

NEW POLYMER INCLUSION MEMBRANE. PREPARATION AND CHARACTERIZATION

C-V. GHERASIM^{a,*}, M. CRISTEA^b, C-V. GRIGORAS^b, G. BOURCEANU^a

^a*Department of Chemistry, "Al. I. Cuza" University of Iasi, 11 Carol I Boulevard, 700506 Iasi, Romania*

^b*"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, Iasi 700487, Romania*

The use of polymer inclusion membranes (PIMs) for environmental friendly separations of heavy metals from waste waters is a very promising technique for a variety of reasons among which are the low cost and high degree of reusability of the membrane. Although PIMs usually contains an additionally added plasticizer, it is possible to prepare it without additional plasticizers, and without loss of their extraction and transport properties. In the present work we report the preparation of a PIM containing only the polymer poly (vinyl chloride) (PVC), and the carrier bis-(2-ethylhexyl) phosphoric acid (D2EHPA). The PIM containing 50%D2EHPA/50%PVC was characterized by several techniques, namely Fourier Transformed Infrared Spectroscopy (FT-IR), Dynamic Mechanical Analysis (DMA), Dielectric Spectrometry and Scanning Electron Microscopy (SEM). The investigation revealed that the carrier is dispersed in physical form in the polymer matrix, and confirmed the plasticizing role of the carrier D2EHPA against the PVC polymer matrix.

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1. Introduction

The Polymer Inclusion Membranes (PIMs) contains a *polymer* and a chemical substance named *extracting agent* or *carrier*, able to extract or transport chemical species (ions or molecules) from aqueous solutions. Usually, these membranes also contain *plasticizers*, which improve the membranes properties. The PIMs are thin, flexible, and stable films, prepared by dissolving the polymer, carrier and plasticizer in an adequately solvent, and followed by the slow evaporation of the solvent.

The extracting agent (or the carrier) from PIM is generally a complexing agent or an ion-exchanger, which chemically interacts with the species from the aqueous solution and retains it on PIM. Additionally, the PIM can be mounted between the two compartments of a double-cell device, one-containing the solution which must be purified (*source solution*), and the other-containing a properly choosed solution for the target solute recovery (*receiving solution*). In this case, the carrier transports the target solute (ions or molecules-depending on the carrier type), from source solution into the receiving phase by a "relay mechanism"[1]. The PIM-embedded transport cells possess many advantages over conventional solvent extraction or sorption methods. For example, the speed is considerably enhanced by the extraction and back-extraction processes simultaneously occurring on both sides of the membrane [2]. Moreover, PIMs present a lot of other advantages of liquid membranes, *i.e.* high diffusion coefficients, high selectivity due to the above mentioned chemical mechanisms of retention, low cost, low energy consumption. Also, PIMs have higher chemical stability and mechanical resistance compared with the most commonly used liquid membranes, *i. e.* emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs) [3]. It is extremely important that PIMs possess excellent separation properties towards

* Corresponding author: cristina.gherasim@chem.uaic.ro; cris_gher@yahoo.com

the classical filtration membranes. Thus, PIMs can be used in very selective separation processes for one single target solute from mixtures, while the filtration porous membranes are able to separate only groups of solutes of the same size (dimensional sieving). Therefore, the selectivity, stability and efficient transport of solutes, are selected properties that make PIMs valuable technologies for removing toxic components from liquid effluents, or to recover high cost materials from sludge or waste waters [1].

The base polymer plays a crucial role in providing the mechanical resistance of the membranes. Despite of the fact that a great variety of solid polymers are used in many industrial application, only poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) are used in the most of the investigation on PIMs area. However, in the last years other polymers were studied for PIM's preparation, *i.e.* cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) and cellulose tributyrate (CTB) [1].

