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Photosensitive polyurethanes based on castor oil

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Summary

Films of photosensitive polyurethanes based on castor oil and bearing increasing amounts of cinnamoyl groups were obtained and submitted to tensile tests and thermogravimetric analysis. The test samples were cut into strips, with the long axis making angles of 0, 30, 45, 60, 90, 120, 135, and 150° with the suspected direction of anisotropy. In another series of experiments, films were irradiated with a high pressure mercury lamp during different periods of time and again submitted to tensile tests.

Introduction

Photosensitive polymers are materials which, under irradiation, undergo a solubility change. They may have crosslinks being formed, rendering the material insoluble, or they may become more soluble due to some kind of degradation. No matter which process will be going on, these materials are of great commercial importance, being the basis for such applications as photoresists, protective coatings for optical fibers, inks, sealants, adhesives, dental materials, etc.

Among the photosensitive polymers, the photocrosslinkable ones possess in their structure chromophores chemically interlinked when irradiated. The most simple and apparently most important commercially, are those bearing groups, whether in the main chain or in side chains, capable to photodimerize(1).

Historically, the first system of practical importance and which still is the basis for the commercial photoresists is the one involving the photodimerization of cinnamic acid derivatives(2,3). Cinnamic acid undergoes dimerization even in the solid state, giving rise to cyclobutane derivatives. As the reaction may occur in the solid state matrix, this indicates that a minimum molecular mobility is required for the reaction to proceed. These small movements should be enough to allow molecular segments to rearrange into a more favorable conformation, so as to make possible a reasonable approximation of the chromophores. In this regard, structures presenting a preferential orientation may show a higher effectiveness toward the photodimerization reaction.

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In this work, castor oil polyurethanes with increasing amounts of photosensitive groups were synthesized, and the effect of these groups on tensile properties, taken at different directions, was evaluated.

Experimental

Castor oil and excess TDI were mixed at room temperature until a visible viscosity change occurs. To the reaction product, a pre-polymer with available NCO groups, 2-hydroxyethylcinnamate (HECI) and/or 2-hydroxyethylmethacrylate (HEMA) were added under moderate stirring to avoid bubbles. When necessary, a small amount of MEK was introduced to assure an adequate viscosity to the solution and, consequently, films with proper thicknesses.

The amount of cinnamoyl groups varied from 0 to 100 mol%. Films were cast onto polyethylene from MEK solutions and dried in air, under atmospheric pressure. They were irradiated with a high pressure mercury lamp for periods of time ranging from 0.5 to 5.0 minutes.

Tensile tests were carried out on a Instron-4202 equipment, at an extension speed of 50 mm/min and the parameters tensile strength at break (τ), strain at break (ε), elastic modulus (E) and toughness (H) for the extension deformation mode were analysed. From each sheet, samples were cut into 5x15 mm strips with their long axis making angles of 0, 30, 45, 60, 90, 120, 135, and 150° with the suspected direction of anisotropy.

Thermogravimetric analysis was conducted on a Perkin-Elmer TGA-7 Thermogravimetric Analyzer.

Films for irradiation were cut in only one direction.

Results and Discussion

From curves in Figure 1, it can be seen that the values of tensile strength at break have a reasonable variation with the amount of cinnamoyl groups. The highest values are those for irradiation time of 0.5 and 1.0 minute, up to 80%

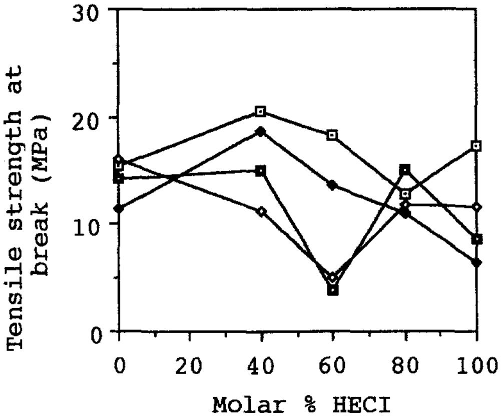

Figure 1: Tensile strength at break as a function of the amount of cinnamoyl group, for PU films irradiated during different periods of time

HECI. Longer times lead to a deterioration of this property, probably due to the beginning of degradation processes in the material.

It can also be observed that the sistematic increase in the amount of cinnamoyl groups does not necessarily lead to more resistent materials. There is an ideal concentration of reactive groups, around 40%, from which a significative decay in the tensile strength at break occurs, increasing again at 80%. Apparently, at this point the irradiation time does not have significant influence.

