

Acid-Sensitivity and Physical Properties of Polymethylmethacrylate and Polyurethane Films Containing Polymeric Styryl Dye

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Abstract: Solution-cast films of polymethylmethacrylate (PMMA) and polyurethane (PU) containing polymeric styryl dye up to 5 % by weight were prepared to investigate their acid-sensitivity and mechanical and thermal properties. Original red samples due to styryl dye turned out yellow very rapidly as they were exposed to acid vapor of hydrochloric acid or p-toluenesulfonic acid. According to UV/VIS spectroscopic measurements, characteristic peak intensities near 430 nm and 520 nm increased or decreased relatively with exposed amounts of acid, respectively. Both PMMA and PU samples showed uniform color distribution due to a good miscibility between polymer and dye which can be evidenced by measurements of glass transition temperature. No significant difference in acid-sensitivity was found between PU and PMMA except relative absorbance. However, dependence of their mechanical properties on dye content was somewhat different with PU or PMMA. In case of PMMA, modulus and breaking stress increased up to about 50 % with increasing dye content, whereas those of PU samples showed only slight increase. It was ascribed to whether the matrix polymer was in the glassy or rubbery state.

Keywords: Styryl dye, Acid-sensitivity, Polymethylmethacrylate, Polyurethane

Introduction

Smart materials have recently received an increased attention, which can respond to external stimulus change in temperature, light, electric field, chemicals, pH, and so on. Utilization of polymers or organic materials may be possible to offer more effective smart function to materials because of easier structural control compared with inorganic or metals. Stimulus-responsible function in polymers can be achieved by using intrinsic smart characteristics of polymer itself or by incorporating low molecular weight or polymeric additives having smart function [1-5].

We have recently researched some interesting properties on styryl dyes. They could show stimulus-responsible functions to light or chemicals due to their strong donor-acceptor characteristic by intermolecular charge-transfer [6-8]. Moreover, we have succeeded in synthesizing high molecular weight styryl dye, leading to higher possibility of applications as smart materials. Polymeric dyes have some advantages of good physical properties such as absorption, solubility, migration, and viscosity compared with low molecular weight dyes. According to our previous report [9], acid-sensitivity of polymeric styryl dye in solution gave a rapid change in color from red to yellow when the dye was in an acid circumstance.

In this study, we aim to investigate acid-sensitivity of films incorporating polymeric styryl dye, and to analyze their mechanical and thermal properties as a function of dye content. As a polymer matrix, polymethylmethacrylate (PMMA) and polyurethane (PU) were used.

