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A mechanochromic smart material

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Abstract

A mechanochromic polyurethane elastomer was synthesized and demonstrated. Azobenzene chromophores were introduced into a copolyamide oligomer to provide conformational latches which stabilized the *cis*-azobenzenes by the formation of intramolecular hydrogen bonds. The copolyamide oligomer was chemically inserted into a polyurethane copolymer. The chromophores in the resulting copolymer were transformed to the *cis*-form by ultraviolet (UV) irradiation (λ=365 nm) and then succesively stretched and relaxed to strains of 100 %, 200 %, and 300 %. After 100 % strain and relaxation, the absorbance of polyurethane copolymer at λ=380 nm, which indicates transformation to the trans form, was not significantly increased. However, the absorbance increased with 200 % and 300 % tensile strain followed by relaxation. A mechanochromic relationship between absorbance increase at λ=380 nm in the relaxed sample and the maximum strain to which the sample was subjected was thus demonstrated.

Introduction

Aircraft and automotive industries are increasingly using fiber-reinforced polymer composites in the wings, panels, and other structural elements. Design freedom, weight saving, resistance to corrosion and to crack propagation, improved fatigue life, and superior ballistic performance are some of the advantages for the advanced composites over metals [1].

Nondestructive evaluations (NDE) [2-3] such as ultrasonic scans and X-ray techniques were used to study the structural integrity of composite materials. New methods [4-6] using fiber-optics for a sensory system are under investigation. Active "smart composites" which combine the fiber-optic sensors with the mechanical actuators such as piezochromic and electro-rheological materials can be made sensitive to structural flaws and can change their mechanical properties depending on environmental change such as temperature or mechanical stress. Smart or intelligent materials are materials which respond to environmental change and manifest their own functions according to the changes [7]. Smart skins on a bridge [8] or an aircraft can send out warning signals to avoid catastrophic failure, for example.

One goal of this research is the development of a subclass of smart materials which change color depending on the stress experienced at the interface between a fiber and a polymer matrix. The structural integrity of a fiber-reinforced composite could then be monitored by the color change. Rapid inspection, by this means, can save both time and cost.

This work is a fundamental study for the development of a mechanochromic smart composite which changes its color depending on the strain history. A mechanochromic poly(diacetylene-urethane) segmented copolymer [9] is known. This elastomer changed from blue to yellow when stretched, and unlike the material described here, changed back to the original color when the tension was released.

In this work, a thermoplastic polyurethane elastomer which can irreversibly change its optical absorption spectrum depending on the tensile strain was designed, synthesized, and demonstrated. This polyurethane elastomer is a polyurethane copolymer containing a copolyamide block with an azobenzene chromophore.

A modular approach was used to design the copolyamide oligomers which contained three different modules to perform specific functions. First, attachment modules are functional groups (amine group and carboxyl group) at the chain ends. Secondly, azobenzenes are chromophore modules in the chain backbone. Finally, intramolecular and intermolecular hydrogen bonds work as conformational latches.

p,p'-Diaminoazobenzene is an organic dye which shortens its contour length during photochemical *trans*-to-*cis* isomerization [10]. The photoproduced *cis*-form is thermodynamically unstable and reverts back to the *trans*-form at room temperature and more quickly during irradiation with visible light. Intramolecular hydrogen bonds in the copolyamide molecule are used to stabilize and thereby latch the *cis*-azobenzene [11] until a strain large enough to break the hydrogen bonds is applied. This polyurethane elastomer is mechanochromic in the UV region and is a strain recording smart material (Figure 1). The record of the strain is preserved because the *trans*-azobenzene produced by the strain is stable when the strain is removed.

