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New photosensitive polymer composites based on oriented porous polyethylene filled with azobenzene-containing LC mixture: reversible photomodulation of dichroism and birefringence

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A new type of polymer–liquid crystal (LC) composite with photovariable dichroism and birefringence is described. Porous stretched polyethylene (PE) films with pores size in the range 50–500 nm were used as polymer matrices. A photochromic cholesteric mixture based on a commercial nematic mixture doped with azobenzene and merocyanine dopants was prepared. Highly birefringent deeply coloured flexible films possessing strong dichroism were obtained by introduction of the photochromic LC mixture into the stretched PE films by capillary forces. UV irradiation leads to E–Z isomerisation of azobenzene-containing molecules inside the composite films and results in a significant decrease of the dichroism almost down to zero due to isothermal transition from the mesophase to isotropic melt stimulated by the isomerisation process. This process is reversible and the visible light irradiation or annealing lead to a back transition to the uniaxial birefringent and dichroic state. The composite films show a high fatigue resistance during the alternating cycles of the UV–visible irradiation. These novel composites can be considered as promising materials for photonics and optical information processing.

Keywords: polymer–liquid crystal composite; reversible photomodulation; dichroism; birefrigence

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are composite materials formed by micron-sized droplets of liquid crystal (LC) embedded in a solid polymer matrix (*1–12*). In recent years they have attracted considerable attention owing to their applications as light shutters, switchable windows, displays and other electro-optical devices. Such interest in PDLCs is associated with the possibility of combining the high mechanical properties of polymer films with the unique optical and electro-optical properties of LCs in the same material. PDLCs are very promising from the point of view of their electro-optical applications (*1–7*) as well as the passive polarising optical elements (*8–12*).

In recent papers we have described a composite material based on nematic LCs doped with different dichroic or photochromic dyes embedded in the highly porous stretched polyethylene (PE) films (*13–15*). The size of pores in such a polyethylene matrix was varied between 50 and 500 nm. In some sense these hybrid polymer films can be considered as a specific type of PDLC system, the optical properties of which can be regulated by light irradiation. We have discovered that the director of nematic LCs embedded in the porous polymer films is oriented along the direction of the film stretching (Figure 1). Study of the polarised absorbance spectra of the dichroic dyes dissolved in LCs allowed us to calculate dichroism values. The values obtained are comparable with those in glass cells coated with rubbed polyimide, which indicates a high degree of LC orientation in the polyethylene films.

In this paper, the behaviour of a PE composite containing LC mixture doped with azobenzene photochromic compound **AZOK6/12** is described. It is well known that azobenzene derivatives undergo E–Z isomerisation, resulting in a significant decrease of their anisometry (*16*) (Figure 1(b)). Such changes of the molecular shape result in decrease of order parameter, birefringence and, in some cases, in an isothermal transition from mesophase to isotropic state (*17–23*).

As a main component for the mixture preparation we have used commercially available low-molar-mass nematic LC material MLC6816 (49.5 wt %). This LC mixture has a relatively small mean refractive index close to PE because the main components of the mixture are based on cyclohexane derivatives.

AZOK6/12 (Scheme 1) was selected as a photochromic azobenzene compound (*24*). This compound has good solubility in the LC host and does not disrupt LC order due to its "rigid" mesogenic structure.