Generally, the polymers used in PIMs' preparation are thermoplastic polymers, containing polymer chains tied together by weak physical bonds. The mechanical strength of the polymer is given by both the intermolecular weak forces, and the entanglement of the long polymer chains [4]. The physical weak forces between the chains determine the PIMs' flexibility. If the used polymers have molecular weight (MW) larger than the critical entanglement molecular weight (MW_c), their chains are long and the entanglement leads to very stable thin films, even if the covalent bonds between the chains are not present. Moreover, the PVC-based membranes are very stable in aggressive solutions (like acidic and basic solutions), and possess a remarkable mechanical strength and flexibility. The CTA-based PIMs have good mechanical properties due their crystalline structure, but are less chemically resistant than the PVC ones.

The *plasticizers* are substances which are added in PIMs' composition in order to improve their flexibility, retention, and transport properties. It penetrates between the polymer chains and increases the distance between them, such that the plasticizing process reduces the intermolecular forces (hydrogen bonds or van der Waals forces) between the polymer chains [5]. A proper ratio between the polar and non-polar groups of the plasticizer determines enhanced plasticizing properties [6]. Besides these structural conditions, a good plasticizer must respect also the following requirements: a good compatibility with the base polymer, low viscosity and volatility, low cost and low toxicity [1].

Some extracting agents (or carriers) can also act as plasticizers (*i.e.* quaternary ammonium salts or phosphoric acid esters), and their use in PIMs' composition does not necessarily require the addition of traditionally plasticizers [7-11]. Due to the fact that plasticizers are generally expensive chemicals, the using of non-plasticized PIMs would lead to a significantly cost reduction of the separation process. Considering the plasticizing properties of the above mentioned carriers [12], we studied in a previous work the transport process of the Pb(II) ions by a PIM containing PVC and the carrier bis-(2-ethylhexyl) phosphoric acid (D2EHPA) (see Fig. 1), without addition of supplementary plasticizers [13].

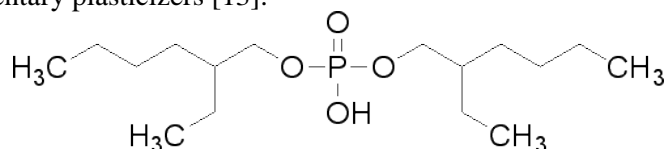
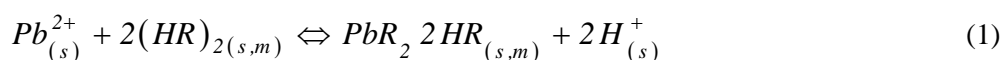


Fig.1 Chemical structure of the carrier bis-(2-ethylhexyl) phosphoric acid (D2EHPA).

We proved that a PIM containing 50%PVC/50%D2EHPA possesses even better transport properties comparing to the plasticized PIMs. The retention mechanism of Pb(II) ions by the carrier D2EHPA molecules can be represented as follows:



where $(HR)_2$ -denotes the dimer form of D2EHPA [14], (m) and (s) - the membrane and the liquid phase (solution) respectively, and (s,m) -the membrane-solution interface. We proved that the

50%D2EHPA/50%PVC PIM transports only Pb(II) ions from mixtures with Co(II) and Ni(II) ions (high selectivity), and presents good reusability capacity confirmed by subsequent transport experiments by the same PIM [13]. Despite of these facts, the characterization of the non-plasticized PVC-based PIMs containing D2EHPA as carrier, have not been reported in the literature.

In the present work we characterized this PIM, which proved in the previous work very good transport properties. PIM's morphology was evidenced by scanning electron microscopy (SEM), and infrared spectroscopy (FT-IR) was used for determining the membrane composition and the type of the interactions which established between their components. The mechanical and dielectric properties were also analyzed with an emphasis on the interactions between the PIM's components and the plasticizing role of the used carrier D2EHPA. The investigation allowed us to explain the relationship between the membrane structure and their properties. Because the PIM under study does not contain added plasticizers, the enhancing of the extraction and transport properties concomitantly with the lowering their price and easy-manufacturing process, represents important advantages for future use of the process on a larger scale.

2. Experimental

2.1. Chemicals/reagents

Bis-(2-ethylhexyl) phosphoric acid (D2EHPA), high molecular weight PVC, tetrahydrofuran (THF) packed under inert atmosphere, were supplied by Sigma-Aldrich, Germany. These chemicals were of analytical reagent grade, and were used as received.

