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A. A. Nishimura^{ab}, H. Komagata^a

^a TOYOBO TEXTILE RESEARCH INSTITUTE, SHIGA, JAPAN ^b Research Department, Dow Badische Co., Williamsburg, Virginia

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Elastomers Based on Polyester

A. A. NISHIMURA* and H. KOMAGATA

TOYOBO TEXTILE RESEARCH INSTITUTE
SHIGA, JAPAN

Summary

Polyester elastomers were prepared by block copolymerization of dimethyl terephthalate (DMT), butanediol (BDO), and polytetramethylene glycol (PTMG). Polyester from DMT and butanediol forms a high-melting hard segment in block copolyester to prevent undue chain slippage when fibers are stretched. High elongation was provided by soft segment which consisted of condensation product from DMT and PTMG.

Experiments were carried out to determine the effect of composition variables on the properties of these elastomers, such as glass transition temperature, elongation at break, tenacity, and elastic recovery. The study on molecular characteristics of the elastic polyester showed that a leather-like region exists between glassy and rubbery regions. These elastomers were melt-spun to give elastic fibers which are competitive with commercially available Spandex-type fibers.

INTRODUCTION

Rubbery polyesters have been known for many years (1). Polyesters having rubbery properties are readily prepared by reacting long-chain glycols with aliphatic, aromatic dicarboxylic acids.

In 1949 Flory published a paper (2) which covered the general problem of crystallization in condensation polymers including random and block copolymers. Anticipating the existence of a copolymer in which the crystallizing units occur in abnormally long sequences, Flory considered theoretically the effect of crystallinity on this type of deviation from a random arrangement, and this is

* Present address: Research Department, Dow Badische Co., Williamsburg, Virginia.

summarized by

$$(1/T_m) - (1/T_m^0) = (R/h\mu) [1/(Y - \zeta e + 1) - \mu'(1 - X_a Z_a)/\bar{Z}^2]$$

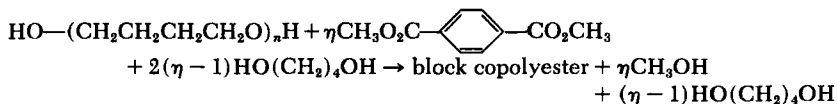
where T_m is the melting point of the copolymer, T_m^0 the melting point of the pure polymer consisting exclusively of repeating unit A, $h\mu$ the heat of fusion, Y the length of the units of the A sequences, ζe the equilibrium length of the crystallite in number of units, μ' the heat of the mixing parameter, X_a the mole fraction of A repeat units present in the polymer, Z_a the number of segments in an A unit, and \bar{Z} the average number of segments per unit.

This equation indicates the relationship of melting point and two important parameters, Y (the length of the units of the A sequences) and X_a (the mole fraction of A repeat units). If $\mu' = 0$, as is the case with copolymers, the term containing X_a disappears:

$$(1/T_m) - (1/T_m^0) = (R/h\mu) [1/(Y - \zeta e + 1)]$$

If Y_1 , the length of the units of A sequences, is sufficiently large, the melting point of these copolymers containing abnormally long sequences of A units will be independent of the mole fraction of A units. This theoretical conception with regard to block copolymers opened the way to preparing copolyesters in which a high melting point is retained even in the presence of an appreciable concentration of a noncrystalline flexible component in the polymer chain. It should be stated at this moment that block copolyesters may be obtained in ordered configuration or in random configuration. If one of the two segments is crystallizable and the other is not, the melting point of the block copolyester will still be only slightly lower than that of the crystalline segment.

Elastomers can be considered to consist of two types of segments: a soft segment and a hard segment. To produce an elastomer with a useful temperature range, the hard segment must be high-melting to counteract the very low-melting soft segment. The hard segment should be capable of restraining the gross mobility of the elastomer chains. This can be accomplished in the form of cross-links, hydrogen bonding, or crystallinity. In polyesters, the rigid crystalline property of the hard segment does this job. Components employed in this experiment are DMT, butanediol, and PTMG.



