STRUCTURAL AND ELECTRICAL STUDIES OF FULLERENE (C60) DISPERSED POLYMER ELECTROLYTES

ŠTUDIJ STRUKTURNIH IN ELEKTRIČNIH LASTNOSTI POLIMERNEGA ELEKTROLITA Z DISPERGIRANIM FULERENOM (C60)

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In this work we report on a modification of the optical and electrical properties of a polymer electrolyte film (PEO : NaI) by doping with C60. Light microscopy was used to study the surface morphology of the polymer electrolyte film doped with C60. For the electrical properties, complex impedance spectroscopy (CIP) was used and the conductivity was calculated. The dielectric, modules and transference numbers were calculated and explained in detail to support the electrical conductivity data.

Keywords: polymer electrolyte, light microscopy (LM), conductivity, dielectric constant, ion transference number

V tem delu poročamo o spremembi optičnih in električnih lastnosti polimerne elektrolitske plasti (PEO : NaI) po dopiranju s C60. Študij morfologije površine elektrolitske polimerne plasti je bil izvršen s svetlobno mikroskopijo (LM). Za električne lastnosti je bila uporabljena kompleksna impedančna spektroskopija (CIP), prevodnost pa je bila izračunana. Dielektričnost, moduli in transportno število so bili izračunani in podrobno razloženi za podporo podatkov električne prevodnosti.

Ključne besede: polimerni elektrolit, svetlobna mikroskopija (LM), prevodnost, dielektrična konstanta, transportno število

1 INTRODUCTION

Ion-conducting polymers, obtained by polymer-salt complexation, are becoming increasingly important because of their application in solid-state polymer batteries, fuel cells, etc. Many good ion-conducting polymer electrolytes have been developed by complexing polymers (for example, PEO) with salts like lithium perchlorate, lithium triflate, sodium chloride, sodium iodide, etc.[1–4] To enhance the conductivity of the polymer electrolyte, various approaches have been adopted, like (a) changing the type of complexing polymer (b) the use of polymers with different chain lengths (c) the use of different complexing salts and (d) modifying the degree of crystallinity by the use of plasticizers and copolymerization.[5–8] However, the doping of fullerene (C60) with a polymer electrolyte is a relatively a new approach to enhance the optical and electrical properties of polymeric films. In this paper we report an important observation regarding a change in the physical and electrical properties of polymer films doped with fullerene (C60).[9–11]

2 EXPERIMENTAL

2.1 Material Preparation

Composite polymer films with a thickness varying between 200 μm to 300 μm were synthesis using the standard "solution cast" technique.[12]

Before the preparation of the polymer film, the fullerene is prepared in the laboratory. To obtain this fullerene, soot is collected by the burning of phenolphthalein, which is dissolved in benzene and stirred continuously for approximately 5 h. Finally, the solution was filtered. A wine-coloured solution was obtained, which was characterized by NMR to confirm the formation of C60. The NMR results showed the formation of fullerenes (methanofullerene) (**Figure 1**) with a small chain attached with the ball. The obtained structure was similar to that required for doping in polymer electrolyte films. Finally, PEO (Mw: 2 000 000) and NaI were weighed separately in the required amounts. These weighed components were then dissolved in distilled methanol. Different weights of prepared fullerene were added to this combination. After this the solution was stirred for a long time to achieve uniform mixing and complexation. Then, the mixture was poured into polypropylene/Teflon moulds for casting in ambient, room conditions. The solvent was then slowly evaporated at room temperature. Finally, the film was dried under vacuum to eliminate any traces of solvents. The as-prepared films were subjected to different characterizations.