2.2. Membrane preparation

Determined quantities of polymer (PVC) and carrier D2EHPA were dissolved in THF under continuous magnetic stirring until a homogeneous solution was obtained. The solution was then poured into a 9.0 cm diameter Petri dish, and covered with a glass funnel in order to avoid the contamination with dust and assure a slow evaporation of the solvent. The organic solvent was allowed to evaporate for 24 h at the room temperature, and the obtained membranes was then peeled from the glass plate. The PIM appear as flexible, transparent, homogenous and good strength thin films.

2.3. Membrane characterization

2.3.1. Membrane thickness

The thickness of the prepared PIMs was measured by an electron microscope VEGA II SBH manufactured by TESCAN. A square piece (about 25 cm²) from the central part of the PIMs was freezing under liquid nitrogen and rapidly broke into 4 pieces. The thickness was measured with the electron microscope in different points of the obtained cross-sections. The average value of at least ten measurements was reported.

2.3.2. Fourier transformed infrared spectrometry (FT-IR)

IR spectra were recorded with a FT-IR Bruker Tensor 27 Spectrophotometer in the transmission mode, in the range of 4000 to 400 cm⁻¹.

2.3.3. SEM analysis

Information regarding membrane morphology was obtained by scanning electron microscopy (SEM), images being recorded with a VEGA II SBH electron microscope manufactured by TESCAN. In order to obtain a clean cross-section image suitable to analyze the internal PIM morphology, the samples were prepared by freezing the membrane under liquid nitrogen followed by rapid breaking. The samples were mounted onto an aluminum support using a C graphite double scotch, and coated with a 15 nm gold layer by sputtering.

2.3.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) of PVC and 50% D2EHPA/50% PVC membranes was conducted on a PerkinElmer Diamond instrument in tension mode, at 2°C/min and 1 Hz, between -30°C and 200°C. The films had the dimensions 10 mm × 10 mm × 0.1 mm.

2.3.5. Dielectric properties

The dielectric behavior was studied by using a Novocontrol Dielectric Spectrometer Technologies GmbH Germany, in the temperature range 0-130°C. The blank PVC and the 50% D2EHPA/50% PVC films were placed into a plane-parallel capacitive measuring system, containing Au-covered electrodes with a 20 mm diameter. The thickness of the films (blank PVC and 50%D2EHPA/50%PVC PIM) was around of 100±4 μm, the amplitude of the AC applied voltage was 1 V.

3. Results and discussion

3.1. Membrane preparation and thickness

The prepared membranes containing maximum 50% D2EHPA appear as homogeneous, transparent, flexible, and with good strength, while those containing more than 50% D2EHPA were soft, sticky, and less mechanically resistant. The average thickness of the 50%D2EHPA/50%PVC PIM measured by an electron microscope (VEGA II SBH manufactured by TESCAN) was 100±4 μm.

3.2. FT-IR spectra

FT-IR is a useful instrument for identifying the interactions which occurs between the components of the studied materials. In the present work FT-IR study was performed in order to highlights the nature of the interactions between the PVC and D2EHPA in the PIM containing 50% D2EHPA. Fig. 2 presents the FT-IR spectra of two PVC films, *i.e.* blank PVC film and the 50% D2EHPA/50% PVC membrane (Fig. 2a and 2c, respectively), and for the pure extracting agent D2EHPA (Fig.2b).

