



Effect of addition of a mixed filler of CoCl_2 and LiBr into PEMA and its morphological, thermal and electrical properties

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Abstract. Poly ethyl methacrylate (PEMA) films doped with various concentrations of a mixed filler (CoCl_2 and LiBr) were prepared by using the casting method and their morphological, thermal and electrical properties were investigated. Scanning electron microscopy showed partial compatibility between the PEMA and the mixed filler. Differential scanning calorimetry was shown to increase their thermal stability with an increase in the concentration of the mixed filler in the films. The electrical properties were investigated using DC electrical conductivity (σ), which showed an improvement in electrical conductivity after addition of the mixed filler.

Keywords. PEMA; CoCl_2 ; LiBr ; SEM; DSC; DC electrical conductivity.

1. Introduction

In the last few years, polymer electrolytes have drawn increasing attention due to their applications in rechargeable batteries, electrochemical devices and sensors. The amorphous nature of poly ethyl methacrylate (PEMA) supporting ionic conductivity, the existence of the $\text{C}=\text{O}$ group in this polymer, as we found in previous work [1], can enhance easy ion movements using polymer parts. PEMA contains electron pairs that are combined with inorganic salts to form polymer–salt matrixes and thereby assisting ionic conduction; owing to these reasons, PEMA was selected as the polymer host in this system [2,3]. Lithium salts such as lithium bromide are stable and dissolve and dissociate easily, and clearly enhance the ionic conductivity and mechanical stability of the polymeric matrix [3,4]. Cobalt chloride (CoCl_2) is used in humidity sensors, which are characterized by the physical colour variation from blue to purple/pink, and is considered as an efficient electron acceptor [2,5]. Sundaramahalingam *et al* [5] prepared samples of polyethylene oxide (PEO)/polyvinyl pyrrolidone (PVP) doped with lithium bromide using a solution casting technique, and found the highest conductivity to be $1.59 \times 10^{-6} \text{ S cm}^{-1}$ for PEO/PVP (30%/70%) filled with 4 wt% of LiBr at room temperature. The variation in the electrical conductivity with temperature suggested the Arrhenius behaviour, and films with maximum conductivity shows lower activation energy (0.80 eV) compared to other

films. Abdelrazek and Elashmawi [6] prepared PEMA complexed with CoCl_2 at different weight percent ratios and found that the thermal decomposition of filled films shifts towards the higher temperature range than that of the pristine sample, which denotes the enhancement of thermal stability of the samples. The scanning electron microscopy (SEM) images of the doped samples contained highly condensed small granules nearly equal in size, which was attributed to the partial compatibility between the PEMA and the CoCl_2 . Measurements of DC electrical conductivity exhibit the values of hopping distance (R_0) in the range of 0.8–1.6 nm. The effect of $\text{CoCl}_2/\text{LiBr}$ -filled PEMA films on their morphological, thermal and electrical properties was studied in this work.

2. Experimental

2.1 Materials

PEMA (molecular weight: $50,000 \text{ g mol}^{-1}$ and density: 1.119 g cm^{-3}) were supplied by Merck, Germany. CoCl_2 (purity: 99%) was supplied by Hayashi Pure Chemical Industries, Ltd., Japan and LiBr (purity: 99%) was provided by Aldrich, USA. CoCl_2 and LiBr were provided in powder form. The solvent used is acetone and was provided by El-Nasr Pharmaceutical Chemical Co., Egypt.

2.2 Sample preparation

Mixed filler of LiBr and CoCl₂ (50%/50%) with different concentrations (0.0, 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 wt%) were incorporated into PEMA by casting technique. All components were dissolved in acetone at constant stirring at room temperature for 9 h. The final product was poured into Petri dishes and dried for 48 h in an oven at 40°C to remove the traces of solvent. Finally, the samples were kept in vacuum desiccators.

