Polyesters Containing Sulfur. II. Products of Reaction of Polyesters with Elemental Sulfur

ANNA KULTYS and WAWRZYNIEC PODKOŚCIELNY*

Department of Organic Chemistry and Technology, Maria Curie-Skłodowska University, ul. Gliniana 33, 20-614 Lublin, Poland

SYNOPSIS

New polyester–sulfur compositions with increased tensile strength were obtained by heating polyesters derived from diphenylmethane-4,4′-di(methylthioacetic acid) and ethylene or diethylene glycol with elemental sulfur. The hardness, tensile, thermomechanical, as well as some electrical properties of reaction products were determined. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Linear polyesters containing sulfur in their structure until now have been synthesized mainly with aliphatic monothio- or dithiodicarboxylic acids and various diols. They find wide application as nonvolatile plasticizers for such polymers as poly(vinyl chloride) and rubber modifiers. They are also useful for modifying or plasticizing elemental sulfur, which may be reacted therewith by heating a mixture of the sulfur and polyester to produce such useful products as caulking compounds and compositions for striping or marking highways and other surfaces.[1]

Some U.S. patents[1,2] disclose the manner of plasticizing and modifying with elemental sulfur monothiopolyesters based on monothiodipropionic acid and monothiodiisobutyric acid as well as dithiopolyesters based on dithiodiacetic acid, dithiodipropionic acid, dithiodibutyric acid, dithiodiheptanoic acid, dithiodioctanoic acid, and dithiodibenzoic acid.

The above-mentioned thiopolyesters were heated with elemental sulfur in amounts of about 10–90% by weight at a temperature range of 150–250°C, for 5 min to 2 h, until a clear melt was obtained. The optimum reaction temperature depended on conditions such as the proportions of sulfur and thiopolyester and the nature of the thiopolyester.

The nature of the reaction occurring between the elemental sulfur and the thiopolyester has not been adequately explained. On heating the mixture, a clear melt is obtained, which, on cooling, becomes an opaque plastic material, the exact properties of which depend on the amount of sulfur used, the nature of the thiopolyester used, the rate of cooling, and other variables. However, it appears that at least a portion of the added sulfur is actually incorporated into the polymer chain, and the new thiopolyester formed, containing added sulfur in the chain, is soluble in sulfur and forms a clear melt at the reaction temperature. Additionally, it is believed that the reversion of polymeric sulfur, formed during the heating period, back to crystalline sulfur is retarded by the presence of the thiopolyester. In any case, as has been mentioned above, the resulting products are unique and useful.

The tensile strength of the polyester–sulfur compositions can be improved by adding such fillers as glass wool and poly(ethylene terephthalate) fiber. The use of cross-linked polyesters containing sulfur also can increase the tensile strength of these compositions.

Depending on the nature of thiopolyester and the amount of elemental sulfur used, products were obtained with various degrees of hardness and elasticity, characterized by tensile strength in the range of

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 49, 1615–1618 (1993)
© 1993 John Wiley & Sons, Inc. CCC 0021-8995/93/091615-04

0.04–9.9 MPa and elongation at break in the range of 17–240%. The subject of the present article is the investigation of some physicomechanical properties of polyester–sulfur compositions obtained by using polyesters derived from diphenylmethane-4,4′-di(methylthioacetic acid) and ethylene or diethylene glycol. The incorporation of the diphenylmethane unit into the polyester chain with active methylene groups makes it possible to obtain sulfur-cross-linked products with increased tensile strength.

EXPERIMENTAL

Reagents

Poly[ethylene diphenylmethane-4,4′-di(methylthioacetate)] (Polyester **I**), softening temperature of 51°C according to the "ring-ball" method and reduced viscosity of 0.25 ($\bar{M}_n$ 5665), was obtained from diphenylmethane-4,4′-di(methylthioacetic acid) and ethylene glycol by melt polycondensation.[3]

Poly[oxydiethylene diphenylmethane-4,4′-di-(methylthioacetate)] (Polyester **II**), softening temperature 38°C according to the "ring-ball" method and reduced viscosity 0.21 ($\bar{M}_n$ 5066), was obtained from diphenylmethane-4,4′-di(methylthioacetic acid) and diethylene glycol by melt polycondensation.[3] Crystalline sulfur produced by POCh Gliwice (Poland) was used.

Measurement of Properties

Hardness

The hardness of polyester–sulfur compositions was measured by the Shore A/D method at 25°C. Values were taken after 15 s.

