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Structural, optical and some physical properties of PVDF films filled with LiBr/$MnCl_2$ mixed fillers

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ABSTRACT

Films of polyvinylidene fluoride (PVDF) filled with (X)LiBr$(20-X)$$MnCl_2$ mixture, where $X=0$, 1, 2, 8, 16 and 20 wt%, were prepared by casting method and studied by ultraviolet/visible optical absorption (UV), differential scanning calorimetry (DSC), X-ray diffraction (XRD), infrared transmission (IR) and electron spin resonance (ESR). The optical absorption spectra suggested the presence of an optical gap (E_g) which depends on filler concentration (W) and arises due to the variation in crystallinity within the polymer matrix. Melting and degradation temperatures were identified using DSC. XRD implied a semicrystalline structure (containing α- and β-PVDF phases for all films). Conjugated double bonds and the role of dimethylformamide with a PVDF chain were detected by IR spectra. The ESR analysis revealed the existence of both isolated and aggregated Mn^{2+} ions within the PVDF matrix.

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1. Introduction

Polymers have attracted the attention of scientific and technological researchers because of their wide applications. Polyvinylidene fluoride (PVDF) as a polycrystalline polymer started drawing scientific interest in the seventies, because of its extraordinary pyro- and piezo-electric properties. These properties combined with both high elasticity and processing ability lend this material numerous technological applications [1].

Recently, PVDF has been used widely in biotechnology [2], photorecording [3], microwave modulation [4] and in rechargeable lithium batteries [5]. Filling PVDF enhances its electromagnetic wave sensing feature due to its increased magnetic activity [6].

Another feature that distinguishes PVDF from other polymers is its polymorphism, that is, it may present at least four crystalline phases, namely α, β, δ and γ [7]. Moreover, an increasing interest has been devoted to PVDF as electric and/or magnetic field sensors. For this application, PVDF was filled with transition metal halides [8].

Fillers are used in polymers for a variety of reasons: cost reduction, improved processing, density control, optical effect, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardancy and hardness, and tear resistance [9]. For example, in optical, electrical and magnetic applications, fillers such as LiBr and $MnCl_2$ are used to provide better optical, electrical and magnetic properties.

Manganese is well known as a magneto-active multivalent element; thus its halides can be used as fillers to modify the electric conduction, the optical absorption and magnetic properties of PVDF. On the other hand, $MnCl_2$ is considered as a good candidate for one- or two-dimensional phenomena [10] and for optical memory device [11].

Spectroscopic and physical properties of metal halide doped polymers are extensively studied. But research on a mixture of LiBr and $MnCl_2$-containing PVDF is limited, to our knowledge. Therefore, the present study is devoted to shed some light on the role of filling PVDF with a mixture of LiBr and $MnCl_2$ on optical, structural and electron spin resonance properties.

2. Experimental work

The studied PVDF films filled with (X)LiBr$(20-X)$$MnCl_2$(wt%) were prepared by casting method. Dimethylformamide (DMF) was used to dissolve the used materials. The solution of mixed halides was added to the dissolved polymer at a suitable viscosity. The mixture was cast to a glass dish and kept in a dry atmosphere at 323 K for 2 weeks to ensure the removal of solvent traces. Different concentrations of the fillers were obtained, where $X=0$, 1, 2, 8, 16 and 20 wt%. The thickness of films was in the range of 0.15–0.3 mm. Ultraviolet/visible (UV/Vis) absorption spectra were measured in

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the wavelength region of 200–800 nm using a Shimadzu UV 2101-PC instrument (resolution 0.1 nm). The differential scanning calorimetry (DSC) measurements were performed using (Perkin Elmer-Pyris 1) apparatus in the temperature range 30–420 °C with a heating rate of 10 °C/min. X-ray diffraction (XRD) scans were obtained using ("STOE-STAD IP" powder diffractometer with Cu-K (alpha) radiation) the Bragg angle (2θ) in the range of 5–80°. FT-IR spectra were recorded with a Perkin Elmer FT-IR-1000 spectrophotometer and KBr pellets at 2 $\mathrm{cm^{-1}}$ resolution (8 scans each) were used for measuring the IR spectra in the wavenumber range of 800–3100 $\mathrm{cm^{-1}}$. The ESR spectra were recorded on BRUKER MEX with cavity ER4102 at 100 kHz modulation, 9.65 Ghz, X-band, using 1,1 diphenyl-2-pierylhydrazyl (DPPH) as a calibrant.

3. Results and discussion

3.1. UV/visible optical absorption

Fig. 1 displays the UV/VIS absorption spectra in the range of 200–800 nm of PVDF films filled with two mixed fillers LiBr and $\mathrm{MnCl_2}$. In previous works, our research group investigated the optical absorption of pure PVDF films [12]. This investigation revealed that, the spectrum of the unfilled PVDF is characterized by a sharp absorption edge (SAE) at about 212 nm and there are no absorption peaks at higher wavelengths. The spectra of the filled PVDF films exhibit a shift of the SAE towards higher wavelengths. The shift in absorption edge in the doped PVDF reflects the variation in the energy band gap, which arises due to the variation in crystallinity within the polymer matrix [13].

The small band at about 360 nm in UV spectra is due to crystal field transitions of isolated $\mathrm{Mn^{2+}}$ ions and/or Li ions [14].

