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BIODEGRADABLE LIQUID-CRYSTALLINE AROMATIC POLYESTERS

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ABSTRACT

Two strategies designed for the mechanical reinforcement of biodegradable polyesters, such as poly-(ε-caprolactone), poly (L-lactide) and their copolyesters, are described. Both strategies utilize more or less biodegradable thermotropic aromatic polyesters as reinforcing component. However, the structures of the aromatic polyesters differ largely. For strategy I polyesters composed of substituted hydroquinones and substituted terephthalic acids are used (which may contain anhydride groups), whereas the polyesters of strategy II are made up of natural nontoxic monomers such as β-(4-hydroxyphenyl) propionic acid and 4-hydroxybenzoic acid.

INTRODUCTION

Biodegradable materials of different structure have recently attracted increasing interest for a variety of applications. Almost all biodegradable polymers reported so far are aliphatic polymers, and predominantly polylactones. Several polylactones are meanwhile commercially available in small quantities, but in the case of poly (L-lactide) even a technical production of 200 000 tons per year has been announced (by Cargill Inc.). The fact that all these biodegradable polyesters posses relatively flexible aliphatic main chains has the consequence that the glass transition temperatures (T_g's) are relatively low (-60 to + 60°C) and that the

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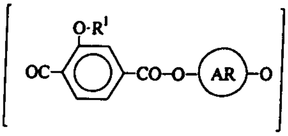
biodegradable polylactiones as engineering plastics it may be useful to find polymers and methods allowing their mechanical reinforcement. In the present work we will shortly describe two strategies designed for the mechanical reinforcement of biodegradable polyesters. Both strategies are based on aromatic liquid-crystalline polyesters (LCP's). The thermotropic character is advantageous to allow an easy processing from the melt (i.e. low melt viscosity) and to obtain a high mechanical strengths. Another prerequirement not met by commercial LCP's is their biodegradability (i.e. hydrolytic degradability).

RESULTS AND DISCUSSION

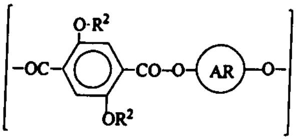
I) Polyesters of substituted terephthalic acids

The first strategy is based on para-linked (rigid rod like) poly(arylene terephthalates)s derived from substituted terephthalic acids (structures 1a - d and 2a - d). The substituents serve three purposes. Firstly, they reduce the melting temperatures (T_m's) to values below 300°C and even below 250°C. Secondly, they significantly improve the solubility in organic solvents. Thirdly, they were supposed to improve the interaction between the LCP main chain and the matrix polymer. Numerous substituted terephthalic acids were synthesized in previous years [1 - 10], and four of them, two monosubstituted and two disubstituted ones, were used for the present study. The substituents attached to hydroquinone had the purpose to improve the solubility further. However, the phenyl group in combination with substituted terephthalic acid has the consequence that the resulting polyesters 1c and 2c are amorphous and not LC-anymore. It was of particular interest to see how these isotropic polyesters perform as reinforcing additives, because they possess the same type of rigig-rod back-bone as the LCP's 1a, b and 2a, b.

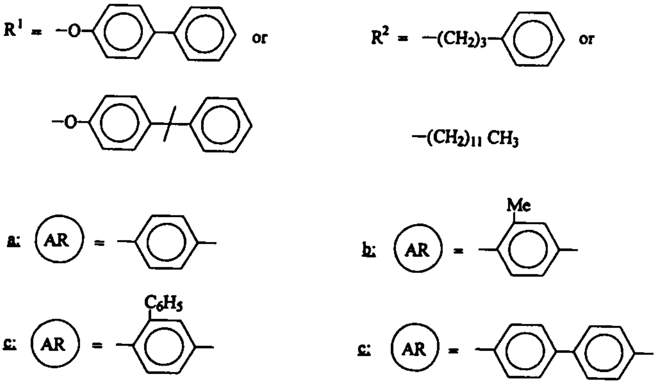
For the present study blends of commercial poly(ε-caprolactones) and LCP's