Polyester from DMT and butanediol constitutes a hard segment and polyester from DMT and PTMG constitutes a soft segment. In the course of the study of a hard segment, it showed the melting point of 260°C when it reached high molecular weight; however, it was noted that the specific polymerization catalyst had to be developed to suppress the decomposition reactions in favor of formation of poly(tetramethylene terephthalate) via ester exchange. Metal double alkoxides of titanium and magnesium proved to promote the formation of polyester. Efficient removal of methanol from the reaction system is essential to reach high intrinsic viscosity. The experiment was run from a small-scale batch (50 g) to a fairly big scale (3 kg/batch). The melt polymerization process here employed is now the conventional procedure; thus DMT involved, together with an excess of glycols, may be initially heated together in the molten state and at atmospheric pressure. After the ester interchange is complete, as indicated by the cessation of the evolution of methanol, the pressure is gradually reduced to the vicinity of 0.1 mm Hg and the temperature increased to a range 240 to 260°C. These conditions were maintained for about 2 hours with stirring, at which time a polymer of the desired intrinsic viscosity is obtained.

EXPERIMENTAL

PTMG with hydroxyl end group was prepared by the ring-opening polymerization of tetrahydrofuran in the presence of acetic anhydride and perchloric acid as catalyst followed by the saponification. For example, 50 g of tetrahydrofuran was polymerized in the presence of 6.5 g of acetic anhydride and 0.20 g of perchloric acid. The saponified polymer gave the molecular weight of 4200.

Polymerization

To a 500-cc flask equipped with stirring rod and distilling column were added 38.8 g (0.20 mole) of DMT, 30.7 g (0.34 mole) of butanediol, 100.4 g (0.04 mole) of PTMG (\bar{M}_w 2510), 1.4 g of dithiopropionic acid, and 0.6 ml of 20% butanol solution of $\text{Mg}[\text{HTi}(\text{OC}_4\text{H}_9)_6]_2$ as a catalyst. After the air in the system was replaced by nitrogen, the temperature was maintained at 200°C for 1 hr. After the ester exchange was complete, the pressure was gradually reduced to 0.05 to 0.1 mm Hg and the temperature increased to 260°C. These conditions were maintained for 2 hr under stirring,

at which time a polymer of the desired intrinsic viscosity was obtained. When the molten polymer has reached the desired intrinsic viscosity, it was extruded from the spinnerette and quenched in water bath. In general, it was preferred that after orientation of the yarn it was allowed to age for 24 hr. This aging procedure appeared to allow equilibrium with respect to crystallization and allows manufacture of a more uniform product.

RESULTS AND DISCUSSION

Fiber properties from polyester elastomers are listed in Table 1. For the flexible soft segment, the following factors need to be considered:

TABLE 1
Fiber Properties from Polyester Elastomers

| Expt. | Composition of elastomer | | | $[\eta]^a$ | Tenacity ^b g/d | Elongation ^c at break, % | Elastic recovery, ^d % |
|-------|--------------------------|----------------------------|----------------------------|------------|------------------------------|--|-------------------------------------|
| | PTMG, mol. wt. | DMT (mole)/ PTMG (mole) | BDO (mole)/ PTMG (mole) | | | | |
| 1 | 3337 | 3 | 2 | 2.13 | 1.12 | 845 | 99.0 |
| 2 | 3337 | 4 | 3 | 2.54 | 1.29 | 750 | 99.1 |
| 3 | 3337 | 5 | 4 | 2.49 | 1.33 | 620 | 99.5 |
| 4 | 2510 | 3 | 2 | 2.43 | 0.67 | 865 | 99.2 |
| 5 | 2510 | 4 | 3 | 2.43 | 1.13 | 700 | 99.8 |
| 6 | 2510 | 5 | 4 | 2.22 | 1.14 | 665 | 99.5 |
| 7 | 1940 | 2 | 1 | 1.82 | 0.52 | 780 | 98.5 |
| 8 | 1940 | 3 | 2 | 2.11 | 0.85 | 665 | 99.2 |
| 9 | 1940 | 4 | 3 | 2.09 | 0.92 | 550 | 98.0 |

^a Viscosity was measured in phenol-tetrachloroethane (6:4) at 25°C as 2% solution.

^b Tenacity was measured on an Instron tester for fiber samples.

^c Elongation was measured by placing two marks 2 cm apart on the fiber sample and stretching it along a meter stick until it broke.

^d Elastic recovery was measured at 25°C by stretching the sample 200% and holding it for 10 min.

1. Low glass transition temperature, to provide the greatest possible mobility of the chains, thus assuring good elastic recovery from deformation.

2. Low melting point, to avoid restricting the movement of the chains.

3. Crystallizability by stretching is desirable, assuming that the crystallites melt completely when the stretching force is withdrawn, since it contributes to the ultimate tensile strength of the fiber.

For the crystalline hard segment, the following factors need to be considered:

1. High melting point of the hard segment is best prepared by using symmetrical aromatic acids and symmetrical glycols having an even number of carbon atoms.

