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Antimicrobial Properties and Thermal Stability of Polycarbonate Modified with 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids

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ABSTRACT: Four water immiscible ionic liquids (ILs): 1-hexyl-3-methylimidazolium tetrafluoroborate, 1-heptyl-3-methylimidazolium tetrafluoroborate, 1-octyl-3-methylimidazolium tetrafluoroborate and 1-dodecyl-3-methylimidazolium tetrafluoroborate have been synthesized. Polycarbonate (PC) films containing ILs were prepared by solvent casting from methylene chloride solutions. Scanning electron microscopy measurements showed the high homogeneity of PC/IL films with the IL content up to 4 wt %. The tendency to IL aggregation was observed for polymeric films with higher IL content (5%). PC/IL composites were found to have the reduced thermal decomposition temperature under both an air and a nitrogen atmosphere in comparison with the neat PC. The effect of IL content on the antimicrobial activity of PC films against *Escherichia coli* bacteria was studied. Pronounced antimicrobial efficacy was revealed for PC/IL films for all studied ILs starting from 3 wt % of IL. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40050.

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INTRODUCTION

Polycarbonate (PC) is one of the most widely used engineering polymers due to its unusual combination of optical clarity, heat resistance, high impact strength, and dimensional stability over wide thermal range.[1,2] PC had been popular for the production of electronic devices housing and instrumental panels, optical lenses, transparent building constructions, decorative laminates, protective shields, packaging films, domestic appliance etc.[1,2] Low water absorption, ease of sterilization and biocompatibility of PC have led to its use in a wide range of medical equipment, including critical medical devices.[1–3]

It is well known that the plastic material surfaces can be quickly contaminated with pathogens like bacteria, mildew and fungi when contacted with humid environment or when operated in climate controlled conditions. The microbial growth on polymeric surfaces leads to the odours development, staining, as well as deterioration of their functionality. The microbial transfer is typical for articles handled by many people, such as mobile phones housing, touch-screen displays, computer keyboard etc. The prevention of biofilm formation on the internal medical devices is also of great importance since it can initiate a degradation process of the material, as well as cause infections and health related problems.[4]

There is an increasing interest in the development of PC having antimicrobial properties for its use in the field of health protection, in consumer goods production, food industry etc. To obtain antimicrobial properties, polymers are usually compounded with organic or inorganic biocides.[4–7] However, the use of organic biocides as additives for PC is significantly limited due to their insufficient thermal stability in the temperature range used for PC processing (300–320°C).

Today silver or silver-ion containing nanoparticles are considered the most efficient antimicrobial additives for various thermoplastic polymers including PC because of the broad spectrum of biocide effect, as well as excellent thermal stability and high migration resistance out of polymer matrix.[7,8] The

small size and high specific surface area make silver nanoparticles extremely reactive on the environment.[4] However, the presence of silver nanoparticles in PC may cause its discoloration during melt processing.[8] The antimicrobial PC films with excellent melt stability and colour retention are developed when using silver sodium zirconium phosphate.[8] The incorporation of silver-ions into zeolite particles, which then are mixed with the polymer, is another successful approach to obtain PC/silver composites.[9] However, as zeolite is a hydrophilic material, it may influence the thermal and chemical properties of the polymer matrix.[10] Thus, in spite of high biocidal efficacy of silver-based compounds, the development of new low-toxic and low-cost antimicrobial additives for PC is of great practical importance.

Until recently, ionic liquids (ILs), which are also called as "molten salts" and "green solvents," became widely used in polymer science as media for various types of polymerization processes, as well as components of the polymer matrix.[11] Besides ILs are considered very promising external modifiers for various thermoplastic polymers and can act as ion conducting electrolytes, plasticizers, antistatic agents, flame-retardants, lubricants etc.[11–16] ILs have numerous advantages such as extremely low vapour pressure, high thermal stability, ionic conductivity, non-flammability, low toxicity etc.[12] The antimicrobial properties of water soluble ILs based on alkyl-substituted imidazolium cation have been already reported in the literature.[17–19] It has been found that 1-alkyl-3-methylimidazolium ILs with alkyl chain length from 6 to 16 carbon atoms had significant antimicrobial activity against Gram-positive bacteria, Gram-negative bacteria and fungi.[17,18] Water soluble 1-butyl-3-methylimidazolium tetrafluoroborate, as well as water immiscible 1-butyl-3-methylimidazolium hexafluorophosphate are also found to have substantial inhibitory effect on the growth of microorganisms.[20] Moreover, 1-alkyl-3-methylimidazolium chloride ILs were found to possess broad spectrum of antibiofilm activity against a panel of clinically significant microbial pathogens.[19,21]

