

New Optical Material Emit Blue Light Poly(vinyl alcohol) Films Filled with Lanthanum-N-Ethylmorpholine Complex

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Poly(vinylalcohol) (PVA) films with different concentrations of lanthanum ions were prepared using the method of casting technique. The thickness of the prepared samples was 250 μm . Optical absorption and mechanical properties were measured. The prepared samples irradiated with UV source and the fluorescence emission was measured. Pure PVA sample emitted fluorescence radiation at 557 nm with FWHM 13 nm, while the doped PVA films emitted bright blue light. The maximum fluorescence intensity for the doped PVA samples increases linearly with the increase of excitation wavelength. The emission peak position showed to be changing as the concentration of the Lanthanum changes. The stress – strain measurements were performed. It was found that Young's modulus Y decrease, while the strength σ , and strain at break ϵ_b increase as the lanthanum ions concentration is increased. The morphology of the prepared samples has been studied using scanning electron microscope (SEM). Such luminescent polymer films are expected to find potential applications as a new optical materials.

INTRODUCTION

The addition of lanthanides to polymeric network is of considerable interest for both scientific and technological purposes [1,2]. PVA is one of the most important polymeric materials as it has many applications in industry and is of relatively cost manufacture [3-10]. The optical uses of PVA are concerned with the retardation, polarization, filtration of light, and contact lenses and drug-delivery system [11-17].

On the other hand, The lanthanides have many scientific and industrial uses. Their compounds are used in fluorescent lamps, lasers, magnet, phosphor, optical glass, electronics, motion picture, projectors and fiber optics. Lanthanide ions have unique spectroscopic characteristics such as sharp luminescence emission and strong paramagnetic shift properties. [2,18-19].

PVA doped with different types of lanthanides ions such as Ho^{+3} , Er^{+3} , Sm^{+3} and Eu^{+3} [2,18]. In this context we have recently [1] doped PVA with lanthanum-N-Ethylmorpholine complex and our results showed that the absorption spectra of doped PVA films showed that there is observable change in the band position with filling levels. This is due to the link between the lanthanum metal ion and the polymer OH-groups. The dependence of the absorption coefficient, α , on the photon energy, $h\nu$, has been determined and the band tails and energy gaps were calculated. It was found that the band tail increases, while the optical gaps decrease as the concentration of lanthanum ion is increased. X-ray diffraction technique was used to characterize the prepared films. The results indicated the appearance of several new bands not existing in both lanthanum ion and PVA. The I-V characterization curve was measured for the PVA- lanthanum film with different concentrations showing a remarkable increases in the values of the conduction current of about three orders of magnitude as compared with the pure PVA film.

Continuing our studies on PVA doped with lanthanum-N-Ethylmorpholine complex samples we devoted the this article to study the fluorescence spectra and mechanical

properties (Young 's modulus Y , strength σ , and strain at break ϵ_b) in combination with scanning electron microscope (SEM) of the prepared samples.

EXPERIMENTAL

$\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (10 mmol, 4.3291g) was dissolved in 20 cm^3 of distilled water and added to an equal volume of aqueous solution containing 10 mmol (1.15g) of N-Ethylmorpholine. The mixture was refluxed for 2 hours, after cooling, the separated white solid complex was filtered, washed several times with ethanol and dried in vacuo. The analytical characterization for the solid complex is depicted in Table1 for more details see[19].

Poly(vinyl alcohol) PVA of molecular weight 17000 gm/mole, (BDH England), was used as a basic polymeric material in this work. The present PVA films, with different amounts of lanthanum-N-Ethylmorpholine complex, were prepared by the casting method as follows [6]: PVA powder was dissolved in distilled water and then maintained for 24 hours at room temperature to swell. Lanthanum-N-Ethylmorpholine complex also was dissolved in distilled water and added to the polymeric solution. The mixture was then warmed up to $60 \text{ }^\circ\text{C}$ and stirred, using magnetic stirrer, thoroughly for 4 hours until the mixture was completely soluble. The solution was poured into flat-glass plate dishes. Homogeneous films were obtained after drying in an air oven for 48 hours at $40 \text{ }^\circ\text{C}$. The thickness of the produced films was $250 \text{ }\mu\text{m}$. PVA films filled with lanthanum-N-Ethylmorpholine complex mass fraction 0, 20 and 40 % corresponding to samples a,b and c were prepared. The lanthanum concentration $W(\text{wt } \%)$ was calculated from the equation

$$W(\text{wt } \%) = \frac{w_f}{w_p + w_f} \times 100$$

Where w_p and w_f represent the weight of lanthanum and polymer respectively.