2. Good compatibility with soft segment is required, to obtain high molecular weight. Two blocks (hard and soft) must be compatible when they are melt-mixed, which inhibits the random selection of polymerizing components.

From Table 1, the desired level of the variables in the elastomer, such as molar ratio and molecular weight of PTMG, were found. The main influence on the elongation was the molar ratio of PTMG used; the elongation increased as the amount of PTMG was increased. The tenacity generally increased as the molar ratio of PTMG decreased. Tenacity was also improved when the molecular weight of PTMG was increased from 1940 to 3337. The polyester elastic fiber has excellent elastic recovery at 25°C, as shown in Table 1; however, this was towered when the measurement was done at high temperature (at 100°C). Since elastic recovery depends upon cross-linking, hydrogen bonding or crystallinity in the hard segment, a small amount of these functional cross-linking agents was added to improve the elastic recovery at high temperatures. The result is shown in Table 2 (see also Table 3).

TABLE 2
Effect of Cross-linking at 100°C

| Cross-linking agent | Mole % ^a | Elastic recovery, % | Stress decay, % ^b |
|---------------------|---------------------|---------------------|------------------------------|
| None | None | 82.5 | 27 |
| TMP ^c | 0.5 | 88.0 | 25 |
| TMP | 1.0 | 92.0 | 23 |
| TMA ^d | 0.5 | 95.0 | 20 |
| TMA | 1.0 | 98.0 | 16 |
| TMA | 1.5 | Gel formation | |

^a Mole % based on total acid or glycol in the polymer.

^b 1 min from 100% elongation.

^c Trimethylol propane.

^d Ester of trimellitic acid.

TABLE 3
Solubility Test of Polyester Elastomer

| Solvent | | Solvent | |
|------------------|-------------|---------------------------|----------|
| <i>m</i> -Xylene | Swelling | Methyl ethyl ketone | Swelling |
| Toluene | Swelling | Cyclohexanone | Swelling |
| Butanol | Not soluble | Methylene chloride | Soluble |
| <i>m</i> -Cresol | Soluble | Carbon tetrachloride | Swelling |
| Ethylene glycol | Not soluble | Chloroform | Soluble |
| Butanediol | Not soluble | Tetrachloroethane | Soluble |
| Dioxane | Swelling | <i>o</i> -Dichlorobenzene | Swelling |
| Acetone | Not soluble | | |

Molecular Characteristics of Elastic Polyester

Typical stress-temperature curve for a commercially available rubber is shown in Fig. 1, which is used to determine the glass transition temperature. At this transition temperature comparatively abrupt changes in slope are observed. The stress-temperature method of study is an old one and has been used by a number of workers (3-5). Meyer and Ferri (6) were among the first to employ the method in the study of rubber. The stress-temperature method was selected for the study of this transition behavior, because the existence of free or quasi-free rotations of molecular groups about the single carbon-carbon bonds in the long-chain molecules is a basic requirement of all modern statistical theories of rubberlike elasticity. In this method the sample was stretched to 35% extension at 30°C, and was then held at constant length at that temperature until the rate of relaxation of stress became negligibly small. The temperature was then lowered in steps, the length being held constant, and the stress was observed as a function of the temperature. The stress in this study was defined as the force per unit original unstrained cross section. We may remark here that the theory of elasticity predicts that rubber tends to contract as the temperature is increased. The singular behavior, which is quite opposite from the familiar expansion of ordinary material with increasing temperature, may be seen qualitatively in terms of the kinetic theory. In Fig. 1 it is also noted that at low temperatures the tension decreases upon heating over a certain temperature interval. That is to say, the material tends to expand upon heating, just as

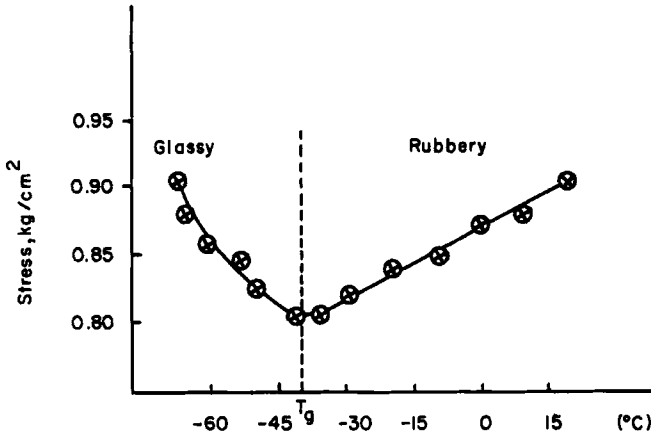


FIG. 1. Stress-temperature curve of butyl rubber (contains 5% zinc oxide and 1.5% sulfur).

with ordinary solids. This is the region in which the rubber is a glassy solid, rather than an elastic substance.