O-R¹
OC
CO–O
AR
O

1a - d


O-R²
–OC
CO–O
AR
O
OR²

2a - d


R¹ =
–O
or
–O
R² =
–(CH₂)₃
or
–(CH₂)₁₁ CH₃
a:
AR
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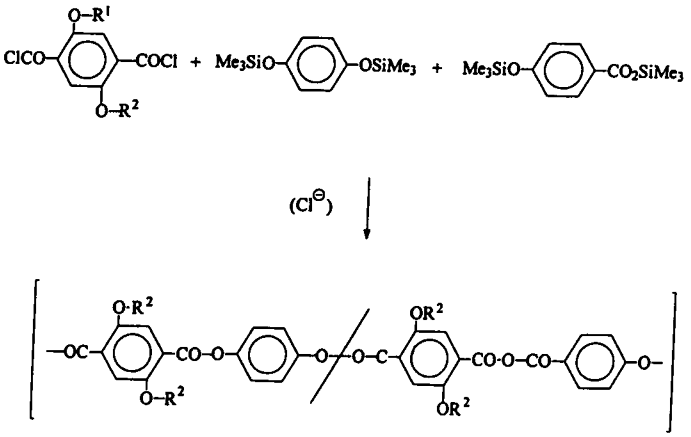
b:
AR
=
Me
c:
AR
=
C₆H₅
c:
AR
=


O–R¹
ClCO
COCl
O–R²
+
Me₃SiO
OSiMe₃
+
Me₃SiO
CO₂SiMe₃
(Cl⊖)
O-R²
–OC
CO–O
O
O–C
O–R²
OR²
CO-O–CO
O–
OR²

(1)

were prepared by dissolution of both components in CH_2Cl_2 (sometimes with addition of a litte trifluoroacetic acid) followed by coprecipitation into cold methanol. It was found that this procedure avoids significant phase separation of matric and LCP.

The resulting blends were examined by DSC measurements, optical and electron microscopy, by dynamic melt rheology, dynamic mechanical measurements and by stress-strain measurements. The following results were obtained [11, 12].

1) Even a small amount of a LCP (e.g. 1-4 weight %) may have a strong reinforcing effect (up to 100 % gain in elastic modulus), see Figure 1.

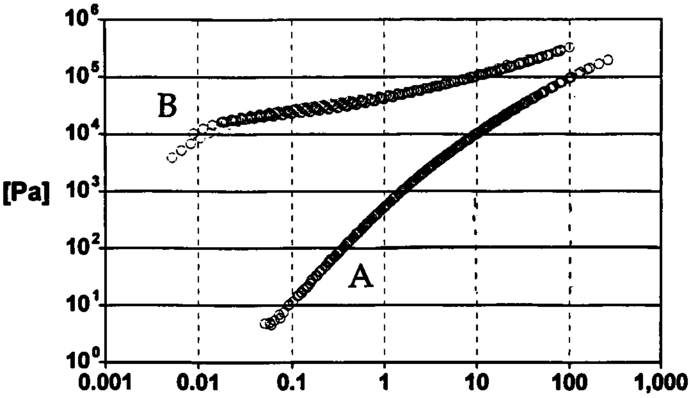
2) The reinforcing effect parallels the concentration of the LCP up to at least 8 weight %.

3) The reinforcing effect increases with the stiffness of the polymer backbone.

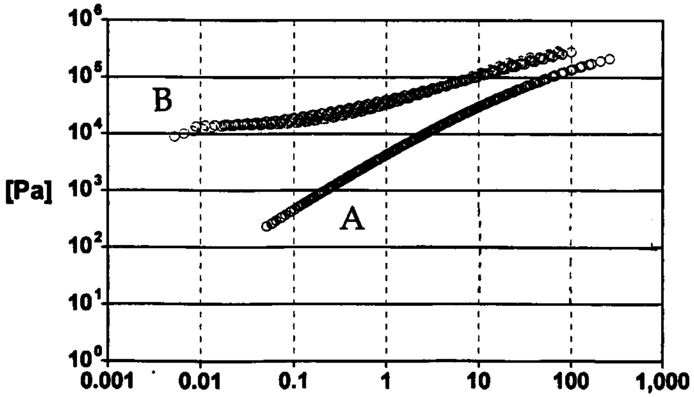
4) Even the amorphous, isotropic polyesters 1c and 2c show a strong reinforcing effect owing to the stiff main chain.

5) LCP's having alkyl substituents (R^2=$(CH_2)_{11}CH_3$) do not cause a reinforcing of the matrix. Obviously the side chains play an important role for the interaction between LCP and matrix and aromatic rings in the side chains favor this interaction.

6) Optical microscopy indicates the existenc of a mobile birefringent phase filling nearly the total volume of the blend, when at least 4 weight % a LCP (including 1c and 2c) are present. This unusual LC-phase consisting of LCP plus matrix is



Storage modulus (T = 80°C)



Loss modulus (T = 80°C)

Figure 1: Rheological measurements of A) neat poly (ε-caprolactone) and B) poly (ε-caprolactone) containing 4 weight % of poly (methylhydroquinone cumyloxyterephthalate with variation of the frequency (given in Hz).

called "lyotropic blend". It collapses above the T_m of the LCP due to phase separation.