The films were divided into three groups a, b, c corresponding to the lanthanum concentrations.

The fluorescence spectrum of sample (a) was measured using Perkin Elmer Precisely LS 55 Fluorescence spectrometer with slit width excitation emission 2.5 nm, excitation wavelength 280 nm and the emission wavelength range 290-700 nm. The fluorescence spectra of samples (b,c) were measured using RF-5301 PC SHIMADZU spectrofluorometer.

The stress–strain measurements were performed using a mechanical test machine (AMETEK) in which a force gauge (Hunter spring Accu force II, 0.01 N resolution) is attached. The readings were automatically recorded through a microprocessor as a function of time. A locally made device with motor with microswitch system was attached to the test machine to control the strain rate. The strain rate throughout the experiment was 0.04 cm/sec.

Scanning electron micrograph of the studied samples were performed using SEM (JEOL-JEM-100) . The SEM specimens were prepared by evaporating gold onto the film surface using ion sputter JEOL, JFC-1100 L. Investigation by SEM under vacuum by using high voltage 40 Kv and beam current 100 μ A at room temperature.

RESULTS AND DISCUSSION

The absorption spectra of the prepared samples (a,b and c) were measured in the wavelength range 190-900 nm as shown in fig.1. The spectrum of the sample (a) contains three absorption bands at 200, 275 and 325 nm. The three absorption bands identify carbonyl groups of the type $-(\text{CH}=\text{CH})_n-\text{C}=\text{O}-$ where $n = 1, 2$ and 3 , which arises from the presence of acetaldehyde in vinyl acetate monomer during polymerization [20]. There is observable change in the band position of the samples b ,c with filling levels as shown in table2. This is due to the link between the lanthanum

metal ion and the polymer OH- groups. The dependence of the intensity of the bands on the filling level provides an evidence for the incorporation of the complex into PVA matrix.

Fig.2 shows fluorescence spectrum of sample (a) at room temperature for wavelength excitation, $\lambda_{exc} = 280$ nm. The maximum fluorescence wavelength (λ_{max}) at 557 nm with FWHM 13 nm.

When sample (a) in fig.1 which contain carbonyl groups of the types $-(\text{CH}=\text{CH})_n-\text{C}=\text{O}-$, of structure types $n=1$ and 2 irradiated with UV radiation at 280 nm the molecules absorb light and an electron is excited from its highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) that corresponds to excitation of an electron from one of the unshared pairs (a nonbonding or n electron) to the π^* orbital of the carbon-oxygen double bond and fluorescence emission at 557 nm emitted from the surface as shown in fig.2. The bigger jumps need more energy and so absorb light with a shorter wavelength [13].

Figs.3,4 show the fluorescence spectra of samples b and c at different excitation wavelengths and table 3 contains the analyzes of the spectra.

For sample (b) the excitation wavelength 390 nm emitted the highest maximum wavelength 460 nm with FWHM 62 nm whereas the excitation wavelength 370 nm emitted the lowest maximum wavelength 451 nm with FWHM 75 nm.

For sample (c) the excitation wavelength 390 nm emitted the highest maximum wavelength 453 nm with FWHM 67 nm whereas the excitation wavelength 330 nm emitted the lowest maximum wavelength 431 nm with FWHM 105 nm. The peak position (λ_{max}) increases linearly with the increase of excitation wavelength.

The maximum fluorescence intensity as a function of excitation wavelength increases linearly for samples b,c as it is demonenstrated in fig.5. Sample b emitted a higher maximum fluorescence intensitiy in comparison with the maximum fluorescence intensity of sample c.

Mechanical properties

The stress-strain behaviors are shown in fig6 and Table 4 summarizes the mechanical properties, Young's modulus Y , strength σ , and strain at break ϵ_b for the three samples (a), (b) and (c).

Table 4 reveals a tendency for a decrease in Young's modulus with increasing lanthanum concentrations while the strength σ , and strain at break ϵ_b increase as lanthanum concentration is increased.