Experimental

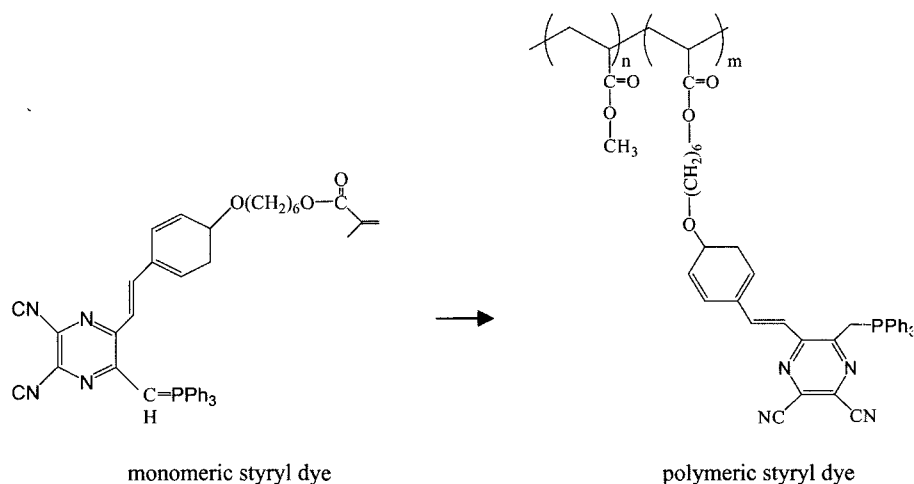
Synthesis of Polymeric Styryl Dye

Monomer dye, 2-[2-[4-(6-methacryloyloxyhexyloxy)-phenyl]ethenyl]-3-triphenyl phosphordiyl methyl-5,6-dicyanopyrazine, was synthesized as a method of previous reference [7,10]. Dye of 0.5 mmol (346 mg) was homogeneously dissolved in benzene (1 g) with distilled MMA of 4.5 mmol (450 mg) and AIBN of 0.05 mmol (5 mg). Reaction of dye was carried out in the homogeneous solution at 70 °C for 12 hours under a flow of nitrogen gas. Final polymeric styryl dye was obtained by dissolving resulting reactant in chloroform and then by precipitating it in methanol, which was repeated several times. A final styryl dye (Scheme 1) was used after polymeric dye obtained was dried completely in an oven. Some properties of dye sample are represented in Table 1, which were obtained using gel permeation chromatography and thermal measurements.

Film Preparation

Commercial PMMA (Mitsubishi Rayon Co.) chips were used in this study, and PU was kindly supplied by SK Chemicals, Korea, being composed of 4,4'-methylenebis(phenylisocyanate) (MDI)/poly(tetramethylene glycol) (PTMG)/1,4-butanediol (BD) at 39/52/9 by weight ratio. They were dissolved uniformly in dimethylacetamide and tetrahydrofuran at concentration of 10 wt%, respectively. Different amounts of polymeric styryl dye (0, 1, 3, 5 wt%) were added to each polymer solution, and were mixed homogeneously using mechanical stirrer. The homogenous solutions were cast onto glass plate, and were dried at room temperature for several days in a vacuum oven.

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Scheme 1. Synthetic scheme for synthesizing polymeric styryl dye used in this investigation from monomeric styryl dye.

Table 1. Some properties of polymeric styryl dye used in this investigation

Composition (mol%)		Molecular weight ^a (g/mol)		Dispersity index ^a	Glass transition temperature ^b (°C)	Degradation temperature ^c (°C)
MMA	Styryl monomer	M _n	M _w			
90	10	21,300	44,380	2.08	124.9	230

^agel chromatographic measurement, ^bdifferential scanning calorimetric measurement, ^cthermogravimetric analysis.

Films cast were used after removing residual solvent from them completely through drying in a vacuum at 50 °C for 24 hours.

Characterization

Color change of polymer-dye solution using dimethylsulfoxide as a solvent was observed by adding a hydrochloric acid or p-toluenesulfonic acid carefully in drops to the solution, and such a change in absorbance of light was measured with a liquid cell by using UV/VIS spectroscopy (UNICAM Helios). For polymer-dye films, changes in acid-sensitivity were observed by exposing samples to vapor evaporated from acid liquids, and UV/VIS spectra were also measured before and after acid-treatment. Measurements of differential scanning calorimetry (DSC) were carried out using DSC du Pont TA 2000 at a heating rate of 10 °C/min to obtain glass transition temperature (T_g) of PMMA-dye films. T_g of PU-dye films was obtained by using a dynamic mechanical analyzer (du Pont DMA983) at a heating rate of 2 °C/min. Tensile tests were performed at room temperature using Instron tensile tester (model 4468) with gauge length and crosshead speed of 25 mm and 10 mm/min, respectively.