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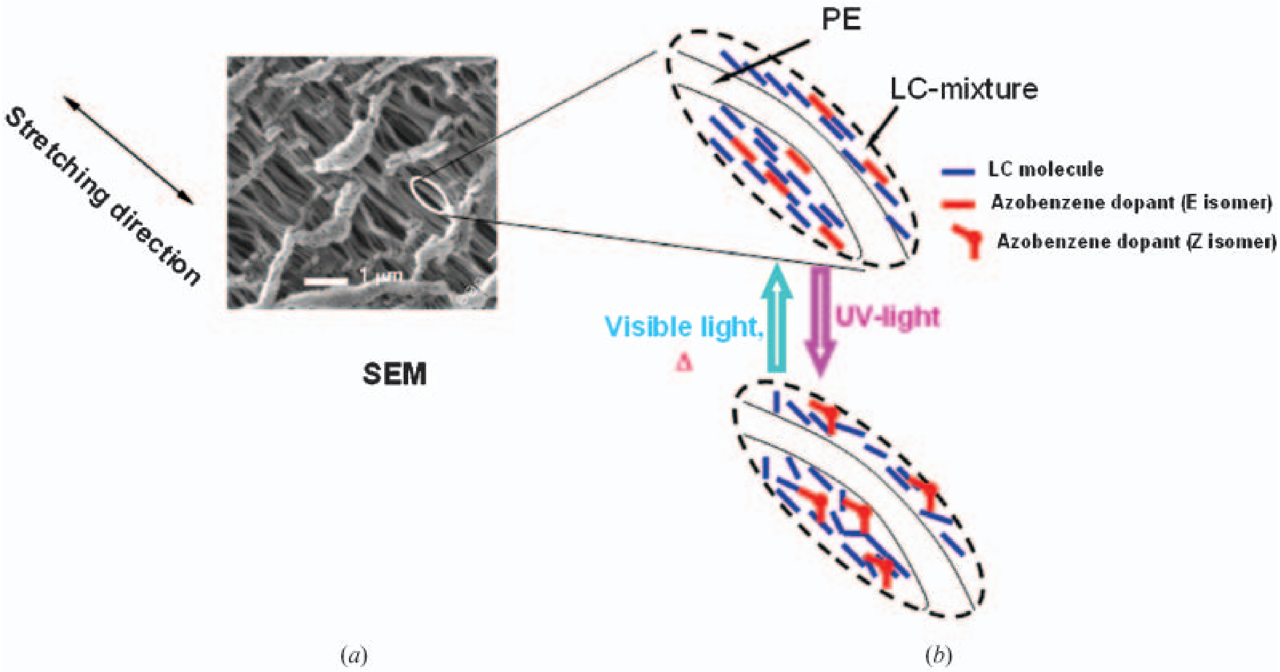


Figure 1. SEM microphotograph showing microporous structure of SPPE film (a) and schematic representation of LC molecules orientation along PE fibrils and photoinduced phase transition initiated by E–Z isomerisation of azobenzene fragments (b).

In addition, this compound has a chiral centre that permits a chiral nematic phase to be induced, which could provide an opportunity for manipulation by helical structure of the obtained composites in future experiments; these, however, are beyond the scope of this paper.

We have also used a trace amount of merocyanine dye **ASh253a** (Scheme 2) (*25*) as dichroic guest for spectral measurements and evaluation of the orientation degree of LC in the composite. This substance is very stable in respect to UV and visible light action, i.e. no photodegradation process takes place under prolonged (hours) irradiation with non-filtered light from a mercury lamp.

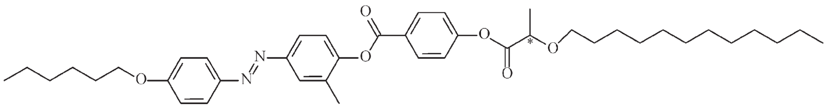
The LC mixture exhibits a cholesteric phase with a clearing temperature around 73–74°C and the helix pitch is greater than 2 µm (as was checked by near-IR spectroscopy). This mixture is quite stable even at ambient conditions, i.e. crystallisation or phase separation does not take place.

The main goal of this work was the study of the photo-optical properties of a new type of photosensitive LC–stretched porous PE composite. The principal advantage of the usage of oriented porous PE matrix is connected with the possibility of orientation of mesogenic, anisometric photochrome, and dye fragments in pores of composite films. Special attention was paid to the investigation of photoinduced changes in dichroism and birefringence in the PE composite films during E–Z isomerization of photochromic dopant **AZOK6/12** induced by UV irradiation in order to demonstrate the possibility of reversible photomanipulation of the optical properties in the new composite materials based on PE.

2. Experimental

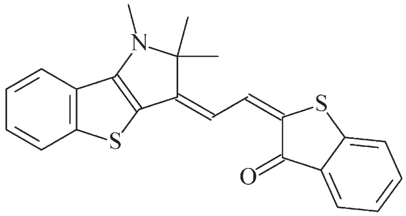
Substances and polymer films

Microporous films of polyethylene were obtained from commercially available polyethylene of low



AZOK6/12, 50.0 wt %

Scheme 1. Structure and concentration of the photochromic azobenzene compound **AZOK6/12**.



0.5 wt % ASh253a

Scheme 2. Structure and concentration of the merocyanine dye **ASh253a**.

density ($M_w=1.4\times10^5$, $M_w/M_n=6$–8, $T_m=132°C$) according to procedure described elsewhere (*26*). During extrusion and stretching processes polymer films are deformed, and a porous structure with pore sizes of about 50–500 nm is obtained. The pore size distribution was measured by the filtration porosimetry method, as described by Palaria *et al.* (*27*).