This could be, explained as follows:

Pure PVA is partially crystalline and consists of crystalline layers or lamellas of folded chains joined together by tie molecules, which form amorphous regions between the lamellas [23]. Increasing of lanthanum ions concentration will lead to an increasing degree of disorder. The increasing degree of disorder causes Young's modulus to decrease according to the electronic structure of amorphous materials [24] while the increase in strength σ , and strain at break ϵ_b returned to the ability of lanthanum to improve the malleability and ductility of PVA [25].

SEM morphology

SEM micrograph of samples (b,c) is shown in fig.7. sample b demonstrated presence of primary structure (so called particle aggregates) and secondary agglomerates structure with broad range in aggregate size. While sample c shows that the particles markedly more uniform, narrowing of the aggregate size range as compared with sample b.

It is clear that the lanthanum ion particle consists of uniform spherical particles.

CONCLUSIONS

Poly(vinylalcohol) (PVA) doped with different concentrations of lanthanum ions of thickness of about 250 μm . Pure PVA sample emitted fluorescence radiation at 557 nm with FWHM 13 nm, while the doped PVA films emitted bright blue light. The maximum fluorescence intensity for the doped PVA samples increases linearly with the increase of excitation wavelength. The emission peak position showed to be changing as the concentration of the Lanthanum changes. This variations could be related to the link between the lanthanum metal ion and the OH group of PVA. Finally, Young's modulus showed to be decreasing as the Lanthanum concentration increases while the strength and strain at break increase as lanthanum ion increased. Aggregate size distribution showed to be related to the variation in behaviour of samples under investigation under absorption and emission .

Generarly, PVA films doped with lanthanum are expected to be new optical material with high potentiall for several applications.

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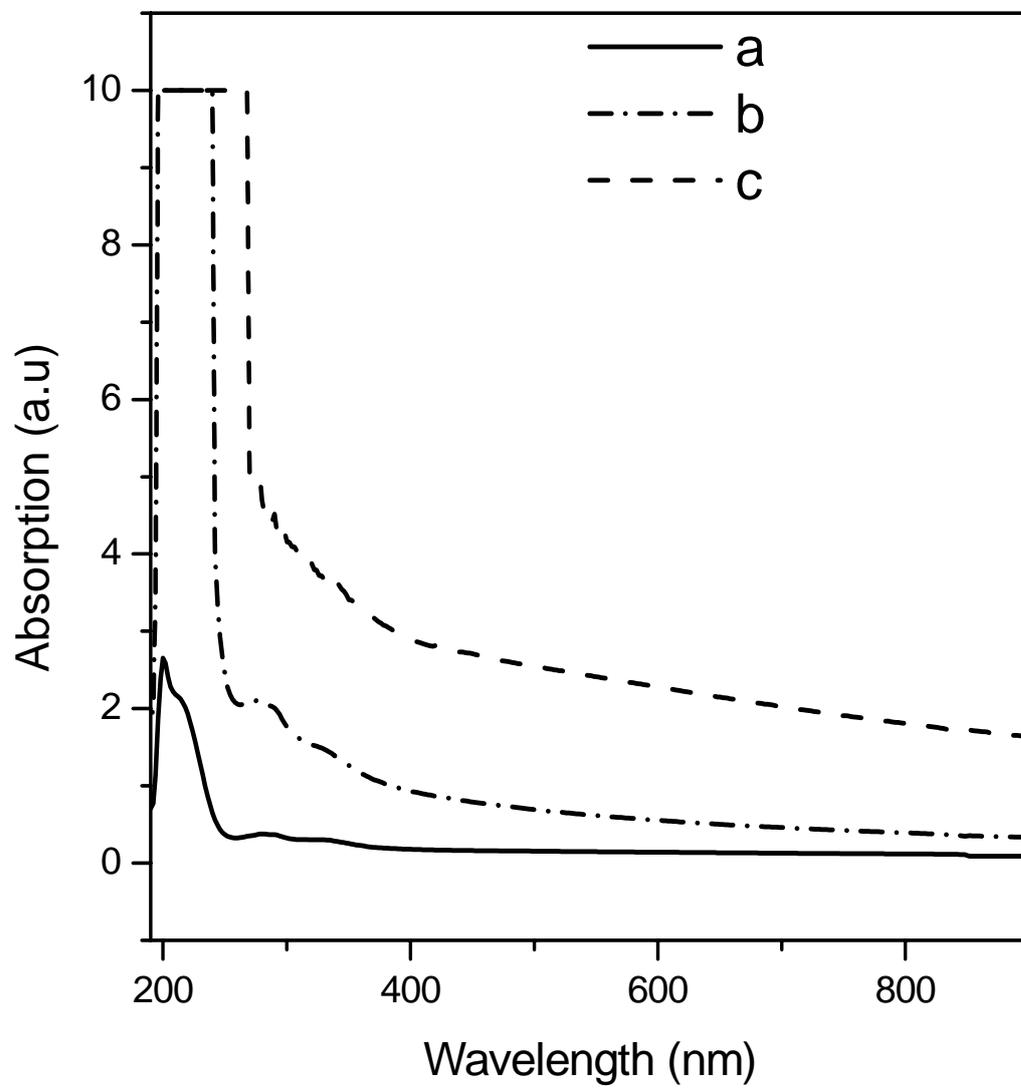