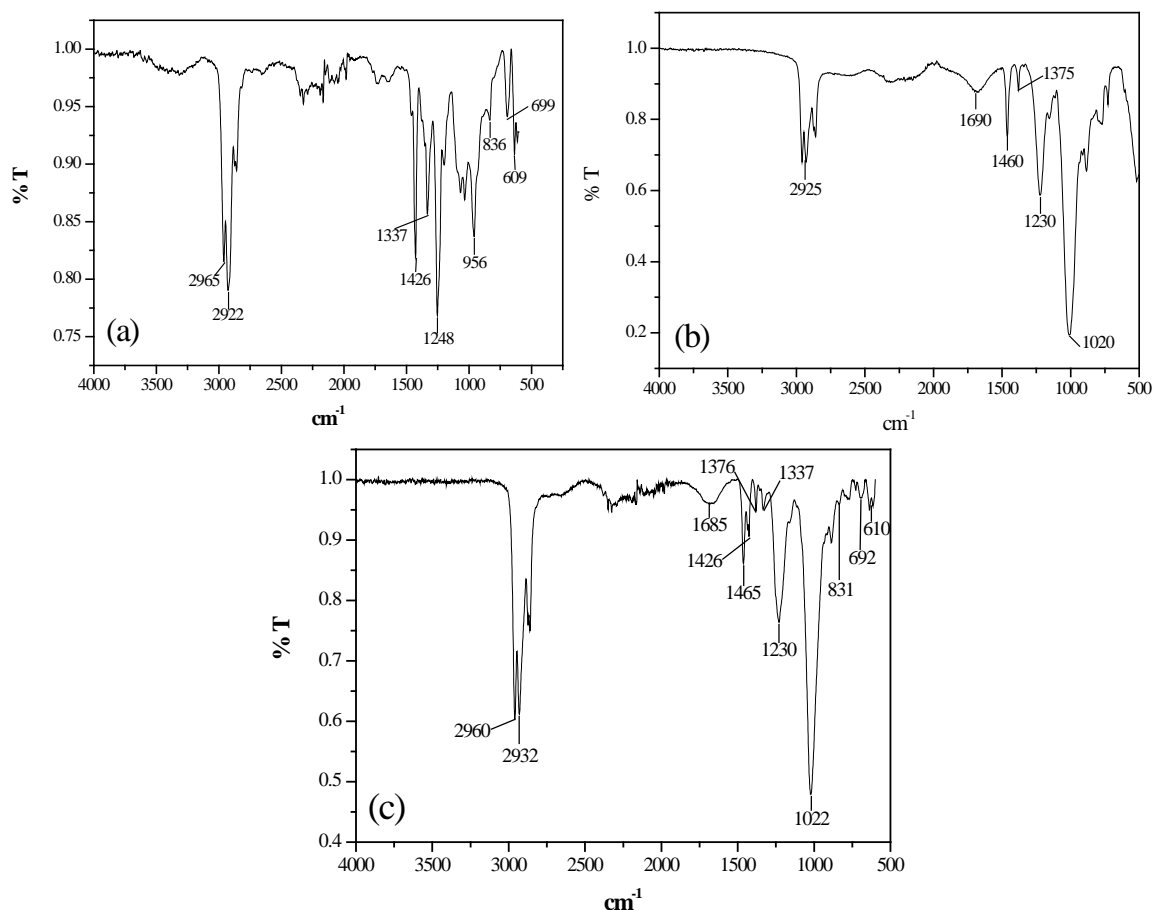


Fig. 2. FT-IR spectra of the (a) blank PVC film, (b) pure D2EHPA and (c) 50% D2EHPA/50 % PVC PIM, respectively.

The band assignments for pure PVC and pure D2EHPA were similar to those reported in the literature for these substances, respectively. Thus, in pure PVC (Fig. 1a) the C-Cl stretching mode can be observed at 836 and 699 cm^{-1} and prominent in the FT-IR spectrum is a strong band with a maximum at 1248 cm^{-1} which is due to CH_2 wagging when the next C atom has a chlorine atom attached ($-\text{CH}_2\text{Cl}$) [15]. The $-\text{CH}_2$ stretch peaks at 2922 cm^{-1} and 2965 cm^{-1} [16]. The $-\text{CH}_2$ deformation modes are observed at 1426 cm^{-1} (scissors) and 1337 cm^{-1} (twisting), while the C-H wagging modes could be observed at 956 cm^{-1} (*trans* CH wagging) and 609 cm^{-1} (*cis* CH wagging), respectively [16,17]. The FT-IR spectra of the pure D2EHPA (Fig. 1b) highlights the presence of the characteristic groups of D2EHPA, namely: P-O-C and P-O-H groups showed an intense band at 1020 cm^{-1} , and the P=O stretch frequency was observed at 1230 cm^{-1} [18]. The O-H stretching vibration is considerably lowered by the occurrence of hydrogen bonding between the D2EHPA molecules, and thus could be observed at 1690 cm^{-1} [19]. The alkyl groups have been assigned at 2925 cm^{-1} (stretching vibration), 1460 and 1375 cm^{-1} ($-\text{CH}_2$ deformation) [15].