As a nematic LC host, a commercial mixture of bicyclohexane derivatives (MLC6816, Merck) with $T_{cl}=76.5°C$ and $\Delta n=0.0605$ was used.

Syntheses of photochromic dopant **AZOK6/12** and merocyanine dye **ASh253a** are described in the literature (*24, 25*).

Mixture preparation and study of phase behaviour and optical properties of mixture and composite films

The liquid crystalline mixture was prepared by dissolving the components in chloroform followed by evaporation of the solvent and drying in vacuum. Polymer composite was prepared by coating of films with LC mixtures and subsequent removal the excess of LC mixture by filter paper. The proportion of LC mixture in polyethylene composite obtained by weighing was about 55%.

Polarising microscopy investigations were performed using LOMO P-112 polarising optical microscope (POM); the temperature of samples was controlled using a Mettler FP-80 hot stage.

Photo-optical investigations.

Photochemical investigations were performed using a special optical set up equipped with a DRSh-250 ultra-high pressure mercury lamp. Using the filter, light with the wavelengths 365 nm and 436 nm was selected. To prevent heating of the samples due to the IR irradiation of the lamp, a water filter was used. To obtain a plane-parallel light beam, a quartz lens was applied. During the irradiation, the constant temperature of the test samples was maintained using a Mettler FP-80 heating unit. The intensity of light was equal to 1.0 mW cm^{-2} (365 nm) and 0.5 mW cm^{-2} (436 nm), as measured by a LaserMate-Q (Coherent) intensity meter.

The linearly polarised spectra of the film samples were studied with a TIDAS spectrometer (J&M) equipped with rotating polariser (Glan-Taylor prism controlled by computer program).

3. Results and discussion

Introduction of the photochromic LC mixture into stretched PE films by capillary forces allowed highly birefringent, deeply coloured flexible films to be obtained. Due to the noticeable birefringence of the pure stretched PE, determination of the clearing temperature of the LC mixture in the composite films by polarising optical microscopy was very difficult. Hence, the transmittance of the composite between crossed polarisers was measured as function of temperature using a spectrometric method. According to the data obtained, the clearing temperature of the LC mixture embedded in stretched PE was almost the same, i.e. 73–74°C (with accuracy of about 1°C).

Figure 2 shows the absorbance spectra of the composite film before and after UV irradiation. Visible and near-IR regions of the spectra consist of two absorbance peaks corresponding to the n–π* electronic transition of azobenzene molecules (with maximum at 440 nm) and peak corresponding to the low-energy electronic transition of merocyanine dye (with maximum at 630 nm). Nonzero absorbance outside these two peaks is associated with the light scattering from composite film. Before irradiation, the film has a strong dichroism at both peaks (figures 2a and 3a). The appearance of dichroism is related to the orientation of the LC mixture molecules as well as azobenzene and merocyanine molecules along the stretching direction of PE film. This effect of orientation has been studied previously (*13, 14*) and refers to an anisometry of the pores in PE films formed by the extrusion process and during the stretching of the films. Moreover, cholesteric helix of LC mixture is already untwisted inside small pores of PE due to boundary effects, as described earlier (*14*).

UV irradiation leads to the E–Z isomerisation of azobenzene molecules and results in a significant decrease of dichroism almost to zero (figures 2b and 3b). Figures 4–5 show the kinetics of absorbance and dichroism changes under UV light action (365 nm) followed by the visible light irradiation (436 nm). Irradiation with the short-wavelength light induces Z-isomer formation with concentration at photostationary state of about 90% (*23*); subsequent visible light irradiation leads to back conversion to