Fig.1

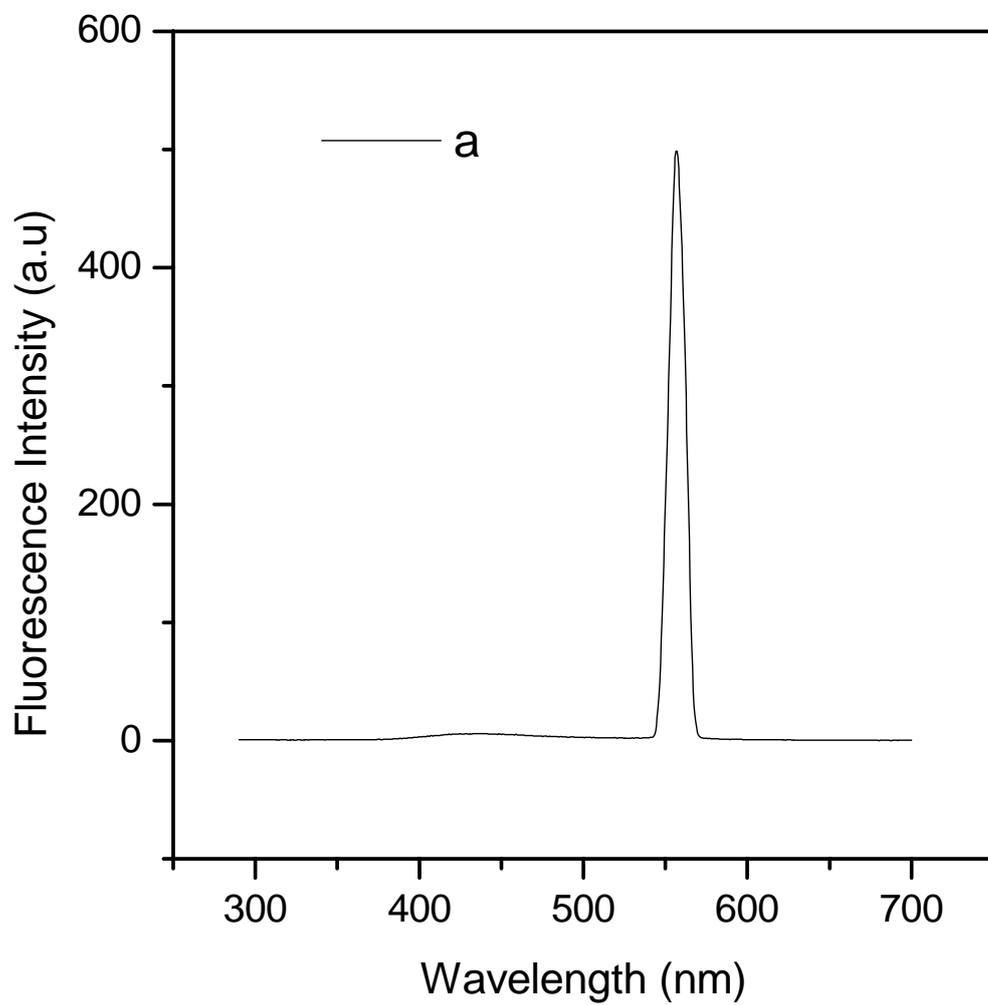


Fig.2