The main characteristic feature of the FT-IR spectra of the 50% D2EHPA/50% PVC PIM (Fig. 1c) is the presence of the bands of the individual components of the membrane. Thus, the bands located at 2930, 2965, 1426, 1337, 831, 699 and 610 cm^{-1} can be observed in the spectra of PVC (Fig. 1a), and the bands at 1685, 1465, 1376, 1230 and 1022 cm^{-1} are attributed to the D2EHPA presence (Fig. 1b). The overlapping of some characteristic bands of PVC and D2EHPA was observed at 2930, 1230 and 1022 cm^{-1} . Therefore, the functional groups of the polymer PVC, and the carrier D2EHPA are present also in the 50%D2EHPA/50%PVC PIM. This observation suggests that chemical interactions do not occur between components during the membrane preparation process. Thus, it can conclude that only weak physical interactions (*i.e.* van der Waals or hydrogen bonds) assure the mechanical stability of the membrane; the carrier D2EHPA is

dispersed in physical form in the polymer matrix, with the entangled long polymer chains acting as a support for the liquid domains containing D2EHPA.

3.3. Scanning electron microscopy (SEM)

In order to accomplish a characterisation of the optimal 50% D2EHPA/50% PVC membrane, we analysed additionally blank PVC film and 25% D2EHPA/75% PVC PIM also. The SEM studies were performed by analyzing both the PIM's surfaces, and their cross-sections.

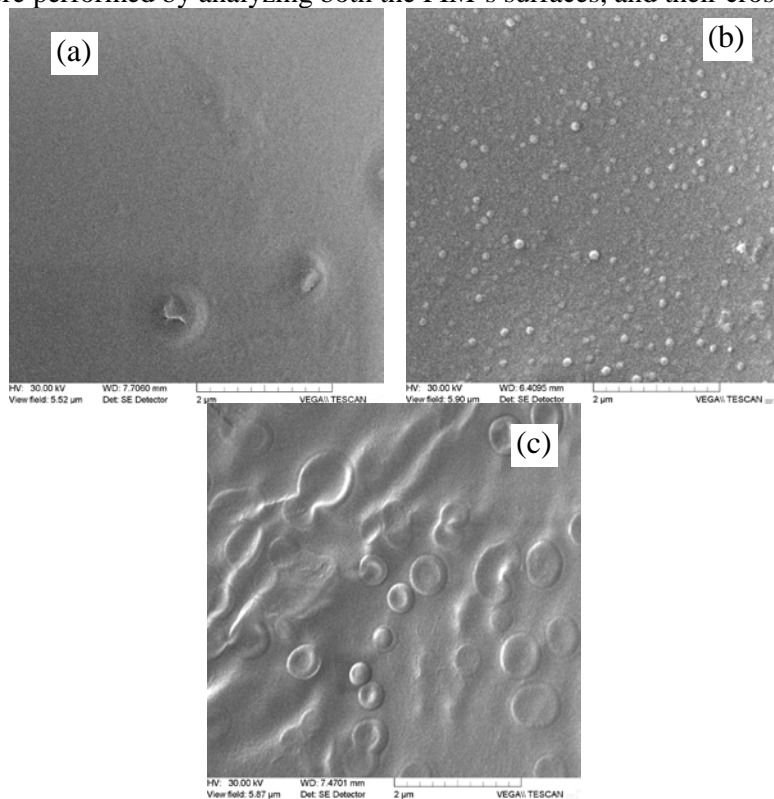


Fig.3 SEM image (surface) of the (a) blank PVC film, (b) 25%D2EHPA/75%PVC PIM and (c) 50%D2EHPA/50%PVC PIM.