Table 1: Data of stress and strain at break, elastic modulus and toughness as a function of the angle between sample long axis and the suspected direction of anisotropy

Amount of HECI %	Angle °	Stress at break MPa	Strain at break %	Modulus MPa	Toughness MPa
20	0	13.90	229.3	8.93	14.18
	45	14.83	207.4	12.97	13.25
	90	11.44	153.7	11.13	8.34
	135	13.61	225.0	9.41	14.10
40	0	13.55	207.9	11.18	11.96
	45	10.92	182.4	8.95	9.03
	90	11.73	184.7	10.59	9.39
	135	15.06	227.8	10.85	14.85
60	0	12.13	215.4	8.73	11.68
	45	8.36	172.7	7.84	6.44
	135	10.72	212.3	7.14	10.38
0	0	15.34	198.0	11.95	14.16
(100% HEMA)	45	15.39	217.7	12.46	13.88
	90	8.19	110.8	11.32	4.54
	135	14.12	189.6	11.08	12.03

The fact that there is no need for high concentrations of reactive groups to accomplish the best performances is already reported in the literature(4,5). It is known that photoreticulation is a fast reaction whose rate is dependent on the concentration of the reactive group. However, as the reaction progresses, the incipient tridimensional network restricts the mobility of the remaining molecules and their access to the reaction conditions. These molecules, entrapped in the polymeric matrix, would act as a plasticizer to the material, until a favorable condition to the reaction could be reached.

It has been also reported(4,5) that, in the solid state, photodimerization is influenced by the configuration assumed by the reactive groups.

So, in order to establish whether the molecules have a preferential orientation in the films, non-irradiated samples of unoriented PU films were tested also at different angles with respect to the suspected film orientation and the values of stress and strain at break, elastic modulus and toughness were taken. These results are presented in Table 1 and Figures 2-5.

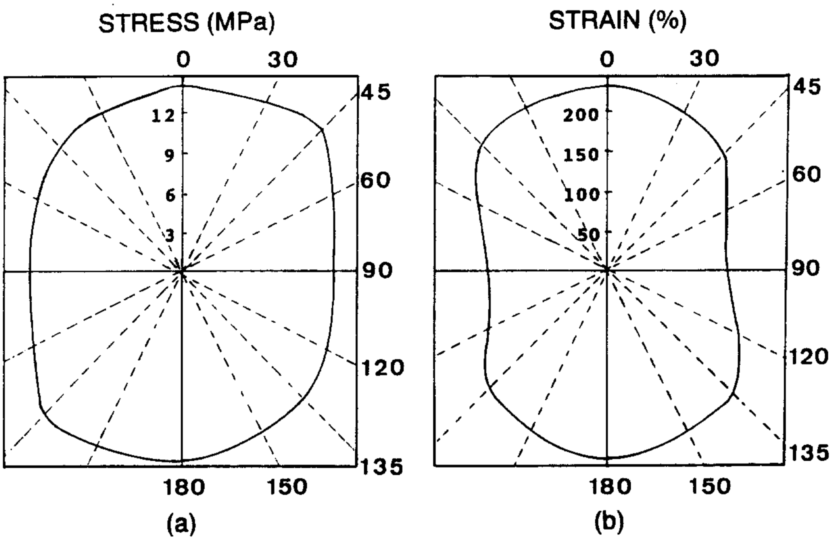

Figure 2: Angle dependence of stress at break (a) and strain at break (b) for PU films with 20% HECI

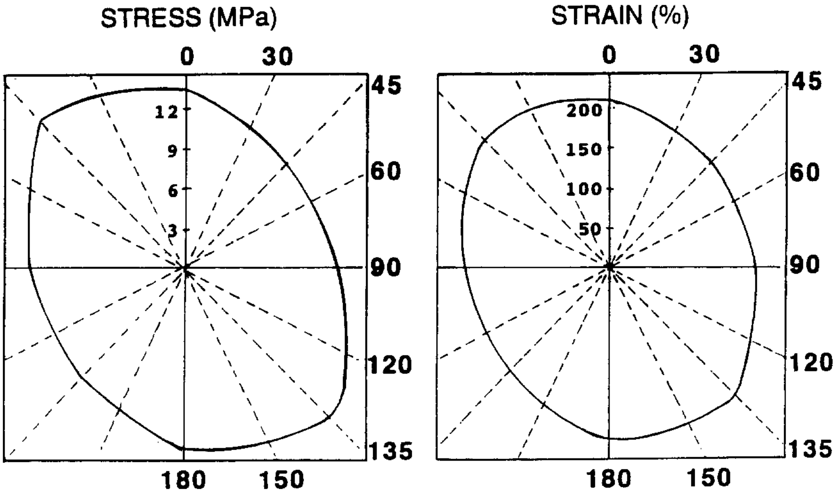

Figure 3: Angle dependence of stress at break and strain at break for PU films with 40% HECI

