



Ionic diffusion in iPP: DC electrical conductivity

B. Škipina , I.M. Petronijević , A.S. Luyt , B.P. Dojčinović ,  
M.M. Duvenhage , H.C. Swart , E. Suljovrujić , D. Dudić

PII: S2468-0230(20)30764-1  
DOI: <https://doi.org/10.1016/j.surfin.2020.100772>  
Reference: SURFIN 100772

To appear in: *Surfaces and Interfaces*

Received date: 16 July 2020  
Revised date: 20 October 2020  
Accepted date: 21 October 2020

Please cite this article as: B. Škipina , I.M. Petronijević , A.S. Luyt , B.P. Dojčinović ,  
M.M. Duvenhage , H.C. Swart , E. Suljovrujić , D. Dudić , Ionic diffusion in iPP: DC electrical  
conductivity, *Surfaces and Interfaces* (2020), doi: <https://doi.org/10.1016/j.surfin.2020.100772>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

## Ionic diffusion in iPP: DC electrical conductivity

B. Škipina<sup>1</sup>, I. M. Petronijević<sup>2</sup>, A.S. Luyt<sup>3</sup>, B. P. Dojčinović<sup>4</sup>, M.M. Duvenhage<sup>5</sup>, H.C. Swart<sup>5</sup>, E. Suljovrujić<sup>6</sup> and D. Dudić<sup>6\*</sup>

<sup>1</sup>Faculty of Technology, University of Banja Luka, Vojvode Stepe Stepanovića 73, 78 000 Banja Luka, Bosnia and Herzegovina

<sup>2</sup>Faculty of Physics, University of Belgrade, Studentski trg 12–16, 11001 Belgrade, Serbia

<sup>3</sup>Center for Advanced Materials, Qatar University, PO Box 2713, Doha, Qatar

<sup>4</sup>Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia

<sup>5</sup>Department of Physics, University of the Free State, P.O. Box 339, 9300 Bloemfontein, South Africa

<sup>6</sup>Department of Radiation Chemistry and Physics, „VINČA" Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

### ABSTRACT

This study provides a new insight into the relationships between absorption and adsorption processes that occur during the treatment of iPP in aqueous solutions of metal-chloride salts, as well as the impact of these processes on the electrical conductivity of this nonpolar polymer. The polypropylene films (0.5 mm) were exposed to three-day treatments in aqueous solutions of chlorine salts of some alkali and transition metals at temperatures of 22 °C and 80 °C. The treatments induced an increase in the electrical conductivity of iPP, up to 800%. DC conductivity is not directly proportional to the concentrations of metals in the treated films due to the complex relationships between diffusion and adsorption processes. The experiment was set up to simulate the real-world conditions and the study provides practical knowledge on the stability of the electrical conductivity of iPP under exposure to aqueous solutions. The influence of electric aging on the electrical conductivity of the treated films was also examined.

Keywords: iPP; diffusion; electrical conductivity; ions; aging.

\* Corresponding author: Duško Dudić (ddudic@vinca.rs)

### INTRODUCTION

Isotactic polypropylene (iPP) is a semi-crystalline polyolefin polymer with a large number of applications. This polymer is characterized by low cost, environmental friendliness (absence of nitrogen and chlorine), low density, non-polarity, crosslinking ability and good mechanical properties (viscoelasticity). Together with polyethylene (another typical polyolefin polymer), iPP is widely used in packaging, household plastic and machine products as well as in thermoelectric insulation. iPP is a particularly interesting material due to good viscoelastic properties, which is a consequence of its semicrystalline structure [1]. On the other hand, semicrystallinity, i.e. the existence of amorphous areas in this polymer, is a driver of degradation processes that reduce the lifespan of this material [2-4]. Changes in the physical properties of iPP due to treatment in aqueous solutions have not been sufficiently investigated. This study contributes to a better understanding of the complexity of adsorption and diffusion processes that occur during the treatments of iPP in aqueous solutions, also shows the changes in the electrical properties of this polymer induced by these processes.

In certain cases, the diffusion of impurities into the polymer can be treated as a degradation. Diffused impurities have little influence on the physical and chemical structure of the polymers, but at the same time they cause significant changes in some physical properties such as electrical conductivity [5 - 7]. By controlled impurity diffusion into a polymer, the desired modification of the properties of that polymer can be achieved.. For this reason, the diffusion is extensively used method for modifying polymeric materials especially in the fields of metal-plastic coatings, ionic polymer composites and organic electronics [8, 9]. There are numerous factors that may influence the process of diffusion from the environment into the polymer: the size, polarity and chemical activity of the diffusing complex as well as the tendency of the

complex to condense on the polymer surface. For example, the diffusion of ionic impurities from solution is more probable than the corresponding atomic-molecular diffusion [10]. On the other hand, the arrangement of the polymer amorphous phase and its polarity also affect the diffusion process [11]. In the case of the processes of ion diffusion from aqueous solutions, the nature of ion hydration is the basic factor that determines the diffusion intensity. Several studies on series of Li - Na - K aqueous solutions clearly demonstrated an increase ion mobility with increasing in ion dimensions due to the change in their interaction with water molecules [9,12]. Of course, this is not a general rule, since in some cases larger ions show low mobility in aqueous solutions [10]. This study shows the effects of ion diffusion on the electrical conductivity of iPP, which, as a non-polar polymer, represents a different environment for the ion transport process relative to water. The presented results indicate that the effects of temperature on the structure of hydrated ions are very important and should be taken into account. It has been shown that the shielding of charges in hydrated ions and their polarity are of significant importance for diffusion processes. This has also been suggested in several studies where the presence of carbon dioxide in solution and/or its pH value was found to affect the diffusion processes [13-16].