The scanning electron microscope image of the blank PVC film shows a smooth surface (Fig.3a) containing only small surface defects. Meanwhile, the 25% D2EHPA/75% PVC PIM presents a surface with small drops of D2EHPA uniformly distributed throughout the PIM (Fig.3b). The surface of the 50% D2EHPA/50% PVC membrane shows a slightly wrinkled surface, containing two separate domains: one consisting of entangled polymer chains which support a second one, liquid micro-domains containing the extracting agent (Fig. 3c). As it can be seen from Fig. 3 b,c, the dimensions of these liquid domains increase with the increasing of the D2EHPA content in PIM. This supports the idea of coalescence of the liquid domains at high D2EHPA concentrations to create liquid pathways which assure either the inner sorption, or the transport process by such PIMs, which occurs by a “relay mechanism” [1,20].

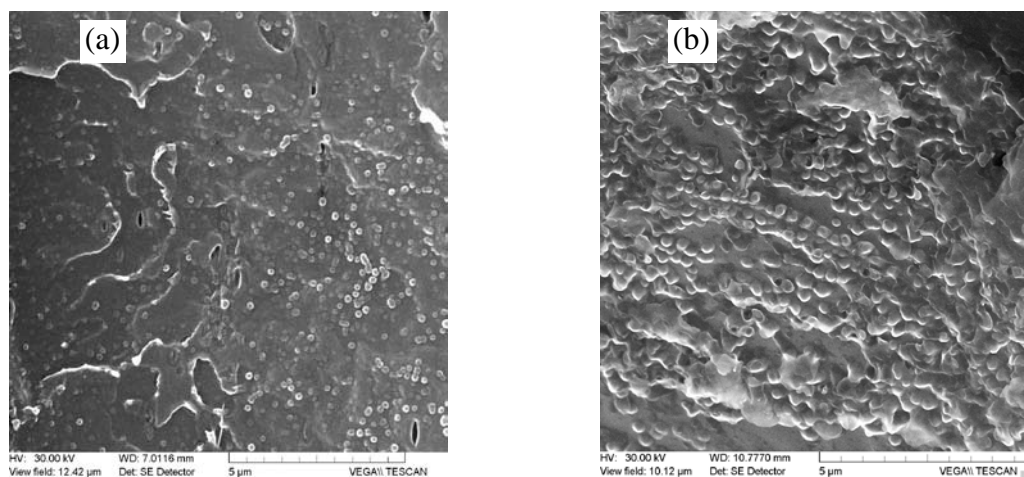


Fig. 4 SEM image (cross section) of the (a) 25%D2EHPA/75%PVC PIM and (b) 50%D2EHPA/50%PVC PIM.

The cross-section images (Fig. 4 a,b) highlight the distribution of the components (the polymer and the extracting agent D2EHPA) in PIMs containing 25% and 50% D2EHPA respectively. As can be seen in Fig. 4 a,b, the distribution of the extracting agent molecules is the same as in the correspondent surface image: small droplets at low D2EHPA content (25%) and organized continuous liquid domains at high D2EHPA concentration in PIM (50%). Fig. 4 b reveals the formation of continuous liquid domains (pathways) through the PIM, which are included within the polymer network. This arrangement of the extracting agent, D2EHPA, explains the enhanced sorption properties of 50% D2EHPA/50% PVC PIM, which assure the transport of the metal ions adsorbed on the surface, to the extracting agent molecules located inside the membrane [20]. These liquid domains through PIMs (Fig.4 b) can be assumed to function as “liquid pores”, which facilitate the transport process by PIMs [13]. Meanwhile, the SEM characterisation is in good agreement with the previous results which highlighted good sorption capacity and transport properties of PVC-based PIMs with 50% D2EHPA contents [13]. Because our 50%D2EHPA/50%PVC PIM does not contain an additional plasticizer, it was possible to include in such of non-plasticized PIM a much higher D2EHPA quantity than in a typical plasticized PIM containing the same carrier. Therefore, the PIM component not involved in the metal’s retention process was eliminated, concomitantly with the price lowering and no loss in the membrane properties.