2.3 Measurements

The surface morphologies were examined by using an SEM (Model JEOL JSM/6510 LV 250, USA), at 2,500 times magnification. The thermal properties were examined using differential scanning calorimetry (DSC) analysis (Model Setaram Labsys TG/DSC-16); samples were heated in the temperature range 30–600°C at the heating rate of 10°C min⁻¹. The DC electrical properties were examined by using an insulation tester, Level type T-M14. The samples were coated with a silver paste to make good contact with the electrodes.

3. Results and discussion

3.1 Scanning electron microscopy

By using SEM information about the sample's surface topography, composition and other properties is obtained. The SEM images of the present films are shown in figure 1.

The SEM images show the effects of variation in the concentration of the mixed filler on the surface structural morphology of the samples. Figure 1a presents the micrograph of the pristine film; the surface is shown to be transparent, soft and uniform morphology revealing a rather smooth surface. After addition of the mixed filler to the PEMA, as observed in figure 1b–g, white granules with bright spots around these rings and granule groups with random distribution appeared on the film surface and did not exhibit any aggregation. At higher concentrations of ≥5 wt%, highly condensed small granules nearly equal in size were noticed. These granules and granule groups were randomly distributed in a medium that manifested to be pure film. The small granules and/or rings which attributed to CoCl₂ with bright spots around these rings were ascribed to LiBr. For more than 10 wt%, the samples show much aggregation of the filler at the surface because of the complexation between the mixed filler and the polymeric samples.

It is clear that all rings were observed and hindered the polymer interface which was assigned to the partial compatibility between the polymeric matrix and the mixed filler [6–9].

3.2 Differential scanning calorimetry

DSC is a tool used to investigate the physical and chemical changes, for example, glass transition temperature (T_g), melting point (T_m) and decomposition temperature (T_d). The temperature range of 30–600°C was used under an argon atmosphere [3]. The DSC curves of pure PEMA and PEMA doped with various contents of CoCl₂ and LiBr are shown in figure 2. T_g , T_m and T_d are listed in table 1.

From DSC curve of pure sample, the broad endothermic peak was noticed at 80.9°C which was assigned to the glass transition temperature T_g of PEMA [10–13]. The endothermic peak (T_m) and another endothermic peak (T_d) at 293 and 389°C, respectively, were observed [10]. For PEMA samples doped with various amounts of CoCl₂ and LiBr, the positions of T_g and T_d were slightly shifted towards higher temperatures compared to pure PEMA. The increase in T_g may be attributed to the increase in the mean molecular weight of the polymeric matrix in the amorphous area [13–16]. Additionally, the increase in T_m may be assigned to the increase in the crystallite thickness in the crystalline phase created through the doping of the mixed filler. Clearly, the embedding of the mixed filler into PEMA samples improves their thermal stability. The obtained data match with the results of X-ray and UV–VIS measurements in previous work [1].

3.3 DC electrical conductivity measurement

The DC conductivity (σ) was calculated in the temperature range of 353–453 K to investigate the conduction mechanism of the polymeric samples. Figure 3 exhibits the variation in the conductivity with the reciprocal of absolute temperature ($1000/T$) for pure sample and PEMA doped with mixed filler. The DC conductivity can be expressed [13] as:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E_a}{KT}\right), \quad (1)$$

where σ_0 is the exponential factor, ΔE_a is the activation energy, K is the Boltzmann's constant and T is the absolute temperature. The linear variation (no phase transition) was observed from these plots which suggests an Arrhenius behaviour.

From the figure, it is clear that the values of the electrical conductivity of the films changed in the range 6.35×10^{-14} to 1.55×10^{-9} S cm⁻¹, which suggests that the mixed filler acts as a good filler to enhance the electrical conductivity of PEMA films; this enhancement is due to the interaction between the PEMA and the mixed filler and gave rise to charge transfer complexes between the PEMA and the mixed filler [17–21].

