Synthesis and rheological study of some maleic acid and fumaric acid stereoregular polyesters

8. Unsaturated polyester fibers*

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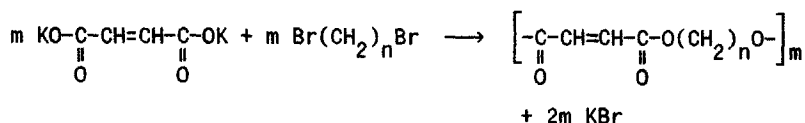[2]Laboratoire de Chimie Macromoléculaire, URA 24, Université Pierre et Marie Curie, 4 Place Jussieu, F-75252 Paris Cedex 05, France

Summary

First unsaturated polyester fibers were prepared starting from stereoregular, macromolecular poly(octamethylene fumarate). Fibers obtained from octamethylene copolyesters of fumaric and terephthalic acids manifested improved mechanical properties and higher melting points. All unsaturated polyester fibers prepared in the study, based on the homopolymer and on copolymers of fumaric acid, even those containing as low as 10 % of fumaric acid residues, are able to be covalently bonded to an unsaturated polyester matrix.

Introduction

Recently, we succeeded in preparing configurationally pure, macromolecular poly(alkylene maleate)s and poly(alkylene fumarate)s by polycondensation of the corresponding potassium dicarboxylate with α,ω-dibromoalkanes in 1-methyl-2-pyrrolidone (NMP), slightly above $100°C$ (1-3):

$$m\ KO-\underset{O}{\underset{\|}{C}}-CH=CH-\underset{O}{\underset{\|}{C}}-OK\ +\ m\ Br(CH_2)_nBr\ \longrightarrow\ \left[-\underset{O}{\underset{\|}{C}}-CH=CH-\underset{O}{\underset{\|}{C}}-O(CH_2)_nO-\right]_m$$

$$+\ 2m\ KBr$$

It is indeed well known that during high temperature polycondensation of maleic acid or maleic anhydride with diols cis-trans isomerization occurs, while in the case of fumaric acid a secondary addition of hydroxyl groups onto fumarate residues prevents preparation of uncrosslinked, high molecular weight products. Both of these disadvantages are eliminated by the above mentioned synthesis route.

The configurationally pure unsaturated polyesters have been used for systematic studies of the influence of the main chain double bonds configuration on transition temperatures and rheological properties of polymers. During the purification and characterization of poly(alkylene fumarate)s, we observed that these crystalline polymers manifested

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*For part 7, see Jaćović M.S., et al., Makromol. Chem. (submitted)
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pronounced fiber-forming properties. So, we undertook a study on preparation and characterization of unsaturated polyester fibers, and this paper presents its initial results. To our best knowledge this is the first published attempt to prepare unsaturated polyester fibers, which are supposed to be useful as reinforcement in composite materials based on polymerizable matrices, as well as specialty fibers susceptible to various chemical modifications.

Experimental

Synthesis and characterization of polymers

The synthesis of poly(octamethylene fumarate) (POF) was previously described (2). Under similar conditions we also prepared one poly(octamethylene terephthalate) (POT), and two poly(octamethylene fumarate-co-octamethylene terephthalate)s (POFT 10 and POFT 20) containing 10 and 20 mole % of fumarate residues, respectively, on the sum of acid residues. ^{1}H NMR spectra were recorded using a Varian instrument EM 390 (90 MHz). Polyesters were dissolved in deuterated chloroform to which tetramethylsilane was added as a standard reference. Limiting viscosity numbers were determined in chloroform solution at 25 ^{o}C. Complex dynamic viscosity was recorded with a Rheometrics mechanical spectrometer RMS-605 in dynamic shear mode between two parallel plates, at constant temperature 5 ^{o}C above the corresponding melting temperature in frequency range from 0,1 to 100 rad/s.