3.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis is a very sensitive method for assessing the relaxations in polymers (α , β , γ). The relaxation temperatures are taken from the result of a temperature scanning experiment, at a constant frequency, as the drops of E' (storage modulus) and the peaks of E'' (loss modulus) and $\tan \delta$ (loss factor). Usually, the α -relaxation is associated with the glass transition.

Figure 5 shows the variation of E' and $\tan \delta$ with temperature for PVC and 50%D2EHPA/50%PVC PIM. Some important values that will be discussed below are included in the Table 1.

Table 1. The main characteristics of the PVC and 50%D2EHPA/50%PVC PIM obtained by DMA.

Sample	$E' \cdot 10^{-7}$ (Pa)			T_g (°C)
	25°C glassy region	80°C glass transition region	125°C rubbery plateau	
Blank PVC film	160	0.8	0.4	65
50%D2EHPA/50%PVC PIM	11.6	5.6	0.2	60 (shoulder) 94 (peak)

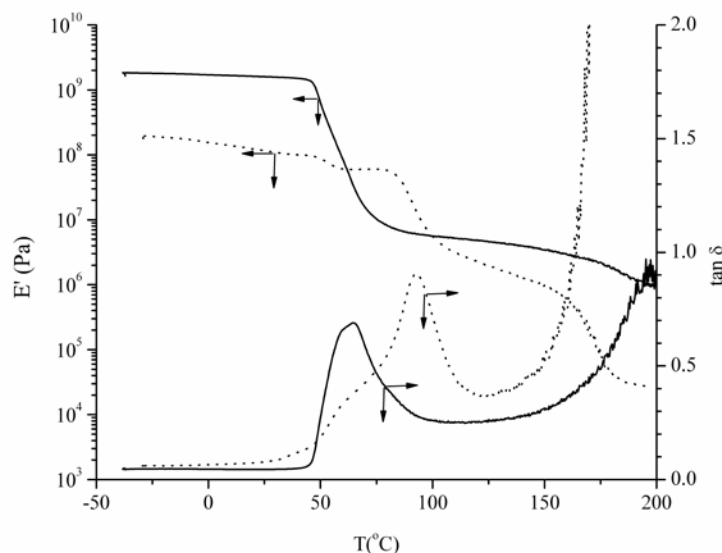


Fig.5 The variation of E' and $\tan \delta$ with temperature for pure PVC (solid line) and for the 50%D2EHPA/50%PVC PIM (dotted line).

At very low temperatures, the PVC has the E' over 10^9 Pa, characteristic for glassy polymers. After the glass transition temperature (65°C , $\tan \delta$ peak), the E' modulus decreases significantly, and the rubbery plateau lasted until the end of the experiment. The E' value for 50%D2EHPA/50%PVC PIM is more than 10 times lower than the E' of PVC, due to the plasticizing effect of D2EHPA. It is curious what is going on during the glass transition region. The broadness of the $\tan \delta$ peak, and the two drops on the E' curve indicate that the 50%D2EHPA/50%PVC film is heterogeneous. The shoulder on $\tan \delta$ curve (60°C) may be associated with the relaxation of PVC segments that are not affected by the plasticizer. Nevertheless, there is a temperature range ($63\text{--}100^\circ\text{C}$) where the E' values for the 50%D2EHPA/50%PVC film are higher than the E' values for the PVC film. It is possible that the accumulation of plasticizer on disparate zones of PVC (as indicated also by SEM), can make the 50%D2EHPA/50%PVC behave as a loose network that has the main $\tan \delta$ peak at a higher temperature than the original PVC. After 100°C the E' values of 50%D2EHPA/50%PVC PIM decrease under the values of PVC. Moreover, after 150°C , flowing takes place. Along with the coordinated molecular motions characteristic for α -relaxation, the polymer chains start to slip past to one another to some extent.

3.5. Dielectric spectrometry

The effect of addition of the carrier D2EHPA in PVC in order to prepare the 50% D2EHPA/ 50% PVC PIM was investigated by means of its dielectric properties. The complex

permittivity ε'' of the 50% D2EHPA/ 50% PVC PIM and blank PVC film was determined as a function of temperature in the range of 0-130 °C, the results being presented in Fig.6.