Results and Discussion

UV/VIS Spectra

Prior to an investigation of acid-sensitivity of polymer

films, UV/VIS spectroscopic measurements of polymer-dye solution using dimethylsulfoxide as a solvent were carried out. Figures 1(a)-(d) show changes in UV/VIS spectra of polymer-dye solutions with increasing an amount of HCl in drops, respectively. Polymer-dye solution with no acid exhibits a characteristic absorption peak at 520 nm indicating reddish color in addition to peak at 400 nm due to the $\pi - \pi^*$ transition of dye [7]. As HCl is added to solution, it can be observed that a reddish color of solution changes to yellow very fast. It was also well reflected in UV/VIS measurements. A new UV/VIS absorption peak appeared near 430 nm with a decrease in absorption peak at 520 nm as a very small amount was progressively added. On further increasing acid, absorption peak intensity at 520 nm continued to decrease gradually whereas one at 430 nm increased. It can be explained in terms of resonant mechanism resulting from structural transition of styryl dye molecule due to presence of proton in added acid as shown in Scheme 2 as described in our previous report [7].

Acid-sensitivity of polymer-dye films was measured with UV/VIS spectroscopy, which is shown in Figures 2(a) and 2(b). Similarly in polymer-dye solution, we can see that both PMMA- and PU-dye films also show rapid color change from yellow to red on exposure to acid vapor. That is, absorption peak at 430 nm increases and that at 520 nm decreases, however, their peak intensities are less sensitive compared with intensity change of polymer-dye solution. It indicates that polymer films containing polymeric styryl dye can have

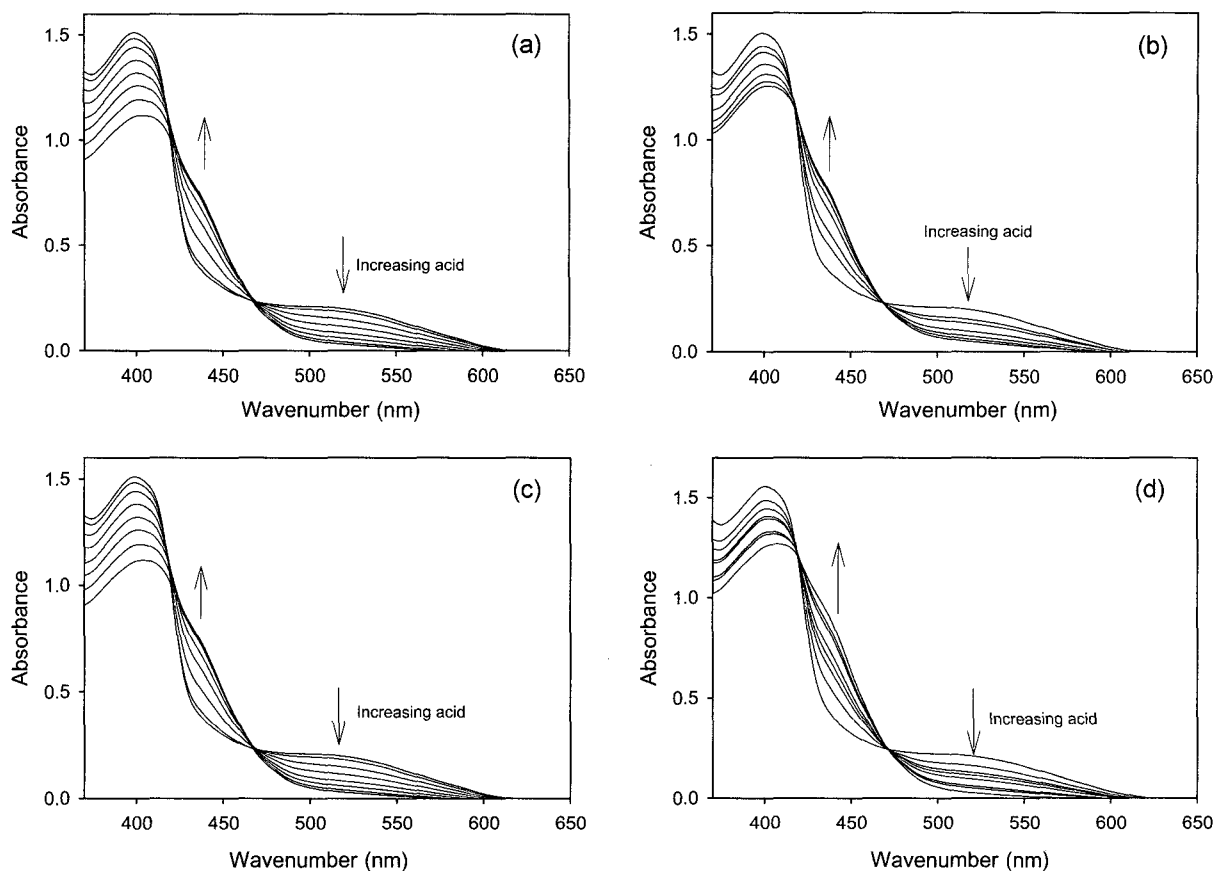
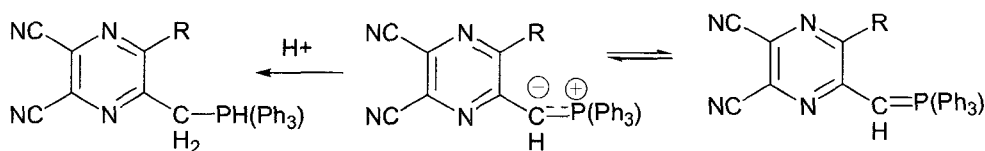