The optical energy gap (E_g) for an indirect transition can be determined using Davis and Mott [15]formula :

$$E_g = h\nu - \left(\frac{\alpha h\nu}{B}\right)^{1/2} \tag{1}$$

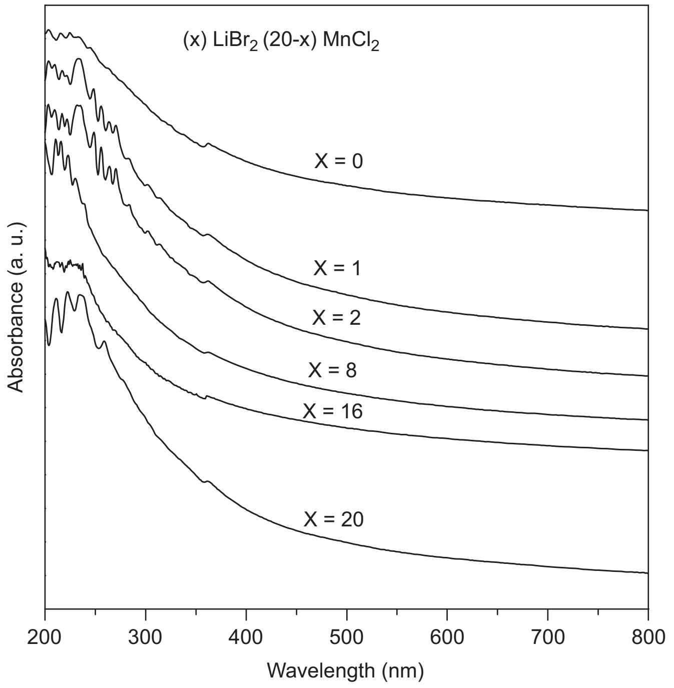

Fig. 1. The UV/vis absorption spectra of FLs in PVDF films.

where h is Planck's constant, ν is the photon frequency, B is a constant and α is the absorption coefficient, which can determined as a function of photon frequency using the equation:

$$\alpha = 2.303\frac{A}{d} \tag{2}$$

where A is the absorbance and d is the thickness of the sample. The plot of $(\alpha h\nu)^{1/2}$ versus the photon energy $h\nu$ at room temperature is shown in Figs. 2 and 3. The extrapolated of linear portion in the range of $3.4 < h\nu < 5.5$ indicates an optical energy gap E_g, which can be considered as an evidence for allowed indirect transition.

Fig. 4 depicts the dependency of E_g on the LiBr and/or $\mathrm{MnCl_2}$ content. It is clear that E_g exhibits a rapid increase up to $W = 8$ wt%: Then E_g increases slowly as LiBr and/or $\mathrm{MnCl_2}$ content increases. The change of E_g may be attributed to the change of induced energy states due to the change of chilation mode at filling level (FL)$=8$ wt% [16].

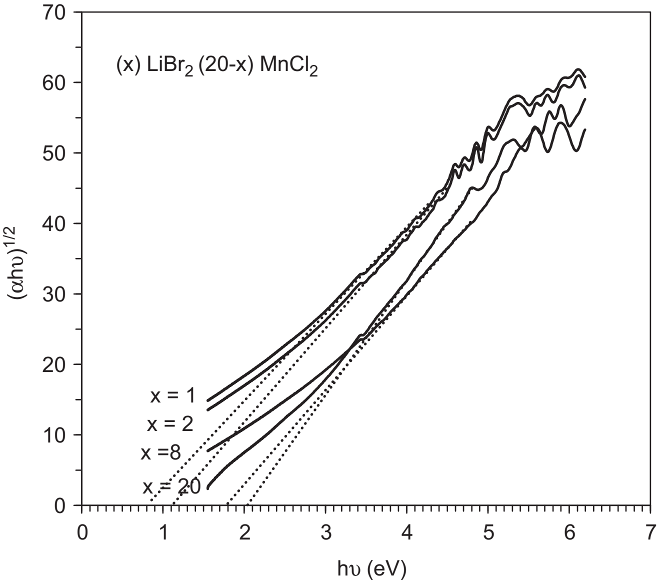

Fig. 2. $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for various FLs.

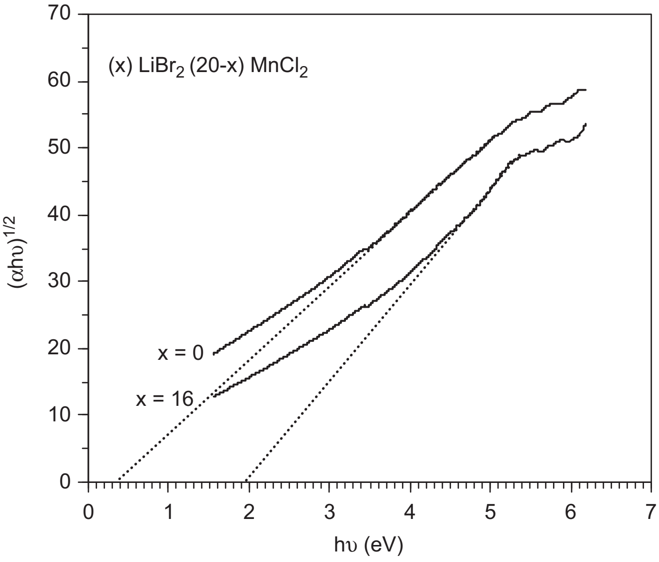

Fig. 3. $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for various FLs.