Degradation of the electrical properties of iPP is the subject of a large number of studies. The presence of trapped charges and changes in the amorphous phase due to various external influences are the dominant factors that induce the degradation of its electrical properties [17-21]. iPP is a non-polar polymer and is expected to behave well as an electrical insulator in humid conditions. But changes in its electrical properties due to the diffusion of impurities from the humid environment are not documented, and this is the main reason for initiating this study. Švorčík *et al.* [22] shows that diffusion from aqueous solutions of alkali metal chloride salts into iPP produce a surface polarization of this polymer, which has been stable for more than three months. The same study shows that saturation concentrations of diffused ions in iPP are achieved after 60-minute treatments of 15  $\mu\text{m}$  thick iPP films at 100 °C. During the cooling of the iPP melt, common in the industrial production of iPP products, uneven crystallization occurs in the polymer volume. Parts of the polymer that are closer to cold surfaces contain a higher proportion of amorphous areas that can show different morphologies, and which can affect the processes of diffusion of impurities. Under normal cooling conditions of molten iPP, these areas reach up to 100  $\mu\text{m}$  from the surface of the molten melt [23]. Having this in mind, in this experiment, we used melt pressed films with a thickness of 500  $\mu\text{m}$  (0.5 mm) in order to get information about this polymer that can be used in real life applications. The time treatment in this study of 72 h was significantly longer than in the the previously mentioned study (60 min) [22], and nearly saturation concentration of ionic impurities in the 0.5 mm iPP films is expected. In our previous paper, we showed that three-day treatments of iPP and polystyrene films in solutions of alkali metal chloride salts induced a relatively small increase (up to a few percent) in the dielectric constant of these polymers [24]. The results presented in this study show that the DC conductivity of iPP increases by several hundred percent after three days of treatment in saturated aqueous solutions of the following metal-chloride salts: LiCl, NaCl, KCl, MnCl<sub>2</sub>, FeCl<sub>2</sub> and NiCl<sub>2</sub>. The results also indicate the need for high-voltage dielectric tests of polymers treated in this way.

## EXPERIMENTAL SECTION

### Materials

The isotropic sheets of isotactic polypropylene, HIPOLEN P EH71 ( $M_w = 110000$ ), were made in a hot press at 460 K and pressure of 1.75 MPa for 5 min, followed by quenching in water at room temperature. The thickness of the sheets thus obtained was in the range of  $0.5 \pm 0.01$  mm and the calorimetric crystallinity about 40%. Both sides of the obtained sheets were gently treated with sandpaper (P900) and then sonicated in distilled water. The foils (10x10 cm in lateral dimensions) were treated at temperatures of 22 °C and 80 °C for three days in saturated solutions of the following salts: lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), manganese(II)chloride (MnCl<sub>2</sub>), iron(II)chloride (FeCl<sub>2</sub>) and nickel(II)chloride (NiCl<sub>2</sub>), all of them from Merck, min 99% purity. After the described three-day treatment

in metal chloride salts, the sheets were sonicated in distilled water for 30 s at  $T = 30\text{ }^{\circ}\text{C}$  and left for more than 30 days under normal atmospheric conditions. For all the experiments, samples were taken from the middle of the treated films. Electrical measurements were performed on disk-shape samples ( $D = 3\text{ cm}$ ) and graphite electrodes were applied.

#### Experimental methods

Fourier transform infrared (FTIR) spectroscopic analyses were performed at room temperature using a Nicolet 380 FTIR (attenuated total reflectance) spectrophotometer in the spectral range  $600\text{--}4000\text{ cm}^{-1}$  (step  $2\text{ cm}^{-1}$ ).

The inductively coupled plasma optical emission spectrometry (ICP-OES) method was used to determine the concentration of metals in the samples. The measurements were performed using an iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, United Kingdom) spectrometer with iTEVA operational software. Measurements were performed on at least three identically prepared samples. More details about the applied experimental procedures in the above method can be found in our previous study [24].

The distribution of metallic impurities in the samples was determined by time-of-flight secondary ion mass spectrometry (TOF-SIMS) using a TOF-SIMS 5 (Gmbh Germany) system. The cross sections of the samples ( $1000 \times 500\text{ }\mu\text{m}$ ) were analyzed using a  $\text{Bi}^+$ -ion beam at 30 kV; the spot was  $5 \times 5\text{ }\mu\text{m}$ , the pressure was  $2 \times 10^{-9}\text{ mbar}$  and applying 50 scans. Due to the weak and diffuse response of the  $\text{Cl}^-$  ion, under the given conditions, the distribution of chlorine in the samples could not be determined.

The surface elemental compositions of the samples were investigated using a scanning electron microscope (SEM) (Shimadzu model ZU SSX – 550 Superscan) coupled with an energy dispersive X-ray spectrometer (EDS). The samples were fixed on conductive double sticking carbon tape without any sputter-coating, and a low electron-beam current and 300 scans were applied.

