



Light-triggered enhancement of mechanical properties and healing effect in azobenzene-based polymer films



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ABSTRACT

One of the disadvantages of using polymers for outdoor applications is the photo-degradation which deteriorates their mechanical properties eventually leading to structural failure. Therefore, rather than a loss of mechanical properties in polymer structures under UV exposure, it would be an accomplishment if the mechanical properties could be enhanced to improve the structural integrity of polymeric structures. This study examines the photomechanical property enhancement in a series of photo-responsive copolymers of methyl methacrylate and methacryloyloxy azobenzene (MOAB) with azobenzene chromophores in the side chains, using nanoindentation. We assume the effect of chromophore concentrations enhances the photomechanical properties. We found that a maximum increase in stiffness of 19% can be achieved with an optimum loading of 30% mol azobenzene. Such an enhancement in stiffness was attributed to photoinduced reorganization of the polymer chains due to the isomerisation of the azobenzene chromophores. UV/Vis spectroscopy of the polymer films suggested that the trans isomer of azobenzene was converted to the cis form within 7 min of exposure to UV light, whereas the reversion from the cis to the trans isomer was achieved within 1 min by visible light. Analysis of the indented thin films by optical microscopy demonstrated healing of the indented region by UV light suggesting that this polymer can be used as self-healing material.

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1. Introduction

Azobenzene is a photoresponsive molecule that uses light energy to undergo a conformational change. Azobenzene and its derivatives have two geometric isomers, the thermodynamically more stable trans with a planar geometry and the less favoured cis forms with a more twisted geometry [1]. These geometrical isomers can be triggered by light of appropriate wavelengths. The trans isomer is stable in visible light (400–500 nm) and in the dark, while the cis form is favoured by UV light (320–390 nm). The changes that occur at the macroscopic level after enrichment of polymers with this chromophore, are of tremendous interest to many researchers especially in the area of smart materials [1–6]. This class of photoresponsive smart polymers has the ability to modify their chemical, optical and mechanical properties when subjected to a specific light wavelength or temperature [2,3]. Various studies have been conducted on azobenzene-based polymers for photoviscosity [7–9], stiffness [10–13] and shape changes

[14–16]. Studies in the measurements of the mechanical properties, such as Young's modulus, of azobenzene-based materials were first reported in 2009 by Verploegen et al. [10] Azobenzene-doped polymer films of polymethylmethacrylate (PMMA) and polyethylmethacrylate (PEMA), with 15 wt% chromophore loading, were examined separately by quartz resonators to assess their elastic compliance as a function of time. UV illumination caused a noticeable increase in the material hardness; 1.5% for PMMA and 0.2% for PEMA. The effect was thought to be due to the trans to cis isomerisation of azobenzene chromophores that stressed the matrix locally and thus improved the resistance to shear stress. In contrast, under irradiation with visible light, free volume was created by photoisomerisation and thus elastic compliance was observed.

Although azobenzene-doped chromophores are capable of undergoing photoisomerisation the photomechanical response appears to be very local and weak in this class of materials [17]. This is due to microcrystallization of the free azobenzene molecules in the polymeric matrix [3]. However, when the azobenzene chromophores are linked to polymer chains, the whole matrix is more uniform. Therefore, studying the polymers with covalently

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attached azobenzene molecules is expected to deliver higher macro-level changes.

Kondo et al. [11] found that 20% azobenzene in crosslinked liquid-crystalline polymer films showed the highest photomechanical contraction (four times greater) and mechanical force (seven times greater) than in the film made by dispersing the azobenzene moieties alone in the polymer. A noteworthy nano-indentation study involving functional azobenzene/MMA random copolymer films containing 6% and 10% mol of chromophores demonstrated changes in the elastic modulus [18]. Upon exposure to UV irradiation the stiffness of the polymer film showed a notable increase by 10% and was attributed to trans to cis isomerisation of the azobenzene chromophore. Furthermore, upon irradiation with visible light, the elastic modulus of the film was found to have partially recovered, probably reflecting cis to trans isomerisation of the azobenzene. However the study was incomplete because only a specific amount of chromophore loading was examined and the optimum azobenzene loading that can demonstrate maximum photo-driven elastic modulus/stiffness changes was not identified.

Here we show photo-induced changes in the stiffness of acrylic-based polymer films as a function of azobenzene concentration in order to estimate the optimum chromophore loading that shows the maximum stiffness change. Moreover, the reversible trans → cis isomerisation by UV and Visible light in the azobenzene-based polymer thin films was investigated using UV/Vis spectroscopy. Self-healing behaviour in the polymer films triggered by UV light is also discussed in this paper.