Experimental

A) Copolyamide Synthesis

A copolyamide was synthesized from *p,p'*-diaminoazobenzene (Eastman Kodak Co.), 1,6-hexanediamine (Aldrich), succinyl chloride (Aldrich), and glutaryl dichloride (Aldrich) with the molar ratio of 1:4:2.5:2.5 in NMP (1-methyl-2-pyrrolidinone) at room temperature. The copolyamide was precipitated in THF (tetrahydrofuran). The copolyamide was reprecipitated twice from its solution in formic acid by addition of THF. The copolyamide was dried under vacuum at 50°C before use. The number average molecular weight of this copolyamide was measured by photochemical end group

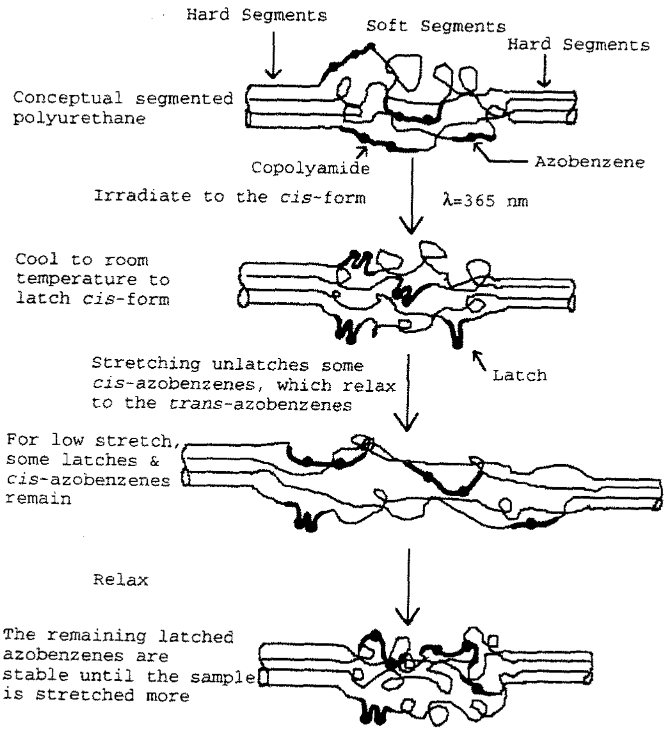

Figure 1. A strain recording smart material.

analysis using the absorbance of the *p,p'*-diaminoazobenzene at the chain end [12]. This method exploited the solvatochromism of *p,p'*-diaminoazobenzene, the color of which, in *m*-cresol or phenolic solvents, depends on its location in the polymer. The color of this molecule is blue in monomeric form, violet when at the chain end, and yellow when in the chain backbone. The M_n of the copolyamide was about 5,000 g/mol.

B) Synthesis and Characterization of Polyurethane Copolymer

A polyurethane copolymer was synthesized from ethylene glycol (EG) (Aldrich, 2.483 g), polyethylene glycol (PEG) (Aldrich, 20 g, M.W.=2,000 g/mol), tolylene diisocyanate (TDI) (Aldrich, 9.061 g, an 80/20 mixture of tolylene 2,4-diisocyanate and tolylene 2,6-diisocyanate), and a small amount of the copolyamide (about 0.1 wt % of total weight). EG was dried under vacuum for 10 hours at 50°C. PEG was dried under vacuum for 15 hours at 80°C. Anhydrous dimethylformamide (DMF) solvent was prepared by vacuum distillation from a DMF suspension with calcium hydride (Aldrich, 95 %) after stirring more than 24 hours. EG, PEG, and copolyamide were dissolved in about 50 ml of anhydrous DMF solvent inside a 300 ml round flask with three necks, by mechanical stirring in flowing dry nitrogen. A small amount of dibutyltin dilaurate (100 mg, about 0.3 wt %) was added as catalyst. Then, TDI was slowly added to the flask to avoid an abrupt increase of reaction temperature. After 20 hours of reaction, the viscous product was poured into methanol to precipitate polyurethane copolymer. Reprecipitation of the polyurethane copolymer from DMF solution with methanol was performed twice to remove unreacted monomers and low molecular weight materials. After drying under vacuum for 24 hours at 50°C, a Dupont 9900 Differential Scanning Calorimetry was used to measure the thermal properties of the polyurethane copolymer, at a heating rate of 10°C/min. The tensile properties of the polyurethane copolymer film cut by a die (ASTM D 412-75 Type C) were measured by an Instron with a 20 cm/min head speed. The thickness of specimen was measured three times with a thickness gauge. The length between the two grips holding the sample was measured and used as the initial length (l_o) for the extension ratio calculation. Tensile strength and modulus were averaged from three test results.