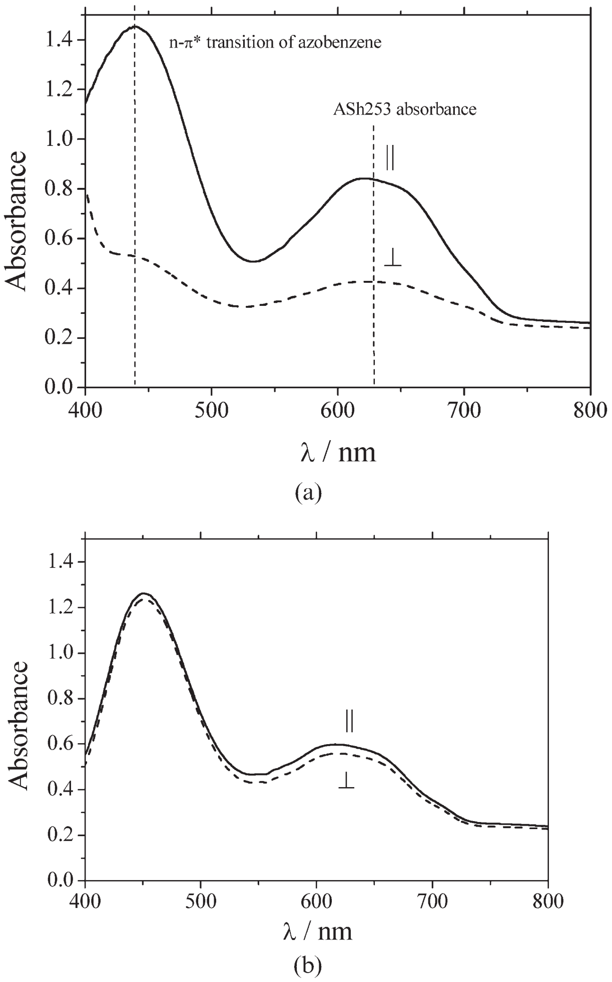


Figure 2. Polarised absorbance spectra measured parallel and perpendicular to the stretching direction of PE film composite (a) before and (b) after 40 min of UV irradiation (365 nm).

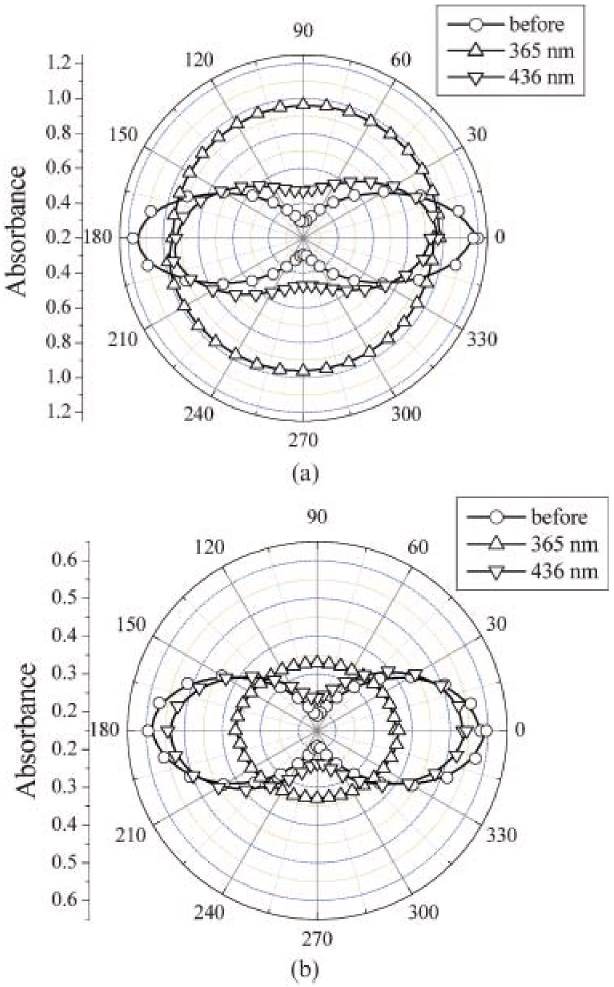


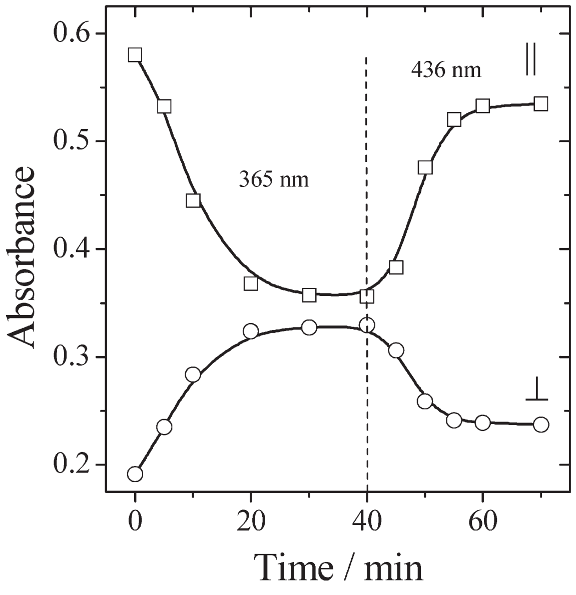
Figure 3. Polar plot of absorbance at 440 nm (a) and 630 nm (b) measured before and after UV (365 nm, 40 min) and visible light irradiation (436 nm, 30 min).

another steady state with the low concentration of the Z-isomer (~10%). On the other hand, annealing of the same sample at 80°C results in very fast (<10 min) and full recovery of dichroism values due to the efficient complete back Z–E thermal transition.