The electrical measurements were performed using a Keithley 2401 ammeter and a DC high voltage source. Electrical measurements and aging were carried out at room temperature using the following order:

- (1) RUN 1 - Measurement of electrical conductivity of the samples during an increase in the electric field at a speed of  $1\text{ MV m}^{-1}\text{ min}^{-1}$ . The range of electric field changes was  $0.1\text{--}10\text{ MV m}^{-1}$ .
- (2) Electrical aging - Immediately after the completion of the first measurement (RUN 1), a constant electric field of  $10\text{ MV m}^{-1}$  was kept on the samples for 20 minutes.
- (3) RUN 2 - Three days after the end of electrical aging, electrical conductivity measurements were performed using the same conditions as before aging (RUN 1), and the previously applied polarity on the samples was not changed.

## RESULTS AND DISCUSSION

FTIR spectra of the samples did not reveal any changes in chemical composition of the surfaces of the iPP films after the treatment. A slight staining was observed for the sample treated in  $\text{FeCl}_2$  at  $80\text{ }^{\circ}\text{C}$ , but even in this case the FTIR method gave a spectrum corresponding to that of pure iPP.

The concentrations of the metals in the iPP films were determined by the ICP-OES method, and the results are shown in Figure 1. For each sample, only the concentrations of the metal from the chloride salt used in the treatment are shown. The molar concentration values of the Li - Na - K alkali metal series in the films are close in the case of Li and K, while the concentration of Na is about ten times larger. Somewhat similar behaviour was observed for the concentrations of the Mn - Fe - Ni series of transition metals in the samples, where the Mn and Ni concentrations are virtually identical, while the Fe concentration in the samples is much higher (Figure 1). In order to understand the differences in metal concentrations in iPP films after three-day treatments in saturated solutions of the metal chloride salts, it is necessary to first

analyze the influence of water-solubility of the salts used in these experiments. Table 1 shows the water solubilities of the metal chloride salts used [25]. Comparison of the results shown in Figure 1 and the results on the solubility of the salts given in Table 1 reveals that significantly higher concentration values of Na and Fe in the polymer samples with respect to the concentrations of other metals are not due to the higher solubility of the NaCl and FeCl<sub>2</sub> salts.

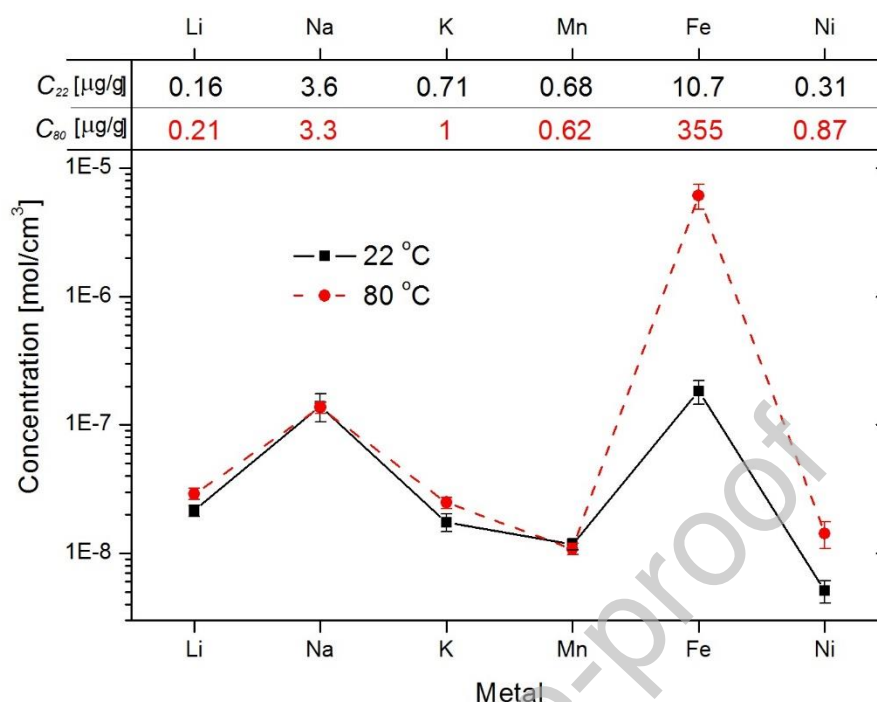


Figure 1. Metal concentrations in treated samples. Molar concentrations are shown graphically, while the corresponding mass concentrations are presented numerically above the graphs. Black color – treatments at 22 °C and red color – treatments at 80 °C.

The increase in the solubility of the metal-chloride salts due to an increase in the temperature of the solution from 22 °C to 80 °C, was found to be about 30% except for the case of NaCl (Table 1). The samples treated at high temperature (80 °C) in FeCl<sub>2</sub> and NiCl<sub>2</sub> solutions showed a significant increase in metal content compared to the corresponding treatments performed at room temperature. This might be a consequence of the thermal expansion and softening of the amorphous iPP phase after increasing in treatment temperature from 22 °C to 80 °C, which allowed greater absorption of ions. However, we cannot exclude possibility that the observed effects originate from the deposition of the salts onto the surface of the films and the possibility that the sonication of the samples after treatment did not remove the salt residues.