C) Thermal Iomerization Kinetics of Azobenzenes in Polyurethane Copolymer Film

Thin polyurethane copolymer film was cast from a DMF solution in a Teflon coated aluminum mold with a diameter of 8.8 cm and a depth of 0.2 cm. UV-Visible absorption spectra of polyurethane copolymer films (0.02 to 0.05 cm thick) were obtained with a Hewlett-Packward 8451A Diode Array Spectrophotometer. Air was used as reference. The photoisomerization of azobenzenes in polyurethane copolymer film was performed by a long wavelength UV lamp (λ_{max}=365 nm, UVP Inc.) with an intensity of 5±2 mW/cm^2. Polyurethane copolymer films were irradiated by the UV lamp for 1 hour at each of three temperatures: room temperature, 60°C, and 100°C. The heated films were cooled rapidly to room temperature at the end of the UV irradiation time. After cooling, the UV-Visible absorption spectra of polyurethane copolymer films were obtained as a function of elapsed time, at room temperature, after the UV irradiation was stopped.

D) Mechanochromism Test of Polyurethane Copolymer Film.

A polyurethane copolymer film (0.05 cm thick) was irradiated by the UV lamp for 1 hour at 100°C, then rapidly cooled to room temperature as the irradiation continued. The UV-Visible absorption spectra were measured after each of three successive cycles of tensile stretching to 100 % elongation and relaxation to zero tension. The successive measurements of UV-Visible spectra were also performed with three cycles of each 200 % and 300 % tensile stretching and relaxation.

Results and Discussion

The number average molecular weight of the copolyamide containing azobenzene was about 5,000 g/mol. The molecular weights of polyols or polyesters used for polyurethane synthesis ranged from 600 to 10,000 g/mol

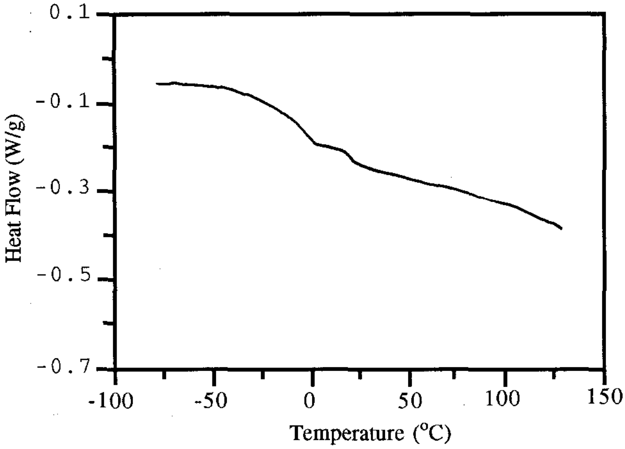

Figure 2. DSC thermogram of polyurethane copolymer.

[13]. The copolyamide chains were inserted into a polyurethane network as deformable segments in the soft segment with the expectation that the macroscopic deformation of the polyurethane elastomer film would break the hydrogen bonds and induce the *cis*-to-*trans* isomerization of the photoproduced *cis*-azobenzene. The elastomeric polyurethane copolymer had two glass transition temperatures, at -12°C and at 16°C, which indicates phase separation (Figure 2). The absence of a melting peak indicates that no extensive three-dimensional crystalline ordering occurred. Asymmetry in the diisocyanate structure, as in tolylene 2,4-diisocyanate, led to an amorphous hard segment domain [14]. Thermal analysis can be used to estimate the degree of phase separation between the hard segments and soft segments. The relatively high T_g reveals that the extent of phase separation between the hard segments and the soft segments is very low. The T_g of low molecular weight (M.W.=4,000 g/mol) poly(ethylene oxide) is -40°C at 0.5 Hz [15]. The tensile modulus of the polyurethane copolymer film was about 3.79 Mpa. Elongation at break was 520±72 %.