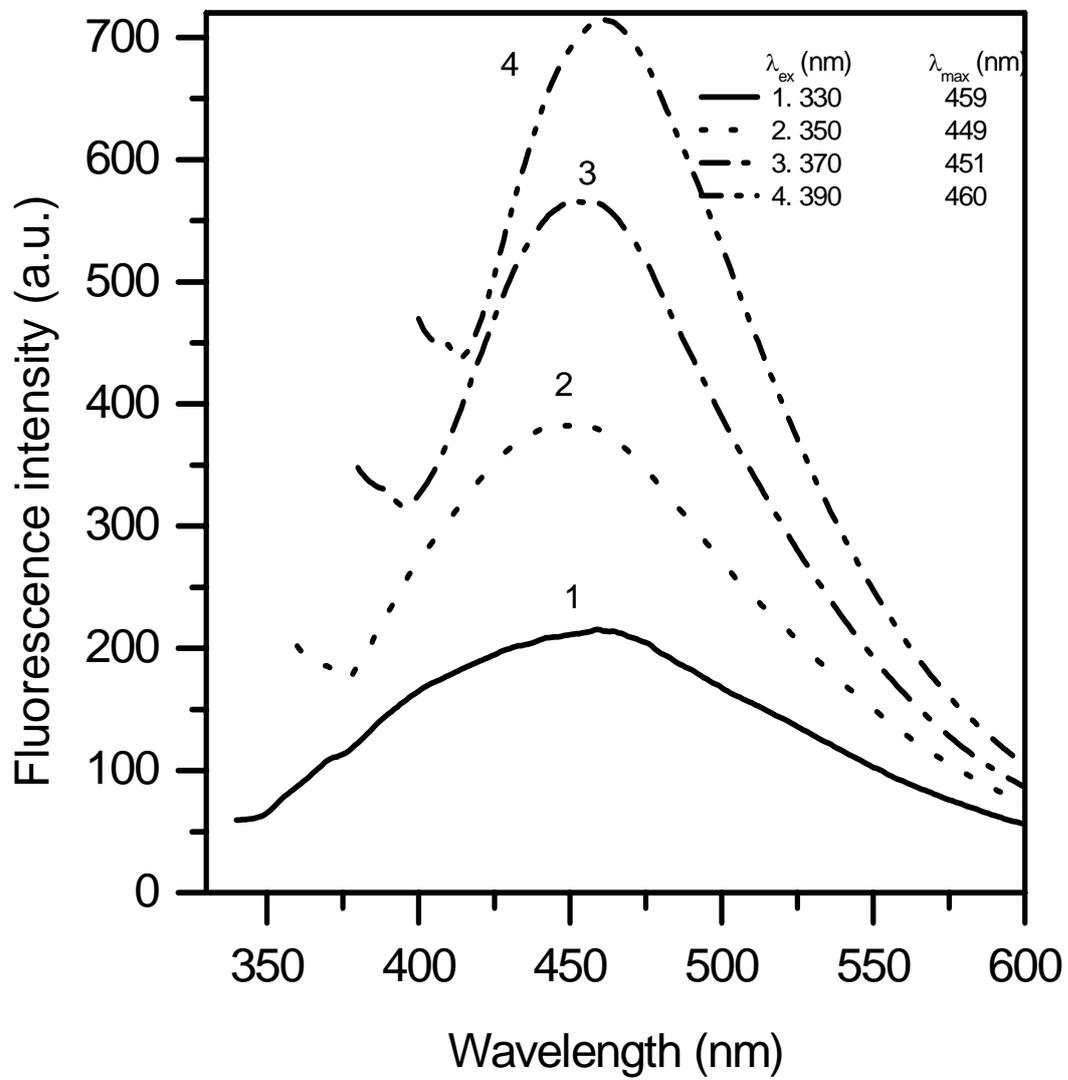


Fig.3

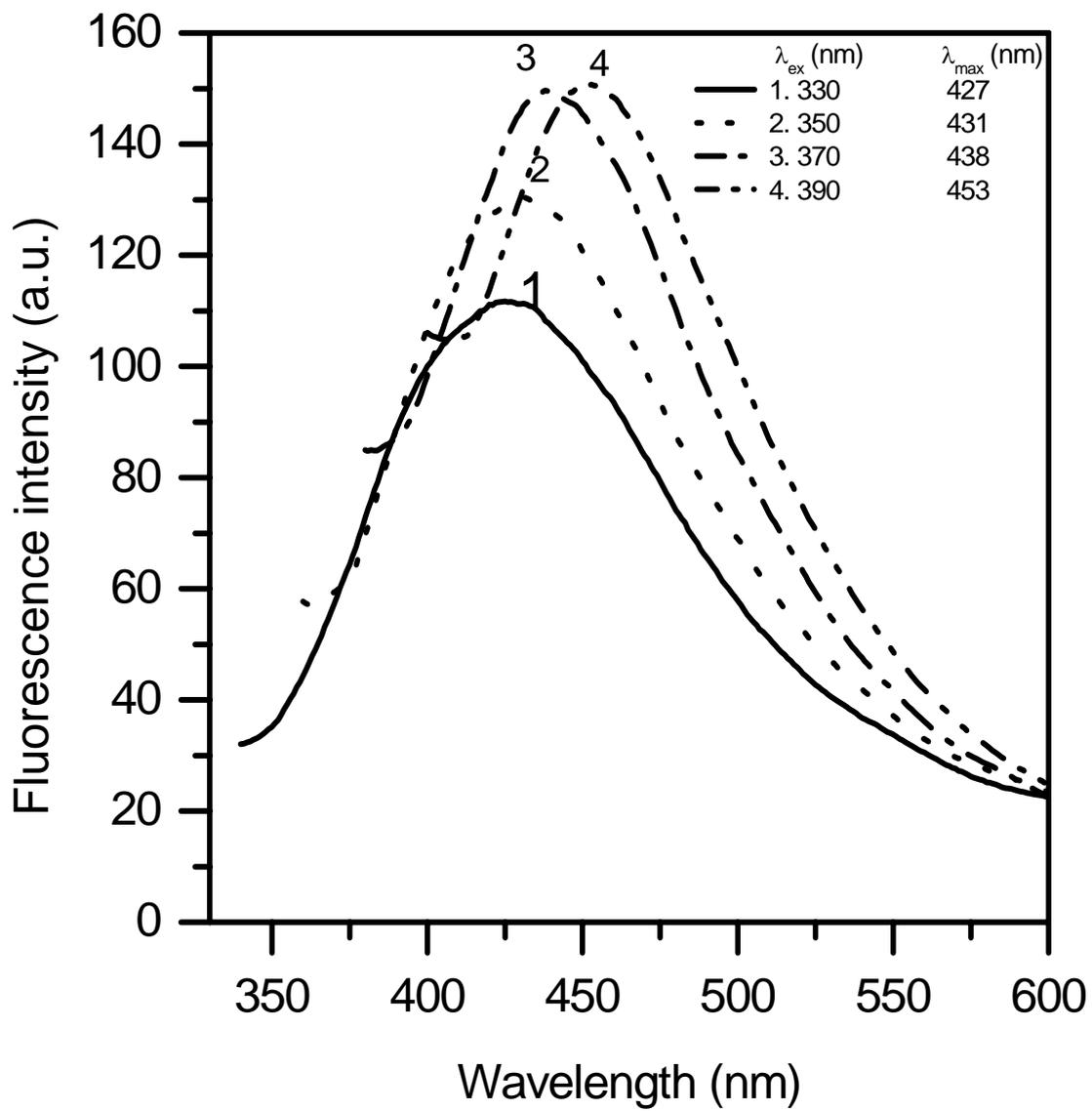