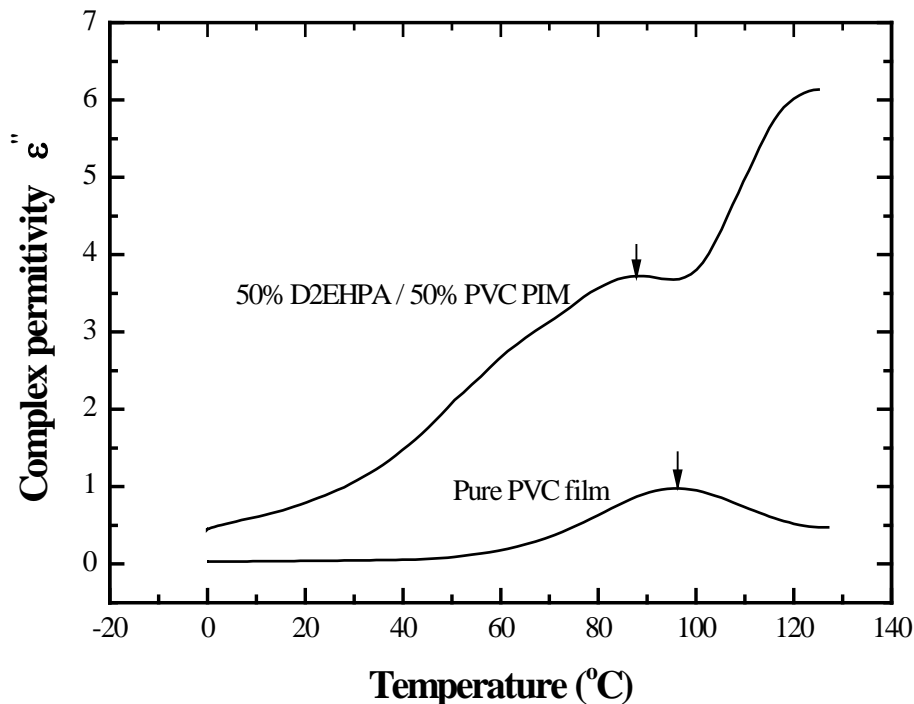


Fig.6 Dependence of the complex permittivity (ε'') versus temperature, for the blank PVC film and for the 50%D2EHPA/50%PVC PIM.

As the Fig. 6 shows, the dipoles relaxation was easier in the 50%D2EHPA/50%PVC PIM than in the blank PVC film. For the 50% D2EHPA/50% PVC PIM, Fig. 6 highlights a decrease of the maximum value of the complex permittivity ε'' with about 10°C comparing to the blank PVC film. Therefore, the D2EHPA molecules interpose between the long PVC chains, leading to an increasing of the distance between these chains, which results in a plasticizing effect. Thus, the dipoles represented by the adjacent C-Cl bonds can more easily change their orientation. Additionally, from the relaxation spectrum of the 50%D2EHPA/50%PVC PIM it can be observed another relaxation process of low intensity in the temperature range of 40–80°C. This latter relaxation process can be assigned to the D2EHPA dipoles. Therefore, the addition of 50% D2EHPA into the pure PVC produce noticeable changes in the dielectric properties, namely it leads to a plasticizing effect of the polymer matrix. Thus, the results of this study sustain also the conclusions of the above presented DMA study.

4. Conclusions

A new PVC-based PIM which does not contain additionally added plasticizers was prepared and characterized. The characterization by SEM and FT-IR revealed that the PIM contains the carrier D2EHPA dispersed in physical form in the polymer matrix. Also, the carrier D2EHPA molecules are organized in continuous liquid micro-domains which cross the membranes, and explain the PIM's sorption and transport properties. Both DMA and dielectric spectrometry methods confirm that the used carrier D2EHPA acts also as a plasticizer of the PVC network. The absence of any plasticizers from our PIM composition determines a high potential to reduce the price compared to the plasticized ones.

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