Preparation of fibers

Fibers from unsaturated and saturated polyesters were prepared by melt-spinning, using an Instron capillary extrusion rheometer. The plunger having a diameter of 9,53 mm moved in the barrel at a linear speed of 0,2 mm/min. The capillary had a diameter of 0,42 mm and a length of 25,4 mm. The solidified extrudate, i.e., the filament was taken-up by a roll having a diameter of 30 mm and rotating at 25 rpm. The filament was then cold stretched at an elongational stretching ratio of about 3.

Characterization of fibers

Young modulus and tensile strength of fibers were measured using an Instron machine, model 1184, at 30 mm gage length and at extension rate of 10 mm/min. For each type of fibers 30 samples were tested. Differential scanning calorimetry was carried out under nitrogen atmosphere using a Perkin-Elmer instrument 2B, at a heating and cooling rate of 10 ^{o}C/min. The bonding between unsaturated and saturated polyester fibers, and unsaturated polyester matrix was examined by a multifilament pull-out test (4) and scanning electron microscopy. Specimen preparation for pull-out test consisted of taking two strands of polyester fibers, which were twisted together and embedded perpendicularly in a disc 1 mm thick of unsaturated polyester "Roskydal K-36" supplied by Bayer AG, Germany. The pull-out test was performed at a speed of 10 cm/min.

Composite materials were prepared with various fibers and the same unsaturated polyester matrix Roskydal K-36, and then subjected to failure under tensile stress. Scanning electron microscopy (JEOL JSM 35) was used to examine the fiber-matrix interface on the fracture surface.

Results and discussion

In order to study the preparation and properties of unsaturated polyester fibers, one poly(octamethylene fumarate) (POF) and two octamethylene copolyesters of fumaric and terephthalic acids (POFT 10 and POFT 20), as well as one poly(octamethylene terephthalate) (POT) have been prepared by moderate temperature polycondensation of corresponding potassium dicarboxylates with 1,8-dibromooctane in NMP, slightly above

Table 1. Synthesis and characterization of polyesters from mixtures of fumaric (F) and terephthalic (T) acid potassium salts and 1,8-dibromooctane (O)

Polymer	Reaction time, h	Yield, %	Mole fraction of acid residues, from ^{1}H NMR		$[\eta]$,	T_m [a)	η_N^*
			F	T	dl/g	(DSC), ^{o}C	at T_m+ 5° C, Pa s
POF	24	90	1	0	0,600	85(79)	540
POFT 10	88	88	0,1	0,9	0,470	129(123)	155
POFT 20	88	87	0,2	0,8	0,550	112(106)	776
POT	88	90	0	1	0,490	138(131)	183

a) in brackets, the second T_m appearing in the second run

100 ^{o}C. The method assumed the preparation of uncrosslinked, high molecular weight polymers in high yields (Table 1). The composition of acid residues in copolyesters is equal to the composition of salts in the starting reaction mixture. All polyfumarates are crystalline solids. On their DSC melting curves there is one peak during first melting, but another smaller peak appears in the second run. Such behavior might indicate melting of two types of crystallites, as it was observed for poly(ethylene terephthalate)s and poly(butylene terephthalate)s (5). At temperatures 5 ^{o}C above the corresponding melting points all unsaturated and saturated polyesters prepared for the study show Newtonian behavior. From all unsaturated and saturated polyesters, fibers were obtained by melt-spinning (6). The melt temperature was maintained in each case slightly above corresponding melting point. The melt linear flow rate through the capillary was close to 100 mm/min and the peripheral speed on the take-up roll was about 2300 mm/min which means that the elongational draw ratio was about 23, and the average fiber diameter was about 90 μm. The successful preparation of fibers shows that the critical viscosity for melt spinning is below 200 Pas. The following cold stretching of solidified drawn fibers was performed at about 50 ^{o}C with an elongational stretching ratio ranging from 2 to 3, and the final diameter of stretched fibers was between 50 and 70 μm.