3.3a. *Determination of the hopping distance (R_0):* The Fourier-transform infrared measurement detects the presence of double bonds C=O and C=C which are considered

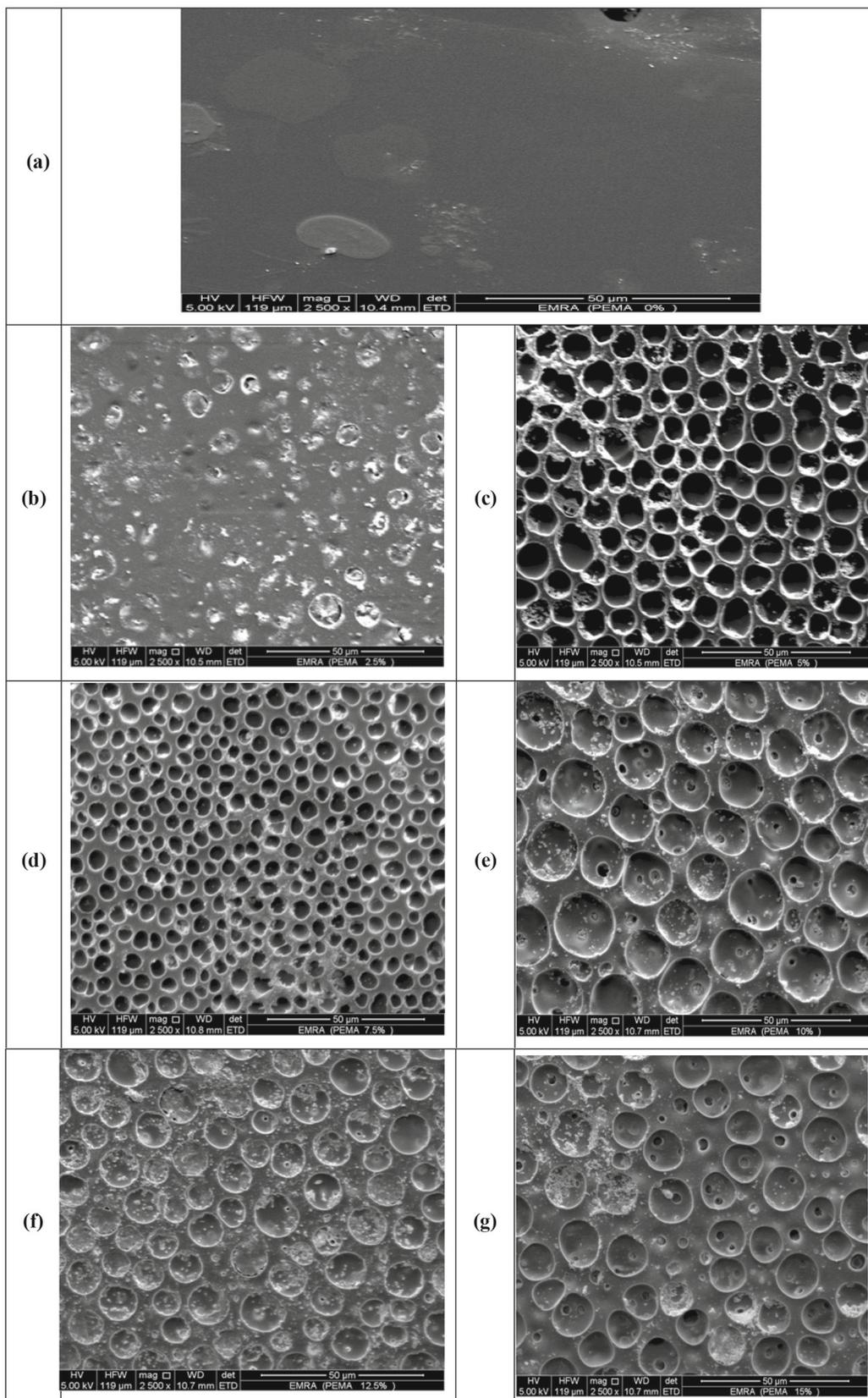


Figure 1. SEM images of the sample surfaces of (a) pure PEMA and its complexes doped with filler of concentrations (b) 2.5, (c) 5, (d) 7.5, (e) 10, (f) 12.5 and (g) 15 wt% at 2,500 times magnification.