The polymer (PEO) and salt (NaI) molar ratio was maintained at 0.065 [13] and the amount of C60 dispersed in the complex matrix was expressed in mass fractions. The composition is represented as (PEO : NaI) + w(C60).
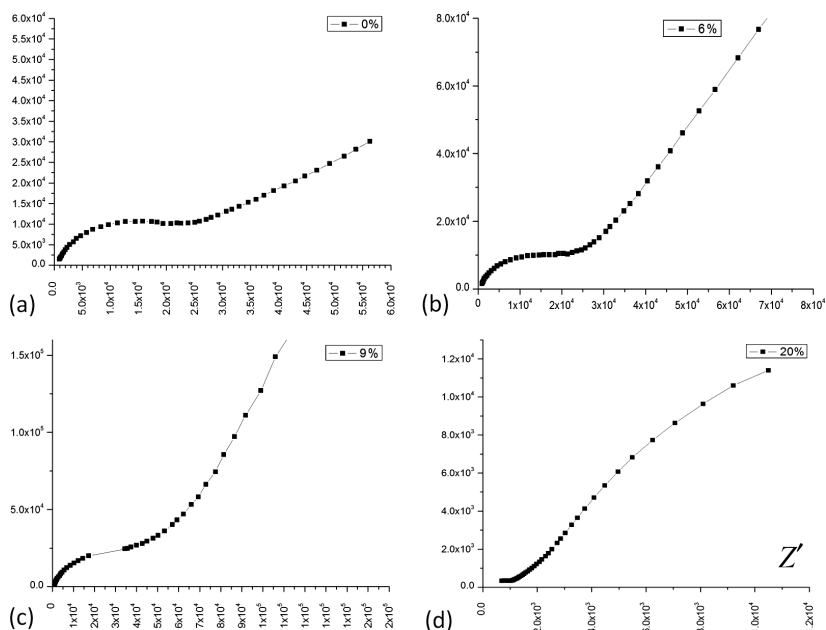
2.2 Material Characterisation

The surface morphology of the composite polymer film was studied with an optical microscope. In order to evaluate the ionic conductivity of the polymer electrolyte film, impedance spectroscopic techniques were used. The conductivity of the polymer films was evaluated from the bulk resistance calculated by ac complex impedance spectroscopy over a frequency range of 100 Hz to 1 MHz. The transference numbers (tion) of the C60-doped polymer electrolyte composite sample were measured using Wagner's polarization method.[4] In this method the sample is placed between two electrodes in such a way that it minimizes the contact resistance. In an ideal case one of the electrodes is blocking, whereas the other is non-blocking. In the present case we used stainless-steel electrodes. A DC potential is applied across the sample in such a way that mobile ion species move towards the non-blocking electrode and a small polarization current flows and, finally, the sample becomes polarized. The initial total current I_i and the final residual current I_f are use to evaluate the ionic transference number.[7]
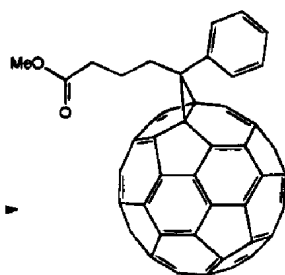
Figure 1: Chemical structure of methanofullerene C61 (CO2Me)[C$_6$H$_6$]
Slika 1: Kemijska struktura metanofulerena C61 (CO2Me)[C$_6$H$_6$]
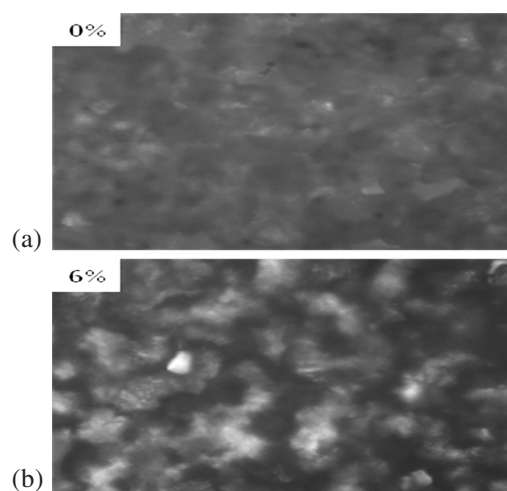
3 RESULTS AND DISCUSSION

3.1 NMR

The samples were investigated in the NMR study. The result confirms the formation of methanofullerene. **Figure 1** shows the structure of methanofullerene C61 (CO2Me) [C$_6$H$_6$].[9]

3.2 Surface Morphological Study

3.2.1 Morphology

Typical light micrographs of the composite polymer electrolyte system (PEO : NaI) + w(C60) are shown in **Figure 2**.