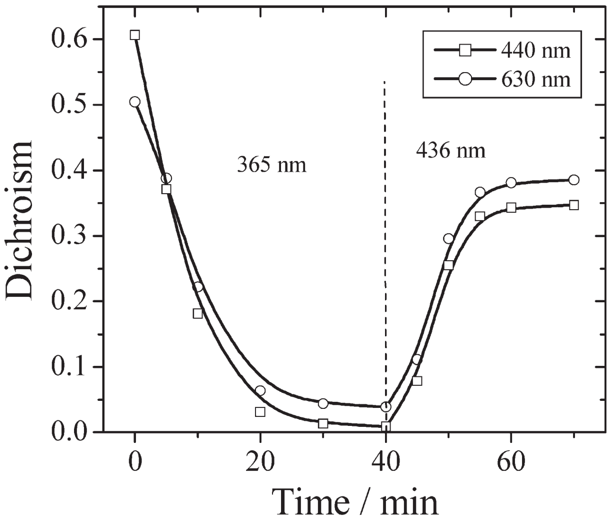
The Z-isomer has very low anisometry and an increase of its concentration induces mesophase disruption and isothermal transition to the isotropic state (see Figure 1), which can be clearly seen during observation of the photochromic LC mixture between crossed polarisers of a microscope or using a spectrophotometry method (Figure 5). Transmittance values at wavelengths outside the absorbance peaks of **AZOK6/12** and **ASh253** (525 nm) oscillate during UV irradiation due to continuous retardation changes (*27*). In the photostationary state, the transmittance becomes almost zero for the photochromic LC mixture in glass cell due to formation of the isotropic state. The high value of the transmittance for the composite film is explained by an intrinsic birefringence of stretched PE film (*26*). Such isothermal transitions, i.e. mesophase–isotropic melt (UV irradiation) and isotropic melt–mesophase (visible light irradiation), are the main reason for the strong dichroism changes shown in Figures 2–3.

Figure 6 shows polarising optical microphotographs of the recorded pattern on the composite film. The film was irradiated by non-filtered mercury lamp light (~20 mW cm^{-2}) for 10 min via a mask. Irradiation locally changes the colour of the film, which is observable by the polarising optical microscopy. During subsequent observation, the erasure of the recorded pattern takes place due to the action of white light from a tungsten lamp.

In order to characterise the quality of photochromic composite films as a material for the



(a)



(b)

Figure 4. Changes of polarised light absorbance at 630 nm (a) and dichroism at 440 nm and 630 nm (b) during irradiation with light 365 nm, followed by 436 nm.

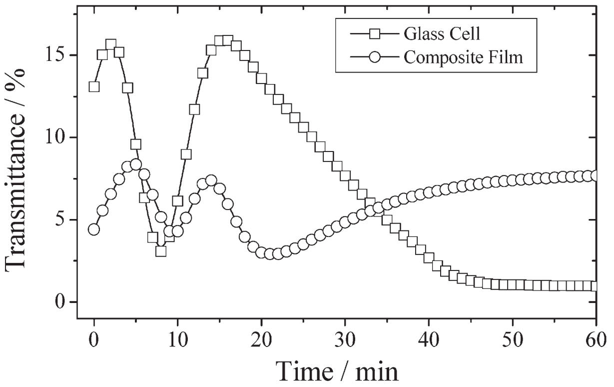


Figure 5. Changes of transmittance of composite films and LC mixture in glass cell during UV irradiation (365 nm). Transmittance was measured between crossed polarisers; optical axis of samples was tilted by 45° to polariser axes.