Tensile Tests

Tensile testing was performed on a TIRA test 2200 tensile testing machine according to Polish Standard PN-82/C-89051 for the modulus of elasticity and PN-81/C-89034 for tensile strength at speeds of 1.5 and 100 mm/min at 23°C, respectively. The tensile test pieces 2 mm thick and 10 mm wide (for the section measured) were cut from pressed sheets.

Dynamic Mechanical Tests

Dynamical mechanical testing was performed by a Zwick torsional pendulum at a temperature of −35 to 80°C and a frequency of 0.1–25 Hz, according to Polish Standard PN-83/C-89042. The rectangular test specimens, 60 × 10 × 1 mm, were cut from pressed sheets.

RESULTS AND DISCUSSION

The polyester–sulfur compositions were obtained using linear polyesters containing sulfur in the main chain and derivatives of diphenylmethane-4,4′-di(methylthioacetic acid) and ethylene or diethylene glycol. For this purpose, the above-mentioned thiopolyesters were heated with crystalline sulfur under nitrogen at 220–225°C for 15–25 min, under vigorous stirring, using various amounts of sulfur in the range of 10–80% by weight in relation to this mixture's weight. The optimum reaction time with the use of 10% sulfur was 25 min, whereas with the use of 20–80% sulfur, it was 15 min.

At the early phase of heating, the mixture of sulfur and thiopolyester at 220°C formed a clear melt, which, as the reaction continued, after some 7–10 min, markedly increased in viscosity due to possible cross-linking with sulfur at this temperature. After the reaction was over, the reaction mixture was cooled to room temperature. Rubberlike products were obtained with various degrees of hardness and flexibility. They were clear and amber-colored when using 10% sulfur and opaque, cream-colored, or yellow when using 20–80% sulfur.

These products undergo dissolving or swelling in common organic solvents like benzene, chloroform, ethylene chloride, tetrachloroethane, dioxane, dimethylformamide, dimethylsulfoxide, and nitrobenzene in contrast to initial thiopolyesters that are very soluble in these solvents. This points to the formation of cross-linked products.

The X-ray analysis and CS_2 extraction showed that the products obtained using 20–80% sulfur contain some quantity of crystalline sulfur formed by reversion of polymeric sulfur during cooling of the reaction mixture.

Mechanical and Electrical Properties

Some mechanical and electrical properties of the obtained polyester–sulfur compositions were studied after pressing at 100–115°C under a pressure of 2.9–10.4 MPa. The results are given in Table I(a) and (b).

From Table I(a) and (b), it follows that the elasticity of compositions varies inversely to the sulfur content. The products from Polyester **I** with advantageous tensile properties were obtained using 20–

Table I Mechanical and Electrical Properties of Polyester–Sulfur Compositions

	Sulfur Content (% by Weight)					
	10	20	35	50	65	80
(a) Polyester I						
Shore A/D hardness	29/6	44/10	61/16	72/21	92/44	97/57
Modulus of elasticity (MPa)	0.70	1.28	4.77	9.04	32.21	258.81
Tensile strength (MPa)	0.72	1.21	1.82	2.43	3.77	7.89
Elongation at break (%)	305.1	220.7	98.7	80.7	18.4	3.0
Dielectrical constants	4.10	3.86	3.76	3.71	3.36	3.30
Tan $\delta \times 10^{-2}$ at 1 kHz (20°C)	8.779	7.843	6.604	5.812	3.305	2.652
(b) Polyester II						
Shore A/D hardness	18/4	30/6	45/10	67/17	94/60	97/72
Modulus of elasticity (MPa)	0.64	0.72	2.50	5.63	49.47	263.38
Tensile strength (MPa)	0.41	0.90	1.45	2.03	8.05	2.62
Elongation at break (%)	244.7	202.8	120.5	84.7	12.0	2.4
Dielectrical constants	5.10	5.60	4.55	3.98	3.75	3.39
Tan $\delta \times 10^{-2}$ at 1 kHz (20°C)	3.217	4.345	6.750	5.381	4.261	3.040

I = Poly[ethylene diphenylmethane-4,4′-di(methylthioacetate)].
II = Poly[oxydiethylene diphenylmethane-4,4′-di(methylthioacetate)].

80% sulfur, whereas the products from Polyester **II** used only 35–65% sulfur. The product from Polyester **II** obtained by using 80% sulfur were too brittle, which is evidenced by a marked fall in tensile strength.