The results were interpreted by the following hypothesis.Nanobundles of LCP's are formed during the preparation (precipitation) of the blend. These bundles strongly interact with the surrounding matrix via the more or less aromatic side chain. In this way the LCP bundles induce anisotropy in the neighboring matrix. This induced LC-character is responsible for the observed mobile anisotropy and for part of the mechanical reinforcement.

The LCP's used for these mechanical and microscopic studies are not biodegradable in the proper sense, because they are (like all aromatic polyesters) rather intensive to neutral water even at higher temperatures. However, their structure can be modified by the incorporation of small amounts of anhydride groups (3) without any loss of the LC-character [13, 14] (eq. 1). In this way their sensitivity to hydrolysis can be improved and controlled.

II) Rosorbable LC-polyesters of phloretic acid

The second strategy is based on the synthesis of aromatic LC-polyesters derived from non-toxic natural monomers. However, very few aromatic hydroxy acids meet the three requirements

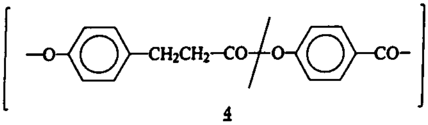
A) to be products of plants or animals, and nontoxic for the human metabolism,

B) to have a structure suited for the formation of an enantiotropic LC-phase

C) to allow an at least slow hydrolysis by the attack of neutral water at temperatures ≥ 40°C.

Four commercial monomers were found which allow the synthesis of copolyesters satisfying the aforementioned properties. These monomers are: 3(4-hydroxy-phenyl) propionic acid (HPPA=phloretic acid), 4-hydroxybenzoic acid (HBA), vanillic acid (VA) and 4-hydroxy cinnamic acid (HCA). Although the homopolyesters of all four hydroxy acids are infusible below 400°C and insoluble in all organic solvents, it was found that the three copolyesters 4 - 6 have T_m's ≤ 250° C and form a broad nematic phase [15, 16]. Particularly interesting is the copolyester 5 because it is noncrystalline and allows an easy processing from the melt even below 200°C either as a neat material of as component of a blend with aliphatic matrix polyesters. The phloratic ascid plays a key-role for the usefulness of these copolyesters for two reasons. Firstly, it improves the flexibility of the chains, and reduces the melt viscosity. Secondly, only its aliphatic ester groups are sensitive enough for a hydrolyses by neutral water [17, 18].

In order to improve the compatibility of the LC-polyesters with the surrounding matrix material, gallic acid (3, 4, 5-trihydroxybenzoic acid) was incorporated in the form of its acetyl derivative (eq. 2). The gallic acid plays the role of branching units, so that randomly branched (hyperbranched) copolyesters were obtained [19, 20]. The hyperbranching has the additional advantage to eliminate completely the crystallinity, and to reduce the processing temperatures. Yet, they also have the disadvantage that a high degree or branching reduced the stability of the nematic phase. To what extent the linear of branched LC-polyesters are useful as reinforcing components of poly(ε-caprolactone) and poly(L=lactide) is currently under investigation.



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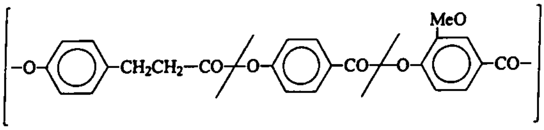

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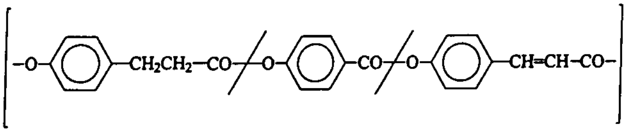

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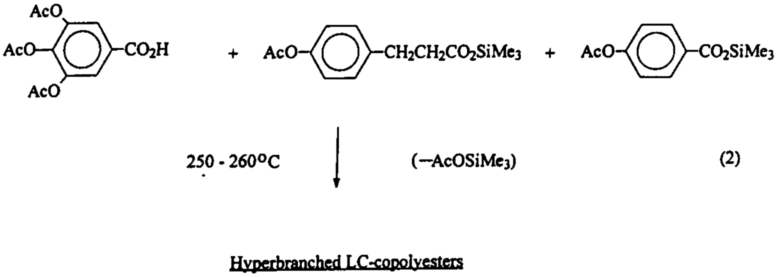

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