In Fig. 2 the typical stress-temperature curve for the elastic polyester fiber is shown. Here a different tendency of curve was observed, in that apparently another region between glassy and rubbery regions was found. We tentatively call it a leatherlike region. The existence of the leatherlike region seems to be a char-

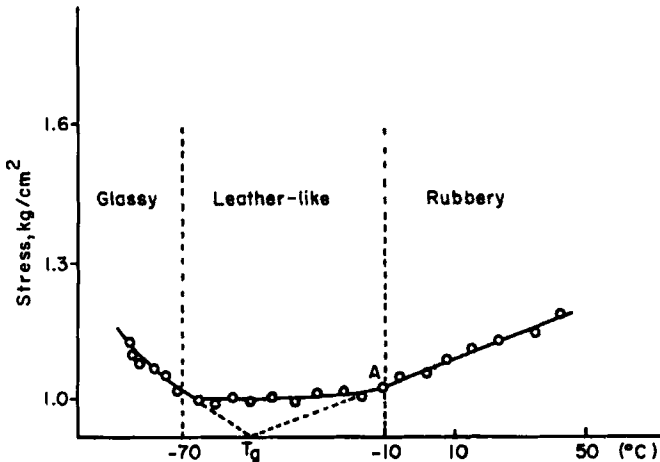


FIG. 2. Stress-temperature curve of elastic polyester fiber (35% extension).

acteristic feature of elastic fiber, which, in category, lies between the rubber and the fiber. The glass transition temperature was determined by the extrapolation, as was shown in Fig. 2. We should note that there is thermal expansion of the stretched elastic fiber, along with contraction. In the leatherlike region, the contraction to be expected from the kinetic theory of elasticity at 35% extension almost equals the expansion typical of ordinary solids, and thus a flat curve resulted. For practical purpose it is desired to lower the temperature at point A (shown in Fig. 2). This was successfully done by using the copolymer rather than pure PTMG as a soft segment. For example, when 10% of 7-oxabicyclo[2,2,0]heptane was copolymerized with 90% of tetrahydrofuran in the presence of perchloric acid and acetic anhydride, this copolymer, when used as a soft segment, lowered the temperature at point A to -20°C .

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Zusammenfassung

Polyesterelastomere wurden durch Block-Copolymerisation von Dimethylterephthalat (DMT), Butandiol (BDO), und Polytetramethylenglycol (PTMG) dargestellt. Polyester aus DMT und Butandiol bilden hochschmelzende, harte Segmente, die übermässiges Gleiten der Ketten verhindern wenn die Fasern gestreckt werden. Hohe Elongation wurde durch weiche Segmente gewährleistet, die aus Kondensaten aus DMT and PTMG bestanden.

Versuche wurden ausgeführt, um den Einfluss der durch die Zusammensetzung bestimmten Variablen auf die Eigenschaften dieser Elastomere zu bestimmen, z.B. die Glasübergangstemperatur, Bruchelongation, Festigkeit und elastische Erholung. Eine Untersuchung der molekularen Charakteristika der elastischen Polyester zeigte, dass ein lederartiger Bereich zwischen den glasigen und gummiartigen Bereichen existiert. Diese Elastomeren wurden als Schmelze versponnen und ergaben elastische Fasern, die mit den handelsüblichen Spandex Fasern konkurrenzfähig sind.

Résumé

On a préparé des élastomères polyesters par polymérisation séquencée du téréphthalate de diméthyl (DMT), du butanediol (BDO), et du polytetraméthylène glycol (PTMG). Le polyester à partir de DMT et du butanediol forme un segment dur à haut point de fusion dans le polyester séquencé, afin de prévenir un glissement indésirable des chaînes lorsque les fils sont étirés. Des segments souples, composés de produit de condensation de DMT et PTMG, fournissent l'élongation élevée.

On a fait des essais afin de déterminer l'effet des variations de composition sur les propriétés de ces élastomères, telles que la température de transition vitreuse, élongation à la rupture, tenacité et récupération élastique. L'étude des caractéristiques moléculaires du polyester élastique a montré qu'une région tenace existe entre les états vitreux et caoutchoutés. On a filé ces élastomères en fusion et on a obtenu des fils élastiques pouvant rivaliser avec les fils commerciaux du type Spandex.