Figure 2: Light micrographs of (PEO : NaI) + w(C60) composite polymer electrolyte system: a) 0 % and b) 6 %
Slika 2: Mikrostruktura polimernega elektrolitskega kompozitnega sistema (PEO : NaI) + w(C60): a) 0 % in b) 6 %

Figure 3: Complex impedance spectra of (PEO : NaI) + w(C60) film at room temperature: a) 0 %, b) 6 %, c) 9 %, d) 20 %
Slika 3: Kompleksni spekter impedance za plast (PEO : NaI) + w(C60) pri sobni temperaturi: a) 0 %, b) 6 %, c) 9 %, d) 20 %

The spherulites are observed (**Figure 2a**) in the pure polymer complex (i.e., for $w(C60) = 0$). The dark boundaries observed between the spherulites show the partial amorphous phase of the films. The morphological pattern of the film changed upon the addition of different amounts of the dispersoid. This effect is well shown in **Figure 2b**. Several dark spots are visible in the case of doping with $w = 6 \%$ of C60. This indicates that a larger addition of dispersoid will make more amorphous phase of the films.[13]

3.3 Electrical Properties Study

3.3.1 Complex Impedance Spectroscopy (CIS)

A CIS analysis of the C60 dispersed polymer electrolyte films was performed to determine the change in the electrical properties. The impedance patterns for the different compositions of the films are shown in **Figure 3**.

It is clearly shown in the figure that as the concentration of the dispersoid increases the impedance pattern of the sample is changed. This impedance graphs are used to calculate the bulk resistance (R_b) of the sample.[10] It is clear from **Figure 3** that the value of the bulk resistance is decreased as the concentration of C60 is increases. Now by using the values of bulk resistance, the area and the thickness of the film we are able to calculate the conductivity of the sample.

3.3.2 DC conductivity

The electrical conductivity of the composite polymer films as a function of doping concentration was calculated. **Figure 4** shows the change in the conductivity in the polymer electrolyte film doped with C60.

Figure 4 shows that the conductivity decreases with the doping of the dispersoid C60. The minimum of the conductivity was seen at 9 % of doping, but the value suddenly increases to a maximum of 7.9×10^{-7} S/cm when doping with $w(C60) = 20 \%$
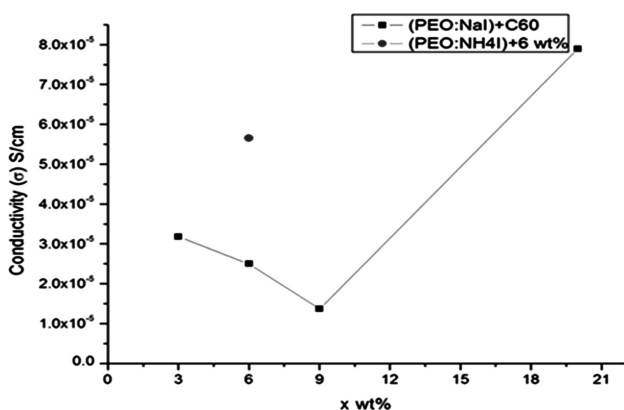

Figure 4: Variation in conductivity of (PEO : NaI) + w(C60) at room temperature
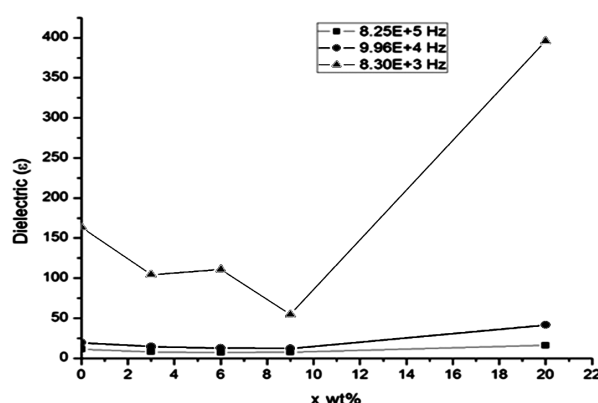**Slika 4:** Spreminjanje prevodnosti (PEO : NaI) + w(C60) pri sobni temperaturi