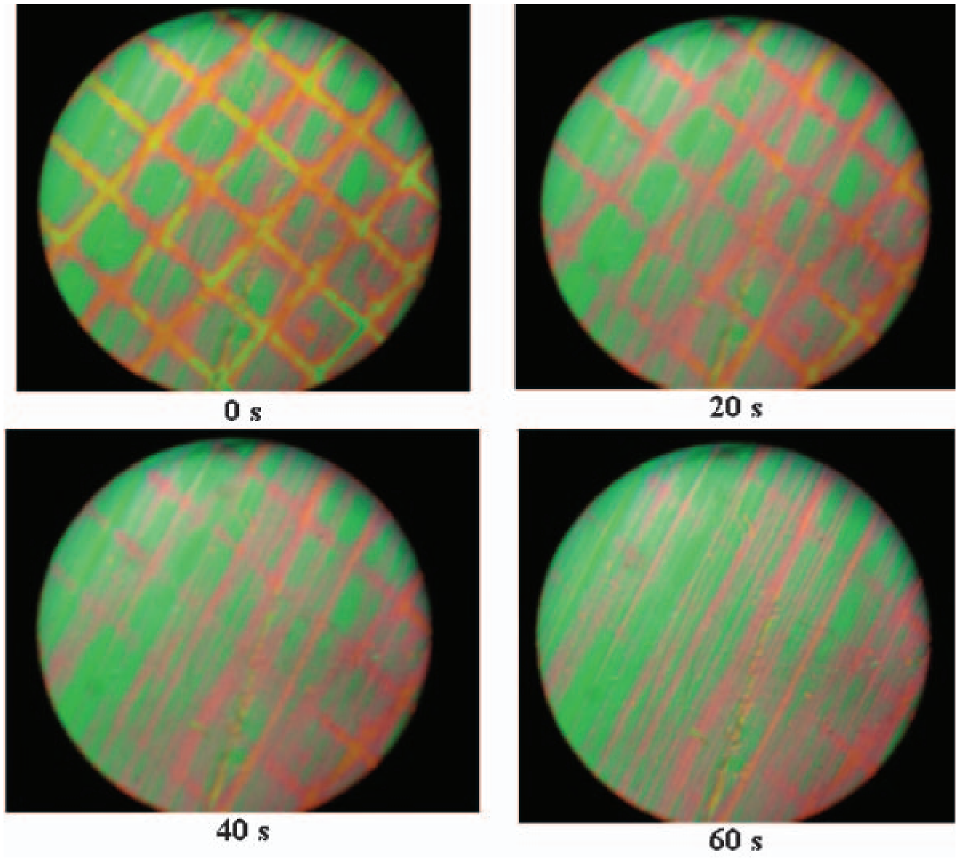


Figure 6. Polarising optical microphotographs demonstrating recorded pattern on PE composite film. Film was irradiated by non-filtered Hg-lamp light (~20 mW cm^{-2}) during 10 min through the mask followed by erasing of recorded pattern during observation in POM (irradiation with white light of tungsten lamp). Time is shown in the figure.

reversible optical recording we performed several cycles of alternating UV and visible light irradiations. As can be seen from Figure 7, the composite films have high fatigue resistance.

Despite a high sensitivity of the recorded images to external light and the short durability of the optical storage due to the diffusion of molecules inside pores, these new composites can be considered as promising materials for optical information processing. For example, the use of photopolymerizable nematic mono- and diacrylate monomers instead of LC mixture MLC6816 allows one to obtain network

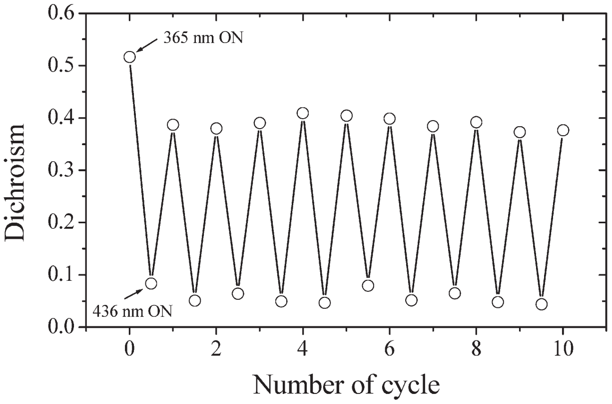


Figure 7. Fatigue resistance properties of composite film under the cycles of alternating irradiation by UV light (365 nm, 30 min) and blue light (436 nm, 30 min).

and to solve the above-mentioned problems of instability of recorded image and can open the possibility for creation of stable composite films based on porous PE for optical data storage.

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