Tensile mechanical properties of stretched fibers are shown in Table 2. The 100 % unsaturated fiber, based on POF, has lower tensile modulus and strength than the 100 % saturated fiber based on POT, as expected. Namely, terephthalic acid residues are contributing more efficiently to the molecular cohesion than fumaric acid residues. The properties of copolyester fibers from POFT 10 and POFT 20 have intermediate values. Melting points of stretched fibers are practically identical to those of starting materials. During the first melting one

Table 2. Preparation and testing of polymer fibers

| Fiber	Average fiber diameter,	Initial Young modulus,	Tensile strength,	T_m from DSC first run,	Pull-out test(4)	
					multifilament is being	MPS,
	μm	GPa	MPa	^oC		MPa
POF	65	1,30	72	84	Broken	–
POFT 10	68	1,94	92	129	Broken	> 2,59
POFT 20	55	3,13	98	112	Broken	> 3,72
POT	50	3,05	100	140	Pulled-out	2,10

peak is observed on DSC curves. In some cases this main peak is immediately followed by another very small peak. In the second run, two peaks are present in each case, as for the starting materials.

The multifilament pull-out test (4) reveals that the unsaturated polyester fibers POF, POFT 10 and POFT 20 are broken in an attempt to be pulled-out from an unsaturated polyester matrix, while the saturated polyester fiber POT is pulled-out without rupture (Table 2). The multifilament pull-out strength (MPS) is defined as:

$$MPS = \frac{F}{\pi d l}$$

where F is the maximum force, d-the diameter of the multifilament, l-the embedded length of the multifilament in the matrix. The result obtained indicates that there is a covalent bonding between unsaturated polyester fibers and the unsaturated polyester matrix. This is confirmed by scanning electron microscopy examination of the fracture surfaces of composite materials prepared from unsaturated and saturated polyester fibers and an unsaturated polyester matrix. (Figure 1).

It seems that an extent of unsaturation of 10 % as in the case of POFT 10, is sufficient to provide a covalent bonding with an unsaturated matrix. As to eventual practical application of unsaturated polyester fibers the advantage of unsaturated copolyester containing terephthalic acid residues is not only in better mechanical properties, but still more in higher melting temperature.
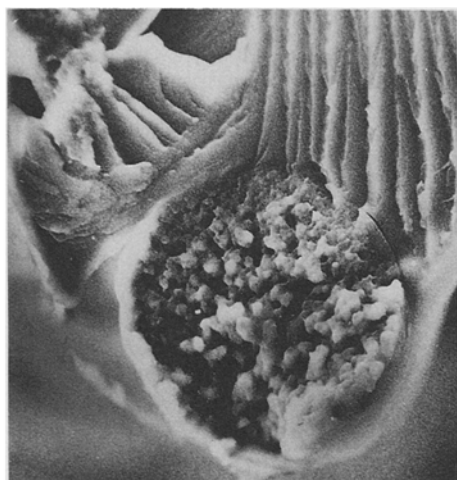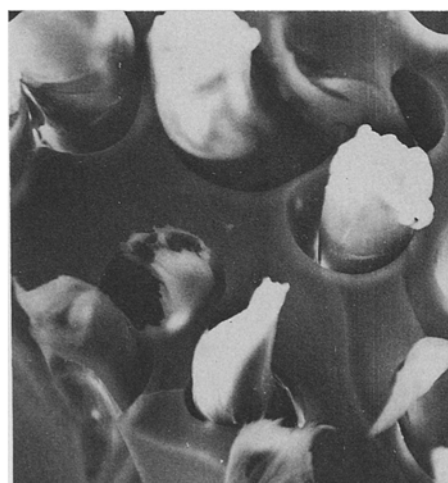
1a (400 X)

1b (1000 X)

1c (400 X)

1d (1000 X)

Figure 1. *Scanning electron microscopy (SEM) photographs of fracture surfaces. Composite materials based on an unsaturated polyester matrix and fibers: POF (1a), POFT 10 (1b), POFT 20 (1c) and POT (1d)*

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