Figure 5: Variation in dielectric of (PEO : NaI) + w(C60)
Slika 5: Spreminjanje dielektričnosti (PEO : NaI) + w(C60)

3.3.3 Dielectric Constant

The frequency-dependent dielectric constant (ε) is calculated for different mass fractions of dispersoid and shown in **Figure 5**. It is clear that the dielectric decreases as the doping of C60 begins, but at 6 % of doping the dielectric increases.

Two increases in the dielectric constant are clearly seen in **Figure 5**, at 6 % and 20 %. This result for the dielectric supports the change in the conductivity.[10,14]

3.4 Dielectric relaxation study

A dielectric formulism is useful in retrieving many particulars about the conductivity behaviour of any material. The dielectric constant is a measure of the stored charge. The frequency dependence of the real (ε') and imaginary (ε'') parts of the dielectric constants are shown in **Figure 6**.

ε' and ε'' are calculated by using the following relations:

$$\varepsilon' = \frac{Z''}{\omega C Z^2} \quad \text{and} \quad \varepsilon'' = \frac{Z'}{\omega C Z^2}$$

where Z" is the imaginary part of the impedance, ω is the angular frequency and C is the capacitance of the empty measuring cell for the electrode area A and the sample thickness L. The capacitance is calculated using the relation:

$$C = \frac{\varepsilon_0 A}{L}$$

At lower frequency the high value is due to the polarization of the electrode.[15] But at high frequency, the periodic reversal of the electric field is so fast that the ion diffusion in the electric field is not feasible. Hence, the charge accumulation at the electrode decreases, leading to a decrease in ε' and ε''.[16]

3.4.1 Modulus Formalism

The sudden change in ε' and ε'' values at lower frequency is possibly due to the contribution of the elec-
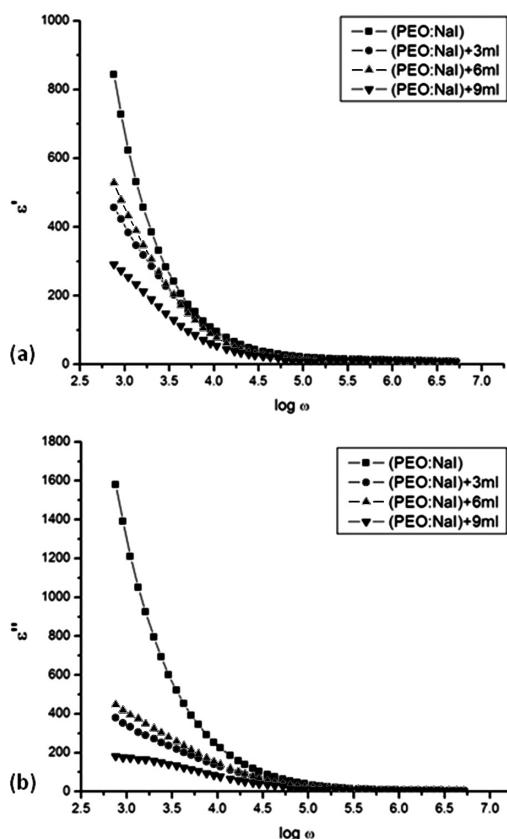
Figure 6: a) Variation in real part of dielectric constant (ε') with w(C60), b) variation in imaginary part of dielectric constant (ε") with w(C60)
Slika 6: a) Spreminjanje realnega dela dielektrične konstante (ε') z w(C60), b) spreminjanje navideznega dela dielektrične konstante (ε") z w(C60)