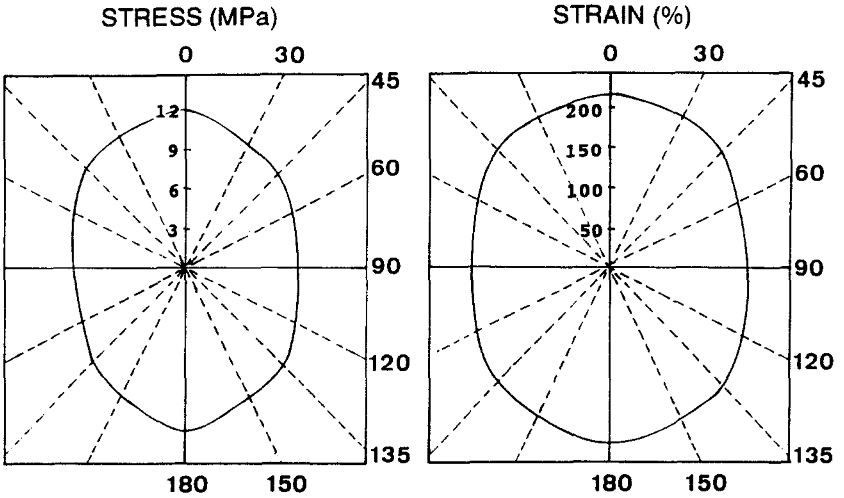

Figure 4: Angle dependence of stress at break and strain at break for PU films with 60% HECI

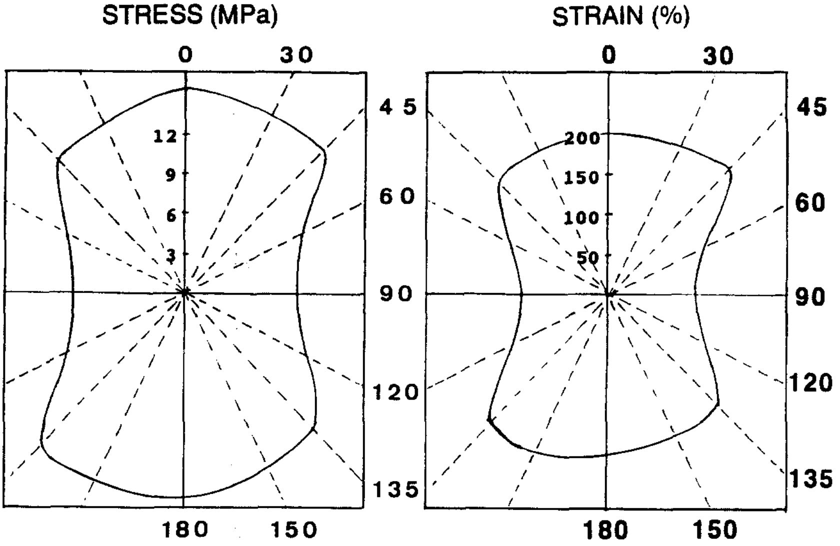

Figure 5: Angle dependence of stress at break and strain at break for PU films with 100% HEMA

It was verified that angle dependences of registered tensile properties for PU films with different percentage of HECI are close to that of the isotropic material. However, when only HEMA is present, an anisotropy is observed in deformation and strength properties, with differences between longitudinal and transverse directions going up to

100%. We can suppose that in this case, HEMA would provide some macromolecular orientation.

Figure 6 shows thermogravimetric curves for the PU films.

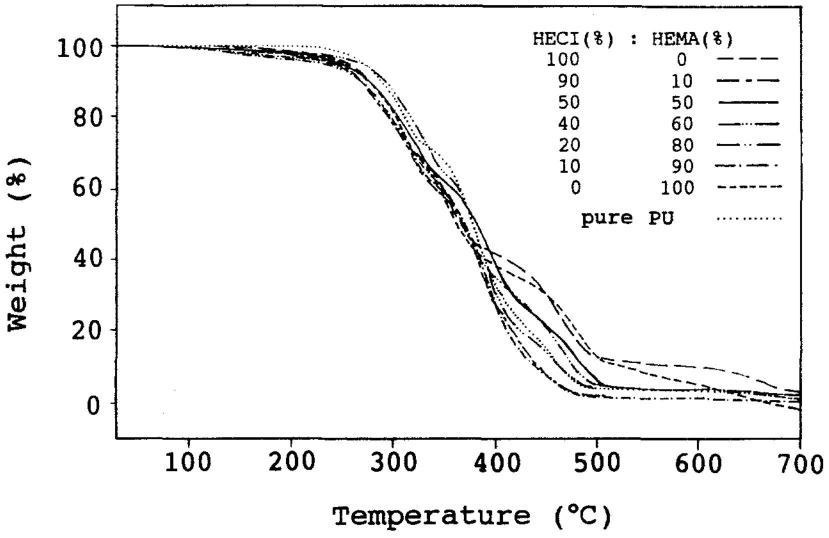

Figure 6: Thermogravimetric curves for non-irradiated PU films containing different amounts of photosensitive groups

It can be seen that all curves present three similar decomposition stages, onset near 278°C. Nevertheless, this value is slightly higher in the case of pure PU and for those films with 100% HECI or 100% HEMA a slightly superior thermal stability is found over 400°C, at the last decomposition plateau, with formation of a small residue. From Figure 5 some anisotropy was already observed that could be thought of as the result of a preferential orientation of the macromolecules. This orientation would favour the photodimerization, leading to a more stable product. When both HECI and HEMA are present, films do not present appreciable anisotropy and consequently their thermal and mechanical properties are poorer.

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