Fig.4

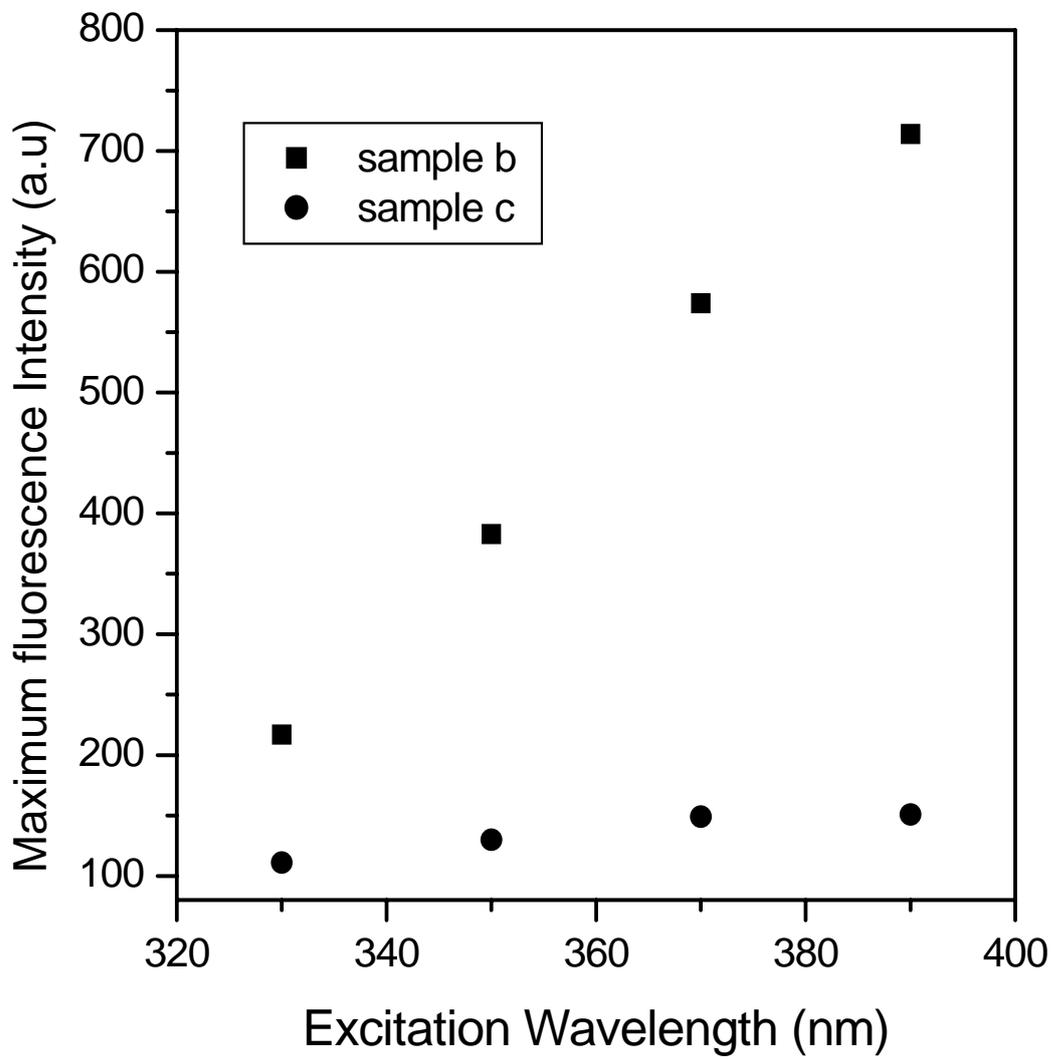


Fig.5