Table 1. Aqueous solubility of the metal chloride salts used,  $S_{20}$  - 20 °C and  $S_{80}$  - 80 °C [25].

Salt	LiCl	NaCl	KCl	MnCl <sub>2</sub>	FeCl <sub>2</sub>	NiCl <sub>2</sub>
$S_{20}$ g/(100 ml)	83	36	34.2	74	62.5	67
$S_{80}$ g/(100 ml)	112	38	51.3	113	88.7	87

The TOF-SIMS method was used to prove the presence of metals in the bulk of the treated samples. In addition to its high detection sensitivity, this method also enables obtaining a concentration profile of

impurities in the material. The TOF-SIMS method confirmed that there was a diffusion of corresponding metals within the entire sample bulk for all the samples. Figure 2 shows typical metal concentration profiles along the cross-section of the treated films. Metal ion counts were normalized by the counting of ions of similar mass originating from iPP due to irregularities (topology) of the scanned cross-sectional area of the samples. Unfortunately, the absolute values of metal concentrations in our samples by the TOF-SIMS cannot be obtained in this experiment. TOF-SIMS spectrometry of the samples showed that the highest metal concentrations in the treated samples were observed in areas several tens of microns away from the treated surface, which could be partly explained by the lower crystallinity of these areas compared to the central areas in the film cross-section. The results also show that the type of ions (salts used) or treatment temperature do not affect significantly the shape of the concentration profiles. Typical examples are shown in Figure 2.

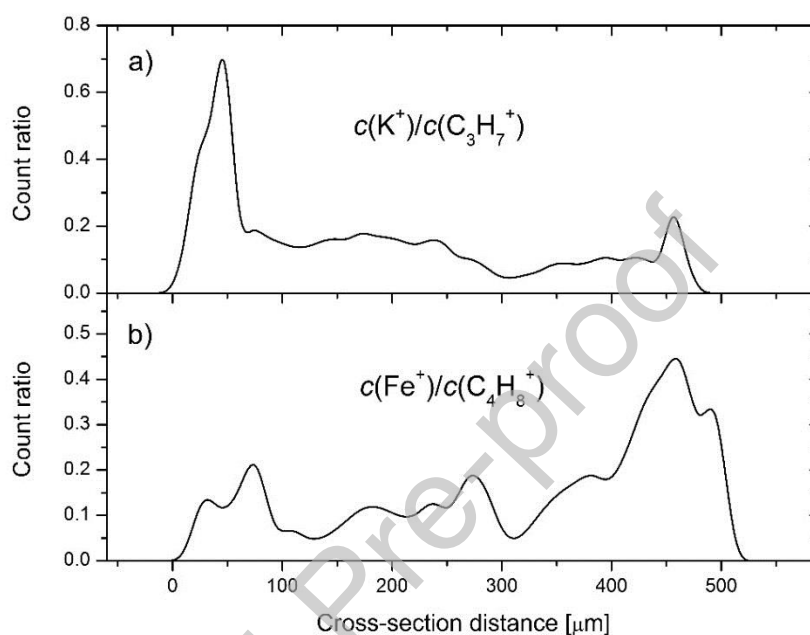


Figure 2. TOF-SIMS counts of a) K and b) Fe versus cross-sectional distance in the samples treated respectively in KCl and FeCl<sub>2</sub> solutions at 22 °C, 1000x500 μm - scan area and 5x5 μm - spot (resolution).

The highest metal molar concentration was observed for the sample treated in FeCl<sub>2</sub> solution at 80 °C. In order to qualitatively compare the content of metal (Fe) present on the surface and in the volume of the film, this sample was tested by the SEM-EDS method (Figure 3).