Figure 1. Changes in UV/VIS spectra of PMMA-dye solution in THF with increasing amounts of HCl (a) and p-toluenesulfonic acid (b), and of PU-dye solution in DMAc (c) and dimethylsulfoxide (d) with increasing amounts of HCl.



Scheme 2. Scheme for explaining a mechanism of color change in polymeric styryl dye due to addition of acid, where P(Ph₃) indicates triphenylphosphine.

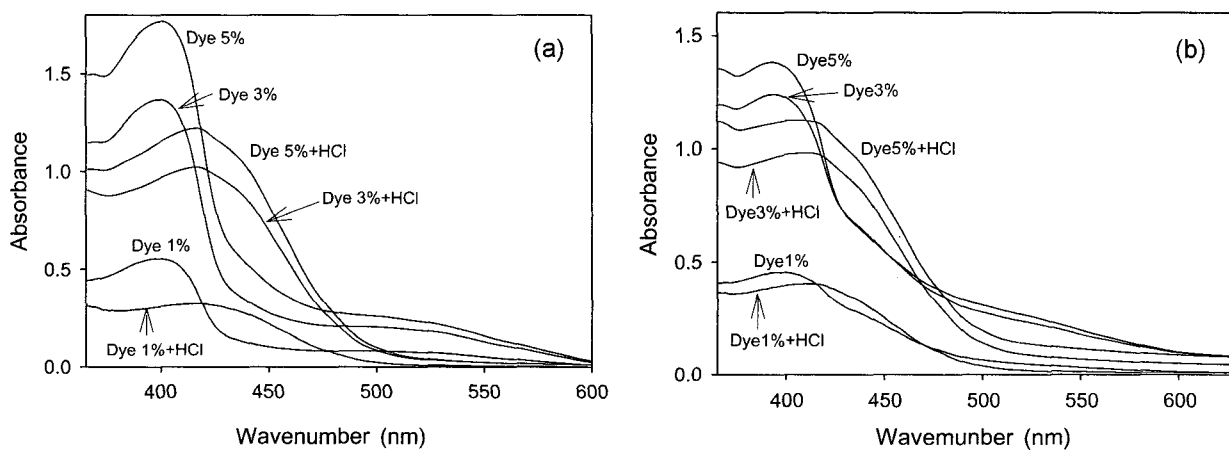


Figure 2. Changes in UV/VIS spectra of PMMA-dye (a) and PU-dye (b) films with an addition of HCl.

acid sensitive function at a relatively high rate. Moreover, uniform color distribution was observed through the entire acid-sensing process in the samples.