2. Experimental section

2.1. Materials and synthesis

Methyl methacrylate, 4-phenylazophenol, ethanol, tetrahydrofuran (THF) and methacryloyl chloride were used as received from Alfa Aesar. Azobisisobutyronitrile (AIBN) and triethylamine (TEA) were supplied by Sigma Aldrich and used without any further purification. The copolymers were synthesized following the procedure described in detail elsewhere [7]. As seen in Fig. 1, the precursor 4-phenylazophenol was initially functionalized to a methacryloyloxy azobenzene (MOAB) monomer via a condensation reaction with methacryloyl chloride in presence of TEA at 0 °C. Subsequently, various ratios of MMA and MOAB monomers were copolymerized in THF at 65 °C for 48 h by free-radical

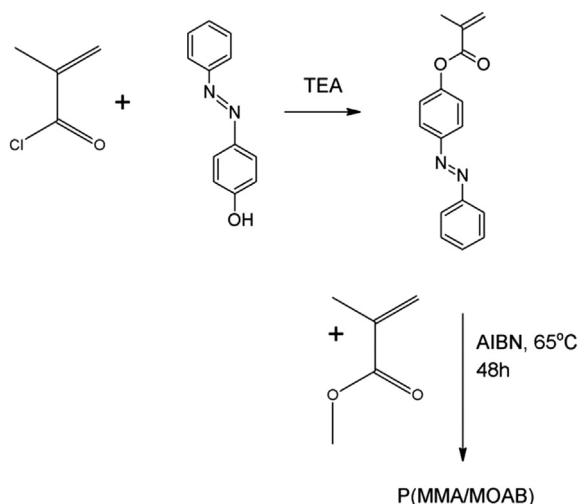


Fig. 1. Reaction scheme for P(MMA/MOAB).

polymerization to produce a series of copolymers with various azobenzene loadings. About 3% mol of AIBN was used as the initiator. The copolymers were precipitated from methanol and dried under vacuum at room temperature.

2.2. Film preparation

Thin films of PMMA, polymethacryloyloxyazobenzene (PMOAB) and of the copolymers P(MMA/MOAB) with 10%, 15%, 20%, 30%, 45%, 65% and 85% azobenzene loadings were prepared by the casting method. The copolymer solution (23% w/v) of toluene was prepared, and films were cast by spreading the solution (1 mL) onto microscope glass slides at room temperature. The slides with the solution were left on a flat table with adjustable legs inside a fume hood for three days in order to evaporate the solvent. The films were then transferred to a vacuum oven and heated at 50 °C for 5 days in order to remove any remaining solvent. Complete removal of solvent was ensured by periodically weighing the films until a constant weight was reached. The thicknesses of the films ranged between 80 and 150 μm for nanoindentation and 7–9 μm for UV/Vis studies. Thinner films were chosen for UV/Vis spectroscopy measurement to ensure absorption peaks were not cut off due to a higher molar absorption co-efficient of the azobenzene chromophores [19].

2.3. Instrumentation

The compositions of the copolymers were assessed by proton nuclear magnetic resonance (¹H NMR) spectroscopy and spectra were recorded using a Bruker 500 MHz spectrometer. Tetramethylsilane (TMS) was used as the internal reference and deuterated dimethyl sulfoxide (dmsO-d₆) as the solvent. The azobenzene concentration in the copolymers was determined using Equation 1,

$$\text{Azobenzene loading (\% mol)} = \frac{A_{\delta=7.9}}{A_{\delta=7.9} + A_{\delta=3.6}} \quad (1)$$

where A_{δ} corresponds to the integral of the peak at the signal δ . In particular, the ratio of the signals at 7.9 ppm, corresponding to four aromatic protons of azobenzene, with that of three protons of the methyl group of methyl methacrylate at 3.6 ppm is used to calculate the azobenzene loading in the polymers.

The glass transition temperature (T_g) of the polymers was determined using a DSC METTLER TOLEDO with STARE Software, Version 9.10 under a nitrogen atmosphere with a flow rate of 80 mL/min. The instrument was calibrated using indium (In) as the pure metal for reference at 156.6 °C. The T_g of the polymers was obtained from the average values of the midpoint of the three heat flow curves. The samples were heated from 25 to 200 °C at a heating rate of 2 °C/min.

The weight average molecular mass (M_w) was determined by gel permeation chromatography (Waters with a 2410 refractive index detector). A calibration curve was established using a number of narrow polydispersed polystyrene standards. The number of units per chain was calculated taking into account the different ratios of the molecular mass for each monomeric unit; MMA and MOAB.

The azobenzene loading, glass transition temperature, weight-average molecular mass and the number of units per chain of all the polymers are listed in Table 1.

The photoisomerisation of azobenzene in the films was studied using a UV/Vis spectrometer (Zeiss, MCS 522 UV VIS) with a Xenon flash lamp (Zeiss, BLX 500/4). The films were irradiated with a 5 mm diameter light guide equipped with a Novacure M2100 light source (EXFO Photonic Solutions Inc.). The output from the light

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