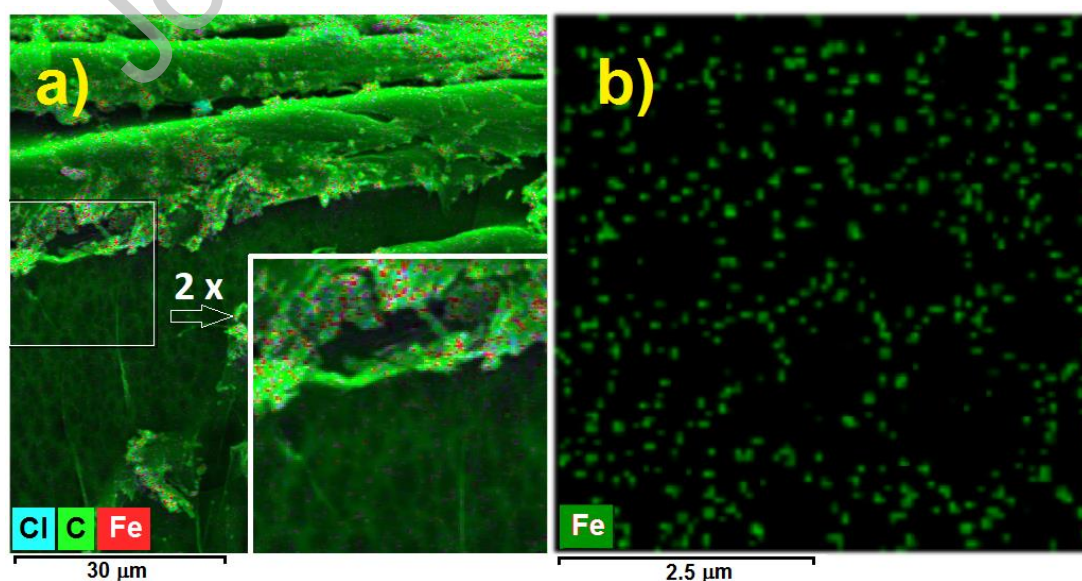


Figure 3. SEM-EDS scans of the sample treated in  $\text{FeCl}_2$  solution at  $80\text{ }^\circ\text{C}$ : a) sample surface and cross-section of the sample; b) cross-section  $50\text{ }\mu\text{m}$  from the surface.

Figure 3a shows a SEM-EDS image of the sample surface (up) and the sample cross-section (down). The treated surface of the film clearly shows the presence of iron (red) and chlorine (blue), while the same image shows that their presence in the cross-section was hardly noticeable. A significantly higher content of impurities was observed on the sample surface than in the cross-sectional area of the iPP sample treated in  $\text{FeCl}_2$  solution at  $80\text{ }^\circ\text{C}$ . This indicates that the surface salt deposition influences to a high extent the values of the molar concentrations of metals obtained by ICP-OES (Figure 1). Figure 3b shows a SEM-EDS cross-sectional view of the same sample  $50\text{ }\mu\text{m}$  from the treated surface. At this depth, only the presence of iron (green) can be noticed. Figure 3b suggests that the impurities diffused primarily through the amorphous regions in the polymer, between the spherulites, and that they were predominantly located in these regions. Based on the presented results, it can be concluded that the detected metal concentrations in the samples (Figure 1) are rather due to the surface deposition than due to the diffusion processes. The results on DC conductivity of the films can offer a better understanding of the observed phenomenon.

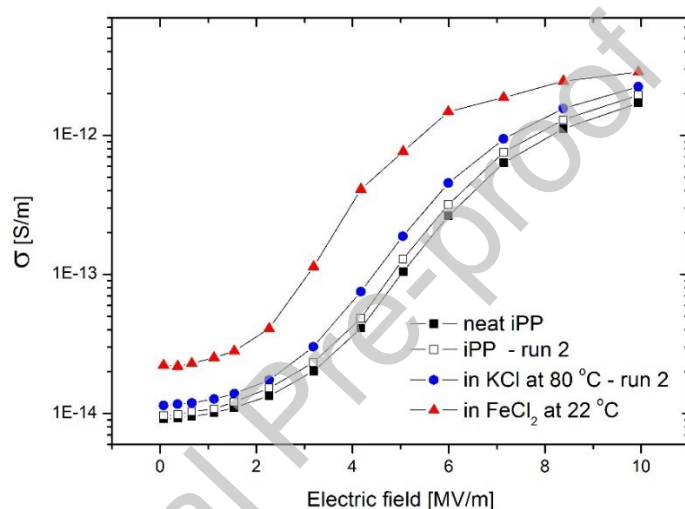


Figure 4. DC conductivity of selected iPP samples versus electric field, the rate of increase of the electric field is  $1\text{ MV m}^{-1}\text{ min}^{-1}$ , *run 2* - indicates that electrical aging has been applied.

The DC conductivities of the selected iPP films are shown in Figure 4. The untreated iPP film shows the lowest DC conductivity (black square symbols) but the conductivity tends to increase after electrical aging (open square symbols). All the samples treated in saline solutions showed an increase in electrical conductivity compared to the neat iPP. The electrical conductivity of the film treated in KCl solution at  $80\text{ }^\circ\text{C}$  only slightly increase after electrical aging (blue circle symbols in Figure 4). The largest increase in electrical conductivity was observed in the sample treated in  $\text{FeCl}_2$  solution at  $22\text{ }^\circ\text{C}$  (red triangle symbols in Figure 4). As can be seen in Figure 4, the DC electrical conductivity of iPP increases nonlinearly with increasing applied electric field, a well-known phenomenon typical for most low electrical conductivity linear polymers [5,18]. The electrical conductivity of iPP increases due to voltage-stimulated induction (in the polymer) and injection (by the electrode) of charge carriers. Also, during the application of the electric field, charge traps are formed in the polymer that stimulate electrical conductivity [20,26,27]. The shape of the dependence of DC electric conductivity on the electric field, shown in Figure 4, depends on the rate of increase of the electric field. The reason for this is the limited movement of the field-induced charge.

Figure 5 shows the percentage increase in DC electrical conductivity of all the samples relative to that of neat iPP as a function of the applied electric field. The treatment-induced increases in film conductivity are the most pronounced at electric field values around  $5\text{ MV m}^{-1}$  (up to several hundred percent). At the

lowest ( $<1 \text{ MV m}^{-1}$ ) and highest ( $10 \text{ MV m}^{-1}$ ) electric fields the conductivity increases are generally up to 100%. The largest increases in the conductivity of the treated samples occur in the electric field range where the pure polymer shows a pronounced increase in the  $\sigma(E)$  dependence ( $\sim 5 \text{ MV m}^{-1}$ ). Such behavior suggests that diffused impurities contribute to the carrier and/or trap generation processes. Also, the presented results indicate that the dielectric testing of such materials should be carried out at electric fields larger than  $2 \text{ MV m}^{-1} = 2 \text{ kV mm}^{-1}$  because the dielectric losses in the treated polymers can be significantly higher than in the untreated ones.