Dynamic Mechanical Properties

Figures 3(a) and 3(b) show DSC thermograms and effect of dye content on T_g in PMMA-dye films, respectively. T_g s of pure PMMA and styryl dye were 100 °C and 125 °C, respectively. For PMMA-dye films, single T_g appeared between T_g s of polymer and dye, and increased gradually with increasing wt% of dye. It indicates that there exists at least some miscibility between PMMA and dye molecules. Here, it should be noted that polymeric dye and PMMA are composed of same main chain of methylmethacrylate unit. Regarding this, it is not difficult to expect relatively good miscibility from PMMA-styryl dye system even though bulky side group pending on dye molecule is introduced. Figure 4(a) shows $\tan\delta$ curves of PU-dye films with different dye content. For pure PU, $\tan\delta$ peak appeared near 10 °C, being ascribed to its glass transition temperature. With increasing wt% of dye, T_g of blends increased linearly as shown in Figure 4(b), reflecting miscibility between

PU and dye. This miscibility in PU- and PMMA-dye systems may be attributed to uniform color distribution of both films.

Tensile Properties

Figures 5(a) and 5(b) show tensile stress-strain curves tested for PMMA- and PU-dye films, respectively. It can be seen that dye has a significant influence on mechanical properties of PMMA. With increasing wt% of dye, modulus and breaking stress of PMMA-dye films increase and breaking strain tends to decrease (Figures 6(a) and (b)). It is due to stiffness of styryl dye [11-13]. PU-dye samples show typical elastomeric behavior for all the samples like pure PU which is composed of hard and soft segments [14-17], and their modulus increases only slightly with increase of wt% of dye, whereas breaking stress does not show any so significant change, though breaking strain is lowered as shown in Figures 7(a) and 7(b). From these results, we can see that there is some difference in its dependence between PMMA and PU films even an increase in breaking stress is related to an increase in dye content. This difference is ascribed to whether matrix polymer is in glassy or rubbery state. In spite of it, another interesting point to be observed is

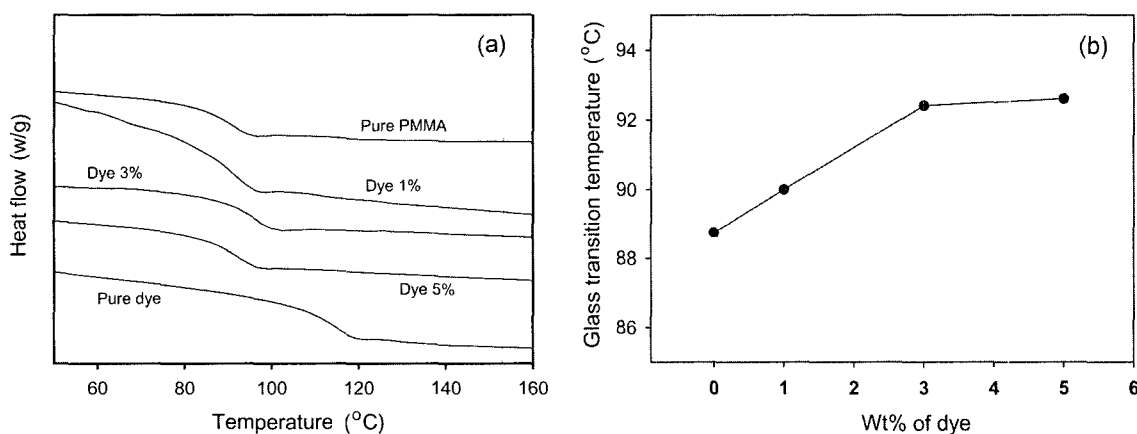


Figure 3. DSC thermograms of PMMA-dye films (a) and dependence of T_g on wt% of dye (b).