as appropriate sites for the generation of polarons and bipolarons in the polymer samples [22]. Therefore, the present results probably discuss on the Kuivalainen basis

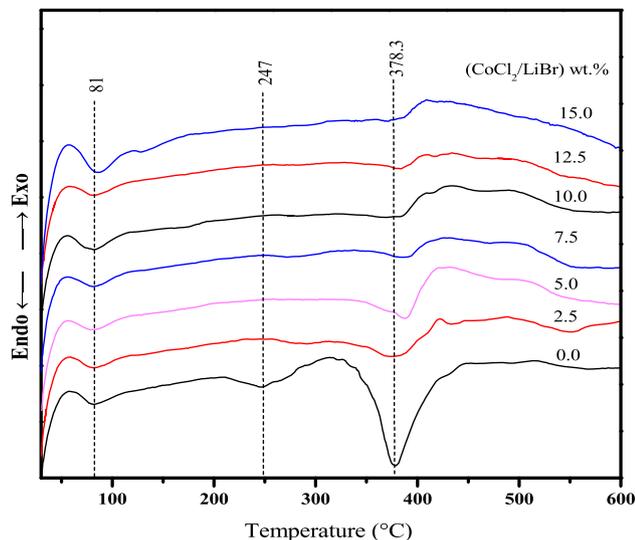


Figure 2. DSC thermograms of pure PEMA and the PEMA doped with various amounts of $\text{CoCl}_2/\text{LiBr}$.

Table 1. T_g , T_m and T_d values of pure PEMA doped with various amounts of mixed filler.

X (wt%)	T_g	T_m	T_d
0.0	80.9	245.3	376.0
2.5	81.4	271.7	376.0
5.0	80.0	—	386.8
7.5	82.3	271.4	385.6
10.0	81.9	284.6	385.1
12.5	80.7	—	402.0
15.0	84.2	—	407.0

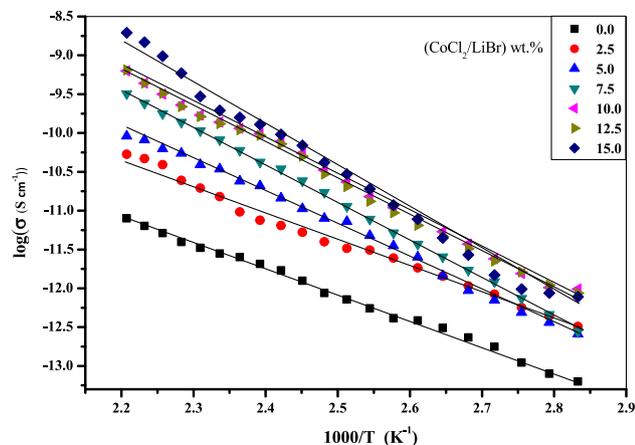


Figure 3. Variation of $\log(\sigma)$ vs. $(1000/T)$ for filled samples.

[23] to interpret these data of conductivity. The electrical conductivity can be expressed as:

$$\sigma = \frac{Ae^2\gamma(T)^2 \zeta}{KT} \frac{y_p y_{bp}}{R_0^2 (y_p + y_{bp})^2} \exp\left(\frac{-2BR_0}{\zeta}\right), \quad (2)$$

where $A = 0.450$ and $B = 1.390$, y_p and y_{bp} are the polaron and bipolaron concentrations, respectively, R_0 represent typical distances between impurities, $(\zeta = \zeta_{||}\zeta_{\perp}^2)^{1/3}$ is decay length of a polaron/bipolaron wave function, $\zeta_{||}$ is decay length parallel to the polymeric chains and ζ_{\perp} is decay length perpendicular to the polymeric chains [6,13]. The transition rate can be written [24] as