Thermomechanical Properties

Dynamic shear modulus (G') and logarithmic damping decrement (λ) of the polyester–sulfur compositions obtained by using 35–65% sulfur were studied at a temperature range of −35 to 80°C. The dynamic glass transition temperature (T_g), the values of shear modulus in a glassy and a high-elastic range, and the temperatures determining the ranges of glassy state, glassy transition, and high-elastic state were defined from the plotted thermomechanical curves of the logarithmic damping decrement (λ) and the shear modulus (G') in relation to temperature.

Numerical data are presented in Table II. The dependence of the shear modulus (G') on the temperature of the polyester–sulfur compositions is given in Figure 1.

Table II Thermomechanical Properties of Polyester–Sulfur Compositions

Polyester	Sulfur Content % by Weight	Free Vibration Frequency (Hz)	Shear Modulus (MPa) in Range: Glassy at −20°C	Shear Modulus (MPa) in Range: High Elastic at 65°C	Glass Transition Temperature (°C)	Temperature (°C): Glassy State to	Temperature (°C): Glassy Transition Range	Temperature (°C): Pure High-elastic State from
I	35	17.4–0.6	1880	2.27	22	3	3 to 48	48
	50	17.0–0.8	2200	5.71	23	−8	−3 to 52	52
	65	19.5–4.1	2970	99.70	24	2	2 to 44	44
II	35	15.6–3.5	1930	0.61	10	−9	−9 to 61	61
	50	16.8–0.8	2260	4.17	12	−8	−8 to 39	39
	65	21.7–3.2	2720	64.50	35	−10	−10 to 59	59

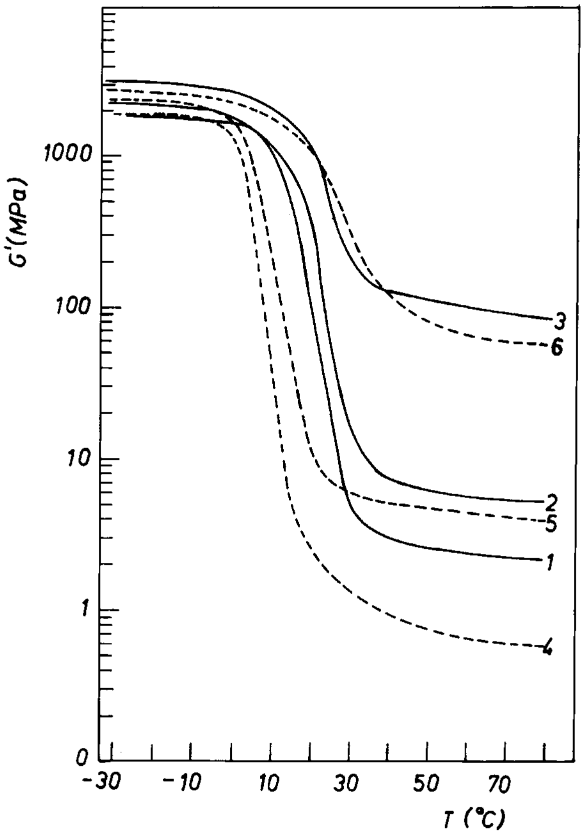

Figure 1 Shear modulus (G') vs. temperature of polyester–sulfur compositions: (——) Polyester **I**: (1) 35% S; (2) 50% S; (3) 65% S; (---) Polyester **II**: (4) 35% S; (5) 50% S; (6) 65% S.

CONCLUSIONS

Polyester–sulfur compositions in the form of rubberlike materials were obtained by using new thiopolyesters cross-linked with sulfur. Differences in hardness and elasticity are dependent on the sulfur content used and the nature of the thiopolyester used. The elasticity of these compositions varies inversely with the sulfur content.

The products with the highest tensile strength were obtained by heating the mixture of 80% sulfur with 20% Polyester **I** and the mixture of 65% sulfur with 35% Polyester **II**. As expected, the compositions derived from Polyester **I** are characterized by higher values of shear modulus in the high-elastic state than those of the corresponding products from Polyester **II**. Values of dielectric constants and dielectric loss factor show good electroinsulating properties of the polyester–sulfur compositions obtained.

REFERENCES

1. W. E. Weesner, U.S. Pat. 3,459,787 (1969).
2. W. E. Weesner, U.S. Pat. 3,513,133 (1970).
3. A. Kultys and W. Podkościelny, *J. Appl. Polym. Sci.*, **39**, 715 (1990).

Received August 5, 1992
Accepted September 1, 1992