Figure 7: a) Variation in M' with w(C60), b) variation in M" with w(C60)
Slika 7: a) Spreminjanje M' z w(C60), b) spreminjanje M" z w(C60)

trode polarization effect. Hence, ionic conduction relaxation is not properly analysed in the dielectric formulism. Here, the modulus is calculated to overcome this problem and widely used to analyse the relaxation phenomenon for different compositions.
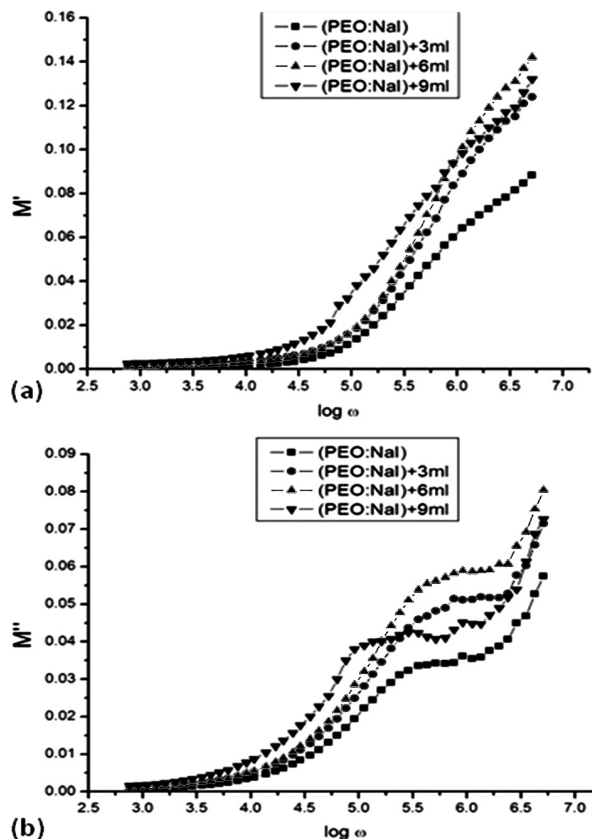
The values of M' and M" were calculated using the following relations:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \quad \text{and} \quad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$

where M' and M" are the real and imaginary parts of the electrical modulus.

Figure 7 shows the modulus as a function of lg ω for different w(C60). The peaks at a very high frequency are invariably present in all the complexes and the height of the peaks changes with the dispersoid (C60) concentration. This indicates that a relaxation phenomenon is occurring.[17,18]

The M' shows a increasing trend with frequency whereas the peaks are observed in the M" spectra in the higher frequency region. The peak in the modulus formalism confirms the ionic conduction in the system.[19,20]

3.4.2 Transference Number (tion)

This parameter will show the conductivity due to ions in polymer electrolyte films. The tion of the prepared films are calculated by dc polarization method. In this method, the dc current is observed as a function of time on the application of a fixed dc voltage (0.25 V) across the sample electrodes. The tion was calculated using the relation:

$$T_{ion} = \frac{I_{initial} - I_{final}}{I_{initial}}$$
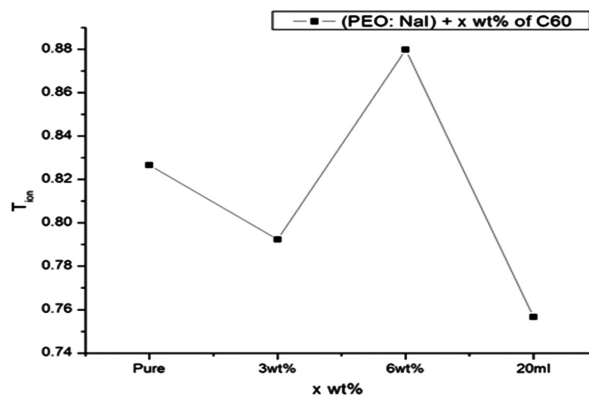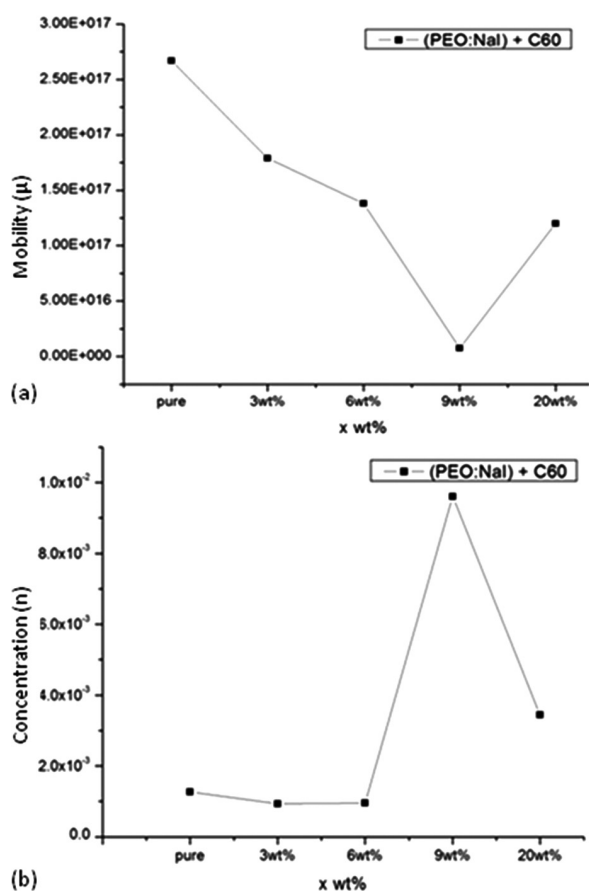

Figure 8: Variation in tion with w(C60)
Slika 8: Spreminjanje transportnega števila z w(C60)

Figure 8 shows a plot of tion vs different w(C60) doped with polymer electrolyte. In this plot it is clear that the ionic conductivity in the polymer electrolyte film initially decreases, but the 6 % dispersed film shows a high ionic conductivity. As the concentration of dispersed C60 is further increased the ionic conductivity of the film decreases. It may be concluded from the plot that the higher doping of C60 makes the polymer film more electronically conductive than ionically conductive.

3.4.3 Concentration and Mobility

The conductivity of polymer electrolytes depends upon the charge-carrier concentration (n), the charge on the carrier (e), and the number of charge carrier. Hence, when the charge concentration is changed by doping, the conductivity is also expected to change. In polymer–salt complexes, the charge-carrier concentration is not directly proportional to the doping concentration. To analyse the origin of the conductivity changes in the present system, the concentration factor (n) and the mobility factor (μ) were calculated with respect to the added w(C60). **Figure 9** shows these changes graphically.

The mobility variation data (**Figure 9a**) are approximately following the trend of the conductivity. This con-firms that ion-pair formation and re-dissociation theory applicable to polymer–salt complexes[10] are also applicable in the present system. The decrease in the mobility may be due to electrostatic hindrance in the movement and because of the increased weight of the charge carriers.[21–23]

Figure 9b shows the variation in the concentration of the charge carrier on the doping of different w(C60). It initially attains a minimum (at 9 %) value, followed by a maximum (at 20 %). Many theories explaining this phenomenon can be found in literature. The change in the conductivity can be correlated with a change in the charge-carrier concentration (**Figures 4** and **9b**).

4 CONCLUSION

A fullerene-based polymer electrolyte was prepared by a standard solution cast technique. The ionic conductivity $\approx 7.95 \times 10^{-7}$ S/cm and the ionic transference number, ≥ 0.87, indicate that the prepared film is mixed conductor. Parameters such as the charge-concentration factor (n) and the mobility factor (μ) were studied with respect to the fullerene concentration. The relationship between the charge concentration factor (n) and the mobility factor (μ) with respect to the fullerene w(C60) is established. At low frequency, the variation of the dielectric constant with frequency suggests an electrode interface polarization process. At a low frequency the high value of the dielectric constant and loss is due to electrode polarization.

Figure 9: Variation of: a) mobility (μ) and b) concentration (n) of (PEO : NaI) + w(C60)
Slika 9: Spreminjanje: a) mobilnosti (μ) in b) koncentracije (n) (PEO : NaI) + w(C60)

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