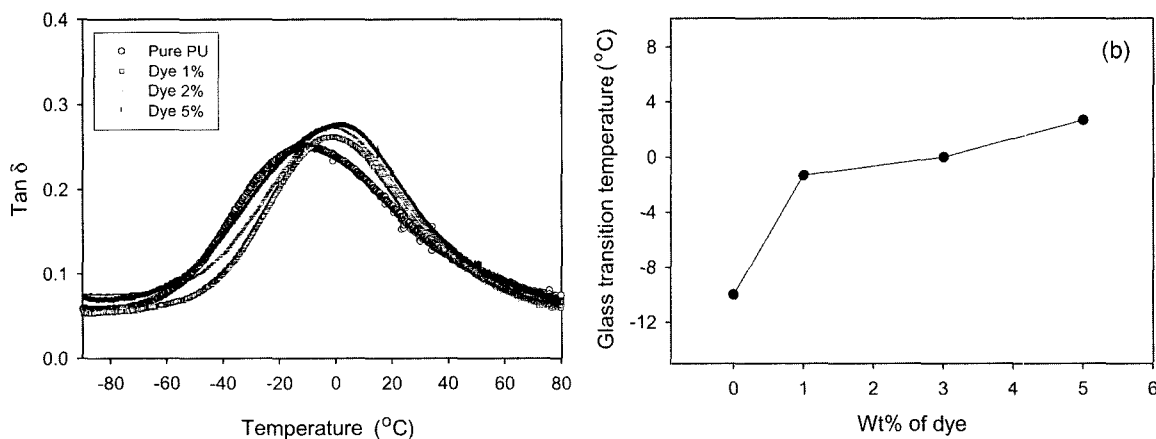


Figure 4. Temperature dependence of $\tan\delta$ for PU-dye films (a) and dependence of T_g on wt% of dye (b).

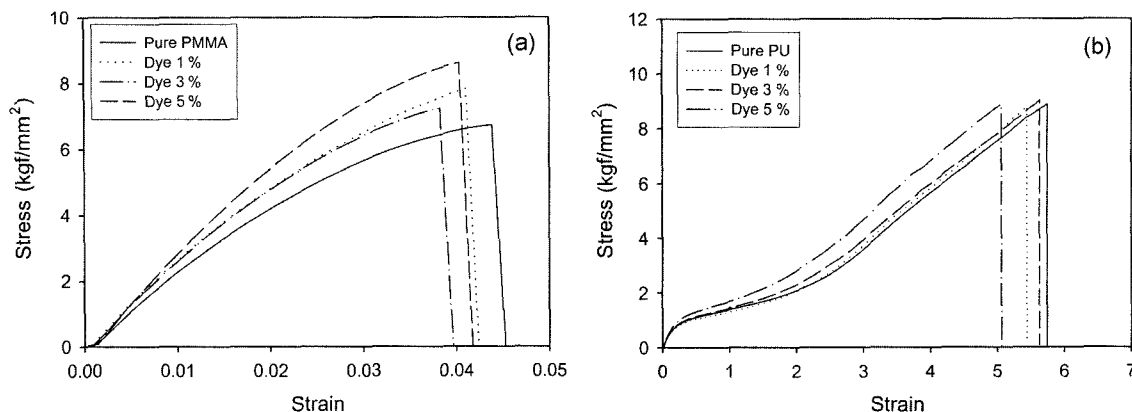


Figure 5. Stress-strain curves of PMMA-dye (a) and PU-dye (b) films.