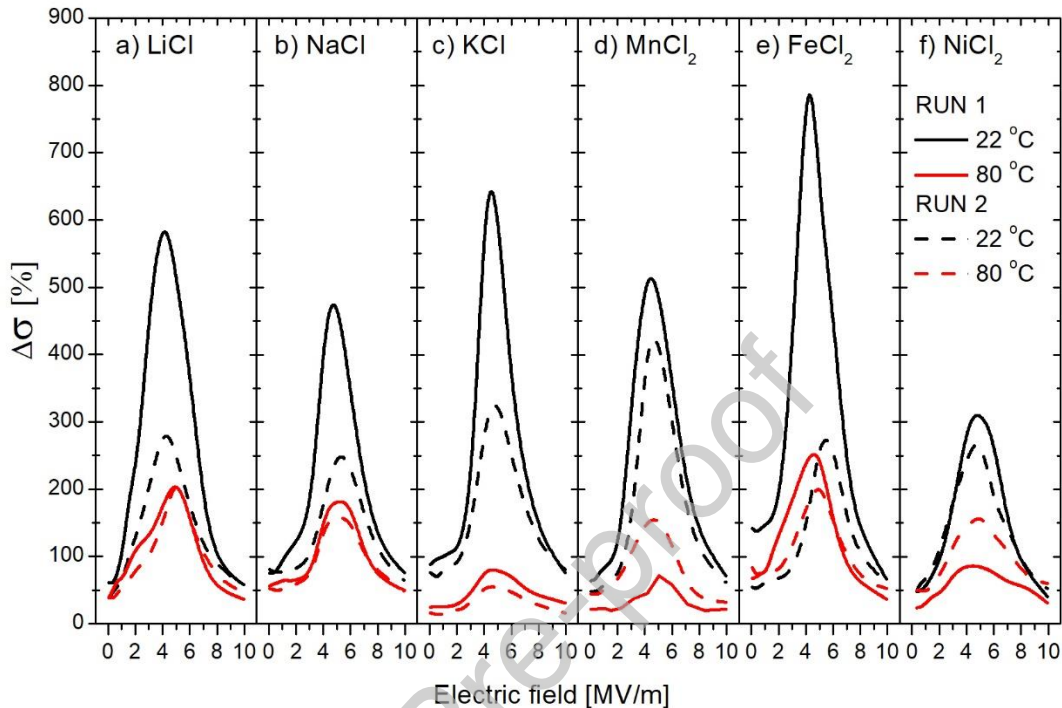


Figure 5. Percentage changes of DC electrical conductivity of treated iPP films relative to DC electrical conductivity of untreated iPP. The salts used in the treatments are indicated in the figure; *RUN 2* - signifies that electrical aging has been applied; the treatment temperatures are also indicated.

Significantly higher increase in conductivity of the samples treated in salt solutions at room temperature (black in Figure 5) than the conductivities of the samples treated at  $80 \text{ }^\circ\text{C}$  (red in Figure 5) are rather strange. Based on the results in Figure 1 and the pronounced coefficient of thermal expansion of polyolefins [28], it was expected that higher temperatures of polymer treatment in solutions will contribute to a better diffusion of impurities and thus to a higher conductivity of the polymer. However, the results in Figure 5 suggest an opposite effect. Existing studies indicate that increasing in temperature improves the absorption ability of polar polymers in polar solvents (water/salt) [7,10]. Given that iPP is a non-polar polymer, the above is obviously not valid. Two main reasons for the reduced diffusion at elevated temperatures can be given: first, the temperature-stimulated ion dynamics in solution reduces the probability of ion diffusion into iPP; and second, the nature of ion hydration during the  $80 \text{ }^\circ\text{C}$  treatment leads to a higher surface salt deposition than in the case of the room temperature treatment. Another reason for the lower conductivity of iPP films treated at  $80 \text{ }^\circ\text{C}$  might be the process of secondary crystallization of iPP during the three days of treatment [29]. Secondary crystallization may affect diffusion due to the reorganization of the amorphous phase of iPP.

Electrical aging has led to a decrease in the DC electrical conductivity of the samples treated at room temperature (black symbols in Figure 5, *RUN 2* - aged samples). A probable reason for this is the aggregation of impurities in the polymer due to the application of an intense electric field over time [4,5,19]. Changes in the electrical conductivity of iPP samples treated at  $80 \text{ }^\circ\text{C}$  after electrical aging are less pronounced, and in the case of samples treated in  $\text{MnCl}_2$  and  $\text{NiCl}_2$  solutions there was a slight increase in



DC conductivity due to aging (red in Figure 5). The differences in the effects of electrical aging on the electrical conductivity of the samples treated at different temperatures indicate that the diffusion of impurities into the polymer was less pronounced during treatment at 80 °C than during treatment at 22 °C. In other words, the aggregation or displacement of impurities in the samples treated at 80 °C during the prolonged electrical aging did not significantly affect the electrical conductivity. For the practical applications of iPP as an electrical insulator, it can be concluded that the insulating properties of the iPP films treated in the mentioned metal chloride salt solutions will not be significantly affected by electric aging with DC electric fields up to 10 MV m<sup>-1</sup>.

