> )	672
Izod impact strength, kg-cm/cm <sup>2</sup>	D-256-56	7.5( <sup>9.9</sup> / <sub>5.3</sub> )	11.2( <sup>15.3</sup> / <sub>8.3</sub> )	13.6( <sup>17.7</sup> / <sub>9.7</sub> )	11.6( <sup>18.0</sup> / <sub>8.5</sub> )	13.5
Rockwell hardness (R-scale)	D-785-51	117( <sup>118</sup> / <sub>117</sub> )	118( <sup>119</sup> / <sub>117</sub> )	118( <sup>118</sup> / <sub>118</sub> )	117( <sup>118</sup> / <sub>117</sub> )	122
Melt index, g/10 min	—	—	11.9( <sup>12.0</sup> / <sub>11.6</sub> )	5.1( <sup>5.3</sup> / <sub>4.8</sub> )	8.4( <sup>8.6</sup> / <sub>8.0</sub> )	—

<sup>a</sup> Figures in columns represent average values, with upper figure in parentheses the maximum value and lower figure the minimum value obtained.

on the contrary, were similar to those of Delrin 500. These results seem to be reasonable, because copolymer C has a very homogeneous distribution of ethylene oxide units in its main chain and a very narrow molecular weight distribution; and also the ethylene oxide content of copolymer C, as listed in Table I, is lower than that of Duracon M90. It is concluded that copolymer C can be expected to be an excellent engineering plastics having both characteristics of Delrin 500 and Duracon M90.

In summary, it is concluded that the mechanical properties of the copolymer obtained by solid-state copolymerization of tetraoxane with 1,3-dioxolane are largely influenced by the amount and addition method of the 1,3-dioxolane-methylal solution and that, on the basis of the characteristics of this copolymerization system, one can easily synthesize the oxymethylene copolymer having various mechanical properties intermediate between those of Duracon M90 and Delrin 500.

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