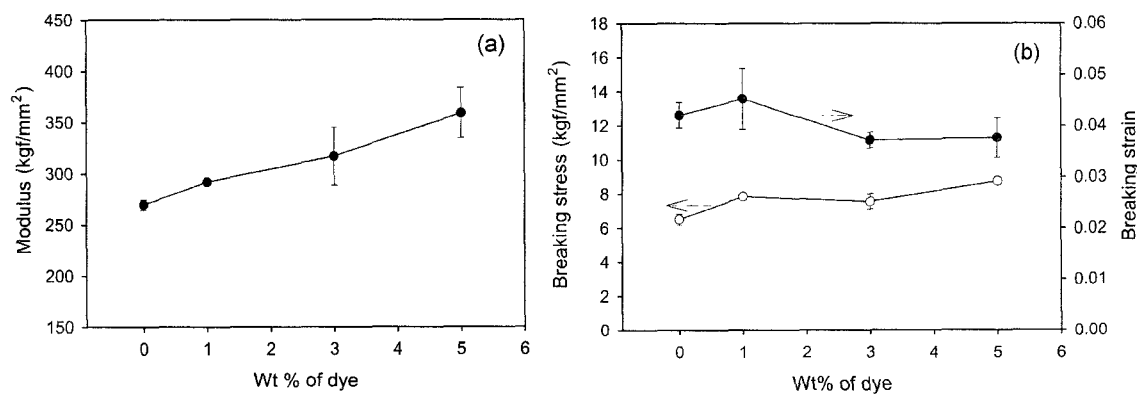


Figure 6. Modulus (a) and breaking stress and elongation-at-break (b) of PMMA-dye films with different wt% of dye.

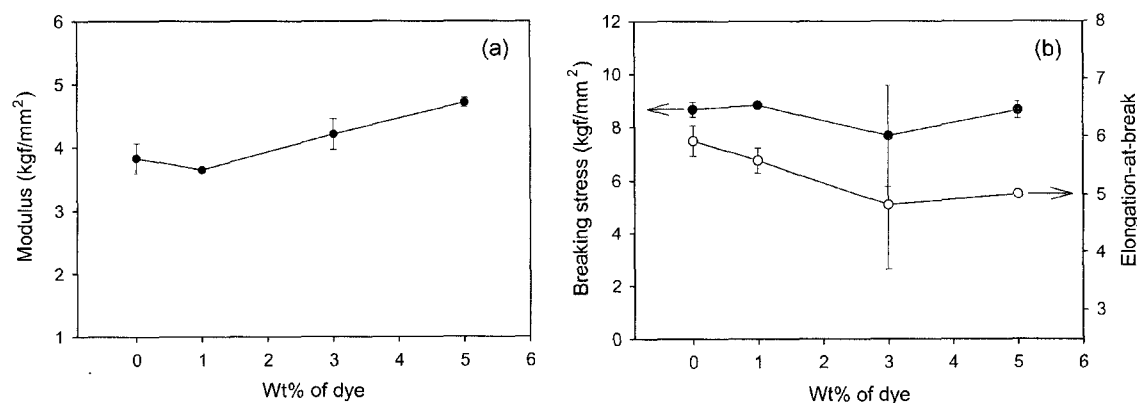


Figure 7. Modulus (a) and breaking stress and elongation-at-break (b) of PU-dye films with different wt% of dye.

that samples containing dye show somewhat increased stress at large elongation prior to breaking point in both cases of PMMA and PU samples as shown in Figures 5(a) and 5(b). This may be very important from a commercial point of view, and it is attributed to the usefulness of polymeric dye with miscibility between dye and matrix polymer. Consequently, it can be said that good acid-sensitive characteristics can be obtained from PU or PMMA films containing polymeric styryl

dye with improvement of mechanical properties, depending on dye content or polymer matrix.

Conclusion

PMMA- and PU-dye films showed good acid-sensitive characteristics, that is, smart function of color change from red to yellow on exposure to acid environment, evidenced by

direct observation and UV/VIS spectroscopic measurements. Due to good miscibility between dye and polymer, uniform color was observed through samples. Mechanical properties of PMMA- and PU-dye samples showed increased breaking stress and modulus and decreased breaking strain with increasing dye content. In case of PMMA, modulus and breaking stress increased up to about 50 % with increasing dye content, whereas modulus and breaking stress of PU samples showed only slight increase.

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