The resulting changes in DC conductivity of the treated iPP samples obviously do not correspond directly to measured metal concentrations. This is due to the different intensities of the metal diffusion processes into the polymer and processes of the adsorption onto the polymer surface. The presented results indicate that the intensities and relative contributions of these processes are influenced by the temperature-dependent distribution of the hydrated ions in the solutions. The previous studies on the mobility of the series of Li-Na-K ions in aqueous solutions showed direct relationship between the size of the ion and its mobility. As the results of the DC conductivity show (Figure 5), these is not preserved in the case of the ion motion through iPP sample.

## CONCLUSIONS

This article describes the changes in DC electrical conductivity of polypropylene films (0.5 mm) after three-day treatments in saturated aqueous solutions of metal-chloride salts (LiCl, NaCl, KCl, MnCl<sub>2</sub>, FeCl<sub>2</sub> and NiCl<sub>2</sub>) at temperatures of 22 °C and 80 °C. According to the FTIR results there were no chemical changes in the samples after the treatment. The TOF-SIMS method confirmed the presence of diffused metals in all the samples, with the highest metal concentrations at several tens of μm from the treated film surface. DC conductivities of the iPP films were measured during an increase in the electric field at a speed of 1 MV m<sup>-1</sup> min<sup>-1</sup>. The salt-treatment induced an increase in the conductivity of the iPP films, with the maximum increase of several hundred percent at electric field values of about 5 MV m<sup>-1</sup>. At the lowest (<1 MV m<sup>-1</sup>) and the highest electric field (10 MV m<sup>-1</sup>) values the observed increases in conductivity was about 100%.

The results indicate that the diffusion and adsorption processes, during the treatment of iPP in solutions, depend on the type of ions and the temperature of the solution. Based on DC conductivity measurements, it can be concluded that the diffusion of impurities in iPP was more pronounced during treatments at 22 °C compared to treatments at 80 °C. DC electric aging using an electric field of 10 MV m<sup>-1</sup> did not significantly change the electrical insulating properties of the iPP films treated in metal chloride solutions. This study suggests the dielectric testing of these materials should be carried out at the electric fields larger than 2 MV m<sup>-1</sup> (2 kV mm<sup>-1</sup>), since dielectric losses might be very pronounced under these conditions.

## Author Statement<sup>1</sup>

I declare that the article, Ionic diffusion in iPP: DC electrical conductivity, contains original scientific results from my research group.

Dusko Dudic

## ACKNOWLEDGMENTS

This work was supported in part by the Ministry of Education, Science and Technological Development of the Republic of Serbia, by the Ministry of Scientific and Technological Development, Higher Education and

### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### References

- [1] Struik LCE. The mechanical behaviour and physical ageing of semicrystalline polymers: 2. *Polymer* 1987; 28: 1534-1542. doi: 10.1016/0032-3861(87)90354-5
- [2] Stojanović Z, Kostoski D, Dudić D, Kačarević-Popović Z. Aging of drawn and gamma-irradiated isotactic polypropylene using high oxygen pressure. *Polym Degrad Stab* 1996; 51: 45-49. doi: 10.1016/0141-3910(95)00199-9
- [3] Dudić D, Kostoski D, Stojanović Z, Djoković V. Recrystallization processes induced by accelerated ageing in isotactic polypropylene of different morphologies, *Polym Degrad Stab* 2000; 67: 233-237. doi: 10.1016/S0141-3910(99)00118-4
- [4] Dissado LA, Thabet A. Simulation of electrical ageing in insulating polymers using a quantitative physical model. *J Phys D: Appl Phys* 2008; 41: 085412. doi: 10.1088/0022-3727/41/8/085412
- [5] Andreas Heilmann, editor. *Springer Series in Materials Science, Vol 52: Polymer Films with Embedded Metal Nanoparticles*. Berlin Heidelberg New York: Springer-Verlag, 2003. doi: 10.1007/978-3-662-05233-4
- [6] Simonović K, Petronijević I, Kostoski D, Dojčilović J, Luyt AS, Dudić D. Effects of acid treatment at different temperatures on the surface dielectric properties of low-density polyethylene. *Polymer International* 2014; 63: 1924–1929. doi: 10.1002/pi.4731.
- [7] Gallardo DE, Bertoni C, Dunn S, Gaponik N, Eychmüller A. Cathodic and Anodic Material Diffusion in Polymer/Semiconductor- Nanocrystal Composite Devices. *Advanced Materials* 2007; 19: 3364-3367. doi: 10.1002/adma.200700394
- [8] Shahinpoor M. Ionic polymeric conductor nanocomposites (IPCNCs) as distributed nanosensors and nanoactuators. *Bioinsp Biomim* 2008; 3: 035003. doi: 10.1088/1748-3182/3/3/035003
- [9] Kim KJ, Shahinpoor M. Ionic polymer–metal composites: II. Manufacturing techniques. *Smart Mater.. Struct* 2003; 12: 65–79. doi: 10.1088/0964-1726/12/1/308
- [10] Devendra Gupta, editor. *Diffusion processes in advanced technological materials, Chapter 7*. Berlin Heidelberg: Springer-Verlag, 2005. doi: 10.1007/978-3-540-27470-4
- [11] Kamcev J, Paul DR, Freeman BD. Effect of fixed charge group concentration on equilibrium ion sorption in ion exchange membranes. *J Mater Chem A* 2017; 5: 4638. doi: 10.1039/c6ta07954g
- [12] Impey RW, Madden PA, McDonald IR. Hydration and Mobility of Ions in Solution. *J Phys Chem* 1983; 87: 5071-5083. doi: 10.1021/j150643a008
- [13] Pommersheim J, Nguyen T, Zhang Z, Lin C. Cation diffusion at the polymer coating/metal interface. *J Adhesion Sci Technol* 1995; 9: 935-951. doi: 10.1163/156856195X00806
- [14] Kamcev J, Jang ES, Yan N, Paul DR, Freeman BD. Effect of ambient carbon dioxide on salt permeability and sorption measurements in ion-exchange membranes. *J Membrane Sci* (2015); 479: 55–66. doi: 10.1016/j.memsci.2014.12.031