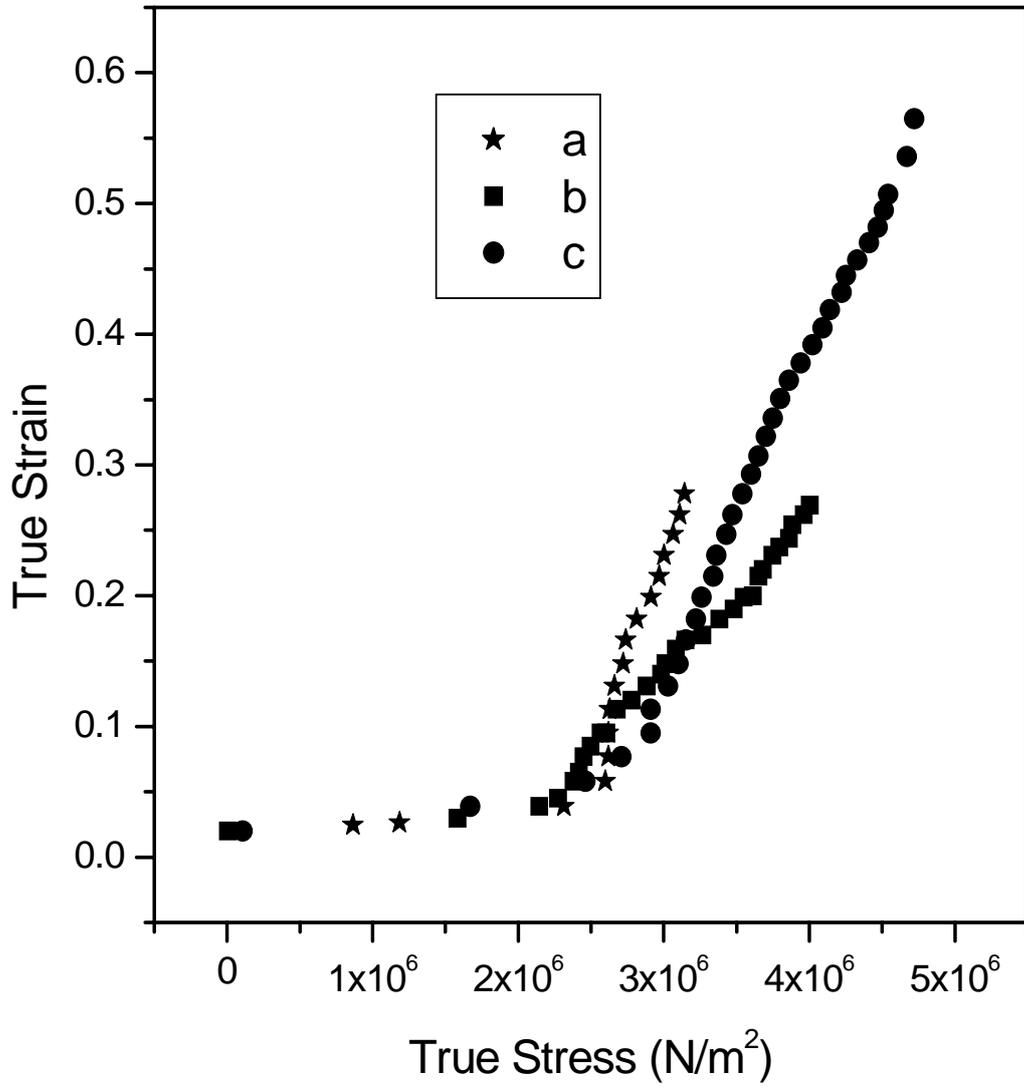


Fig.6