The UV-Visible absorption spectra of polyurethane copolymer film before and after the photoisomerization are shown in Figure 3. A peak at λ=380 nm, which is the absorption peak of the *trans*-azobenzene for the π-π^* transition [16, 17], disappeared after the UV irradiation. The peak of *cis*-azobenzene at 320 nm is superimposed upon the broad and strong peak of polyurethane itself around 300 nm. The first order plot of the thermal isomerization of azobenzene in polyurethane film at room temperature is shown in Figure 4. This is a plot of $\log[(A_\infty-A_t)/A_\infty]$ where A_∞ is the absorbance at λ=380 nm before UV irradiation and A_t is that at time t after UV irradiation. The rate of thermal isomerization at room temperature was much slower in the polyurethane copolymer containing copolyamide than in polyester urethane containing azobenzene in the soft segments [18]. The reasons for the retardation of thermal isomerization in the polyurethane

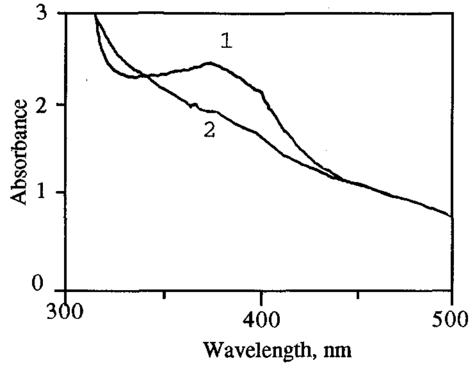

Figure 3. UV-Vis absorption spectra of polyurethane copolymer film before (curve 1) and after (curve 2) the photoisomerization process.

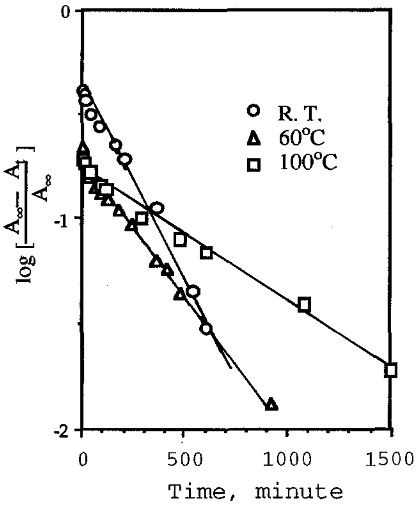

Figure 4. First order plot of the thermal isomerization of azobenzene at room temperature in polyurethane copolymer film which was photoisomerized at room temperature (R.T.), 60°C, and 100°C.

copolymer are the rigidity of copolyamide and the stabilization of photoproduced *cis*-azobenzene by the intramolecular hydrogen bonds. The higher the temperature of photoisomerization, the slower the rate of thermally induced reverse transformation. This retardation effect is believed to be due to the formation of more intramolecular hydrogen bond latches in the copolyamide segments at high temperature. The matrix also rearranges, at 60°C or 100°C, to accommodate the *cis*-azobenzene. Hence the matrix works with the hydrogen bonds to resist the reversion of the *cis*-azobenzene back to the *trans*-form.