- [15] Lamb JD, Nazarenko AY. Lead(II) ion sorption and transport using polymer inclusion membranes containing tri-octylphosphine oxide. *J Membrane Sci* 1997; 134: 255-259. doi: 10.1016/S0376-7388(97)00115-4
- [16] Ansari R, Delavar AF. Sorption of Silver Ion from Aqueous Solutions Using Conducting Electroactive Polymers. *J Iran Chem Soc* 2008; 5(4): 657-668. doi: 10.1007/BF03246147
- [17] Kwan Chi Kao, editor. Dielectric phenomena in solids. London: Elsevier Academic Press 2004. doi: 10.1016/B978-0-12-396561-5.X5010-5
- [18] Chen G, Tay TYG, Davies AE, Tanaka Y, Takada T. Electrodes and charge injection in LDPE. *IEEE Transaction on Dielectrics and Electrical insulation* 2001; 8(6): 867. doi: 10.1109/94.971439
- [19] Han P, Zha JW, Wang SJ, Dang ZM. Theoretical analysis and application of polymer-matrix field grading materials in HVDC cable terminals. *High Volt* 2017; 2(1): 39–46. doi: 10.1049/hve.2016.0067
- [20] Zha JW, Wu YH, Wang SJ, Wu DH, Yan HD, Dang ZM. Improvement of Space Charge Suppression of Polypropylene for Potential Application in HVDC Cables. *IEEE Transactions on Dielectrics and Electrical Insulation* 2016; 23(4): 2337-2343. doi: 10.1109/TDEI.2016.005428
- [21] Mazzanti G, Montanari GC, Dissado LA. Electrical Aging and Life Models: The Role of Space Charge. *IEEE Transactions on Dielectrics and Electrical Insulation* 2005; 12(5): 876-889. doi: 10.1109/TDEI.2005.1522183
- [22] Švorčík V, Rybka V, Švorčíková J, Hnatowicz V, Kvítek J, Vacík J, Červena J, Peřina V. Diffusion into polypropylene of Chlorides of alkali metals. *Eur Polym J* 1993; 29(7): 923-926. doi: 10.1016/0014-3057(93)90287-P
- [23] Dudić D, Kostoski D, Djoković B, Dramićanin M. Formation and behavior of low temperature melting peak of quenched and annealed isotactic polypropylene. *Polym Int* 2001; 51: 111. doi: 10.1002/pi.803
- [24] Petronijević I, Cerović D, Dudic D, Dojčilović J, Dojčinović B, Pergal M. Dielectric spectroscopy of nanocomposites based on iPP and aPS treated in the water solutions of alkali metal salts. *Polym Adv Tech* 2018; 29: 1826-1833. doi: 10.1002/pat.4289
- [25] Atkins P, de Paula J. *Physical Chemistry* 9th Edition. Oxford: Oxford University Press, 2010.
- [26] Dudić D, Škipina B, Dojčilović J, Novaković L, Kostoski D. Effects of Charge Trapping on the Electrical Conductivity of Low-Density Polyethylene-Carbon Black Composites. *J App Pol Sci* 2011; 121(1): 138-143. doi: 10.1002/app.33421
- [27] Luyt AS, Škipina B, Csóka L, Dudić D. Charge-trapping capability and AC conductivity at different humidities of poly(ethyleneimine)-TiO<sub>2</sub>-anthocyanin modified cellulose fibres. *Wood Sci Technol* 2018; 52: 637-351. doi: 10.1007/s00226-018-0994-1
- [28] Motloug BT, Dudić D, Mofokeng JP, Luyt AS. Properties and thermo-switch behaviour of LDPE mixed with carbon black, zinc metal and paraffin wax. *J Polym Res* 2017; 24: 43. doi: 10.1007/s10965-017-1205-8
- [29] Dudić D, Djoković V, Kostoski V. The high temperature secondary crystallization of aged isotactic polypropylene. *Polymer Testing* 2004; 23: 621-627. doi: 10.1016/j.polymertesting.2004.01.015