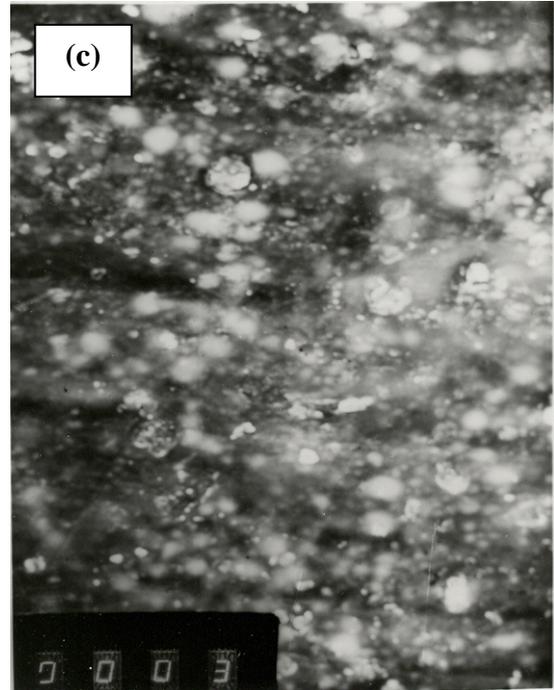
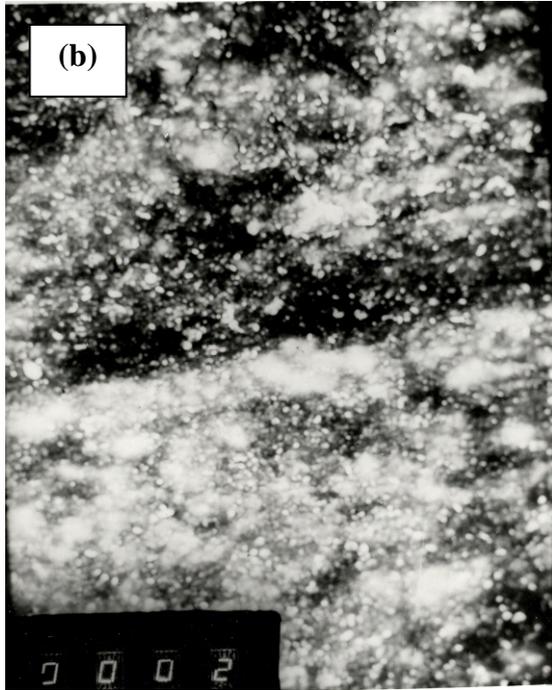


Fig.7