$$\gamma(T) = 1.2 \times 10^{17} \left(\frac{T}{300K}\right)^{11}. \quad (3)$$

Using equations (2 and 3), we can obtain the values of the hopping distance R_0 . The linear temperature dependence of the obtained values of R_0 for different concentrations of the filler is shown in figure 4. A linear variation in temperature dependence of R_0 is noticed. The obtained values of R_0 were in the range of 12.64 to 5 nm, which is 50 to 20 times the monomer length considering the monomer unit length is ≈ 0.25 nm [13,25–27]. This indicates that the present conduction mechanism is of an intrachain one-dimensional hopping type. From figure 5, it is clear that R_0 decreases with an increase in the concentration of the filler up to ≤ 10 wt%, after that the values of R_0 become constant, because for >10 wt%, the samples show much aggregation of the filler at the surface because of the partial compatibility between the mixed filler and the polymeric samples, as shown in the SEM images. These data show the choice of $\text{CoCl}_2/\text{LiBr}$ as a mixed filler to improve the electrical conductivity of PEMA.

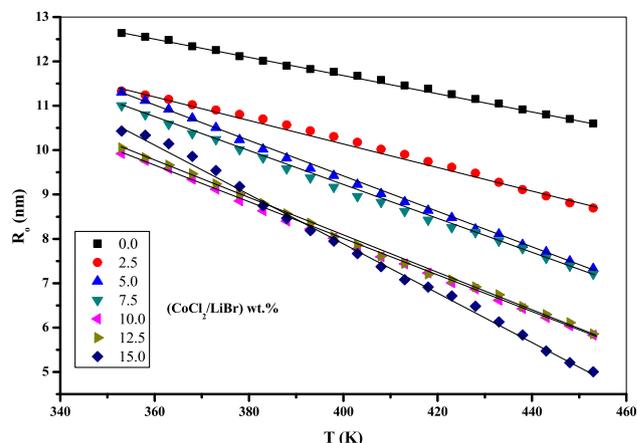


Figure 4. Dependence of R_0 for PEMA doped with various amounts of $\text{CoCl}_2/\text{LiBr}$.

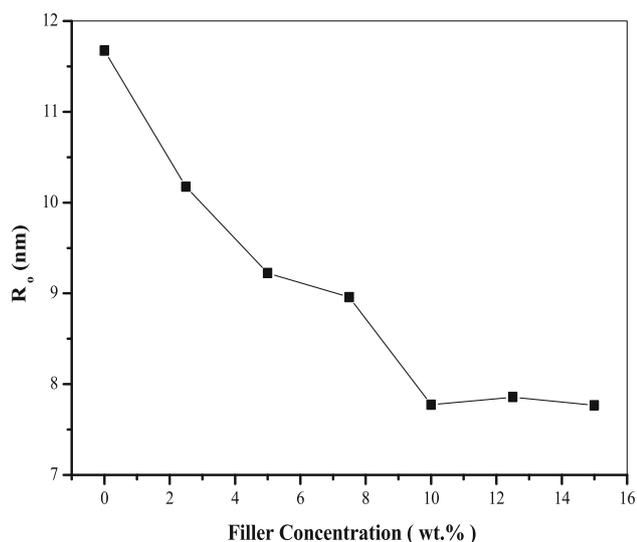


Figure 5. Different concentrations of $\text{CoCl}_2/\text{LiBr}$ dependence on calculated R_0 at constant temperature ($T = 403 \text{ K}$).

4. Conclusion

DSC revealed that the addition of $\text{CoCl}_2/\text{LiBr}$ into the polymeric matrix causes an increase in the thermal stability which is preferred in lithium polymer batteries. SEM shows a transparent, soft and a uniform pure PEMA, whereas after addition of the mixed filler to the polymer small granules with bright spots appear. The conductivity has been improved after addition of the mixed filler. The hopping distance was reduced from 12.64 nm of the pristine sample to 5 nm of PEMA filled with the highest concentration. These results will recommend that the present samples can be used in electrochemical devices especially in lithium polymer batteries.

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