In Figure 5, the base line is curve 2 in Figure 3, which is the UV-Visible absorption spectrum of the polyurethane copolymer after UV irradiation. The solid line in Figure 5 is the difference between the UV-Visible absorption spectra before (curve 1) and after (curve 2) UV irradiation in Figure 3. After three successive 100 % tensile stretch and relaxation cycles, the UV-Visible absorption spectra were almost the same as that before stretching (Figure 5). Possible reasons for the small decrease in adsorption after each cycle to 100 % stretching are a small tensile set, or a change in the amount of light scattering in the sample. After three 200 % tensile stretch and relaxation cycles, a significant increase of the *trans*-form was detected by the increase of the peak intensity at λ=380 nm (Figure 6). Finally three 300 % tensile stretch and relaxation cycles changed almost all the *cis*-form into the *trans*-form

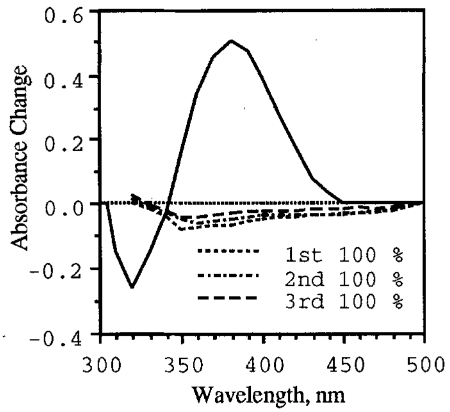

Figure 5. UV-Visible absorption spectra (three dotted lines) of the photoisomerized polyurethane copolymer film after three successive 100 % tensile stretch and relaxation cycles which are subtracted from the curve 1 in Figure 3.

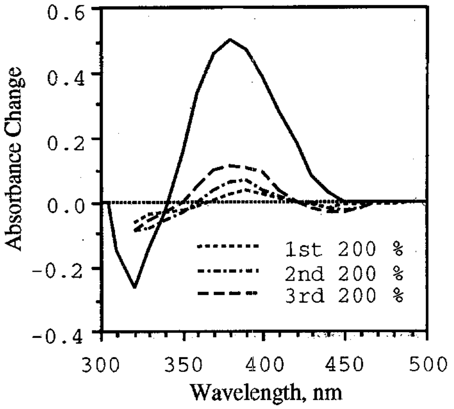

Figure 6. UV-Visible absorption spectra (three dotted lines) of the photoisomerized polyurethane copolymer film after three successive 200 % tensile stretch and relaxation cycles which are subtracted from the curve 1 in Figure 3.

(Figure 7). These data show that non-linear irreversible mechanochromism was obtained with the polyurethane copolymer containing deformable copolyamide chains in the soft segments. The non-linear mechanochromism is advantageous for applications which require a record of only the highest strain experienced. The memory of this particular polyurethane copolymer is limited due to the thermal isomerization which proceeds at a low rate, but the ability to design and synthesize a material with this complex set of properties is demonstrated.

The 5 to 6 hour half-life time of the photoproduced *cis*-form in the polyurethane copolymer matrix needs to be increased fro practical applications. The mechanochromic range located in UV-region (at λ_{max} =380 nm) needs to be changed to visible region. The copolyamide was

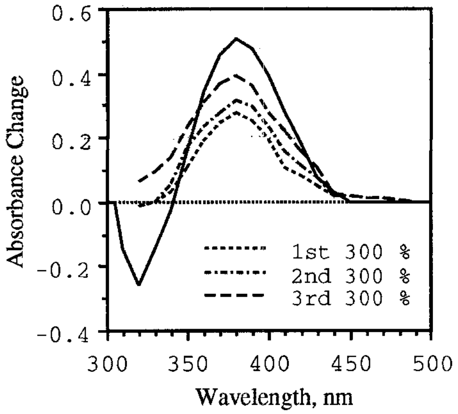

Figure 7. UV-Vis absorption spectra (three dotted lines) of the photoisomerized polyurethane copolymer film after three successive 300 % tensile stretch and relaxation cycles which are subtracted from the curve 1 in Figure 3.

designed to be a smart coupling agent working at the interface between an optically transmitting reinforced fiber (e.g., glass fibers) and the polymer matrix. In this system, the copolyamide should be improved to increase the life-time of photoproduced *cis*-form and the attachment modules should be designed to attach to the fibers and to the matrix. The modular approach we have demonstrated provides guidance toward the design and synthesis of such an improved sensory smart material.

Acknowledgements

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