Various imidazolium-containing polymers, including polyamides and polyurethanes, have been described as very promising for biology and material science applications.[22] Successful approach to impart antibacterial properties to polyesters [polyethylene terephthalate (PET), polybutylene terephthalate (PBT)] has been developed using reactive imidazolium ILs as comonomers.[23,24] In this study, PET internally modified with ILs 1,3-bis(2-hydroxyethyl) imidazolium salts (chloride, tetrafluoroborate, hexafluorophosphate) was synthesized by condensation copolymerization method. The obtained PET/IL materials were found to have good antibacterial performance when contained from 2 to 10 molar percent of ILs. Moreover, the thermal stability of PET material was shown to be enhanced by copolymerization with IL monomers.[23] Random and telechelic imidazolium ionomers have been synthesized with ionic groups covalently and ionically bonded to the PBT backbone.[24] It was found that the introduction of 2 molar percent of imidazolium cations with hexadecyl radical into PBT backbone as a comonomer or end groups impart it pronounced antibacterial activity against *E. coli* and *S. aureus* strains.[24]

Thus, it can be supposed that imidazolium-based ILs may act as promising antimicrobial additives for PC. However, 1-alkyl-3-methylimidazolium ILs with halide anions are water soluble and begin to decompose starting from 240°C[25,26] that makes such biocides unsuitable for the melt processing with PC. It is clear that such additives can be introduced into PC only by solvent casting. For example, electrospinning of PC/chloroform solution with quaternary ammonium IL benzyl triethylammonium chloride was investigated to develop antimicrobial nanofibrous membranes for ultrafiltration.[27] It was shown that such kind of membranes exhibited good filtration efficiency and excellent antimicrobial properties.

It is known that ILs based on alkyl-substituted imidazolium cations and fluoro-containing anions are commonly water immiscible and have much higher thermal decomposition temperature.[25,26,28] For example, 1-alkyl-3-methylimidazolium tetrafluoroborate ILs are thermally stable to at least 360°C.[25,28] Such compounds become water immiscible when alkyl chain length is not less than 6.[25] Therefore, the aim of the present study was to evaluate antimicrobial properties, as well as thermal stability of PC modified with water immiscible 1-alkyl-3-methylimidazolium tetrafluoroborate ILs.

EXPERIMENTAL

Materials

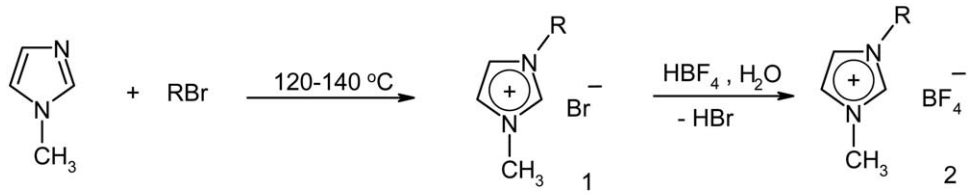
The following chemicals were used for the synthesis of ILs: 1-methylimidazole, 1-bromohexane, 1-bromoheptane, 1-bromooctane (Fluka), 1-bromododecane (Sigma-Aldrich), tetrafluoroboric acid (50% in H_2O, Fluka), ethyl acetate, methylene chloride (Fluka), and sodium sulfate (anhydrous, Sigma-Aldrich). The chemicals were used as received. Polycarbonate Makrolon 3108 was kindly supplied by Bayer MaterialScience AG.

Synthesis of Ionic Liquids

A series of 1-alkyl-3-methylimidazolium ILs (Scheme 1) was synthesized using the methods described in the literature.[29,30]

1-Hexyl-3-methylimidazolium Tetrafluoroborate (C_6C_1IM-BF_4). A flat-bottomed flask equipped with magnetic stirring bar was charged with 1-methylimidazole (10 g, 0.12 mol) and 1-bromohexane (25 g, 0.15 mol) under an argon atmosphere. The mixture was heated to 140°C under constant stirring for 2 h and then cooled to room temperature. The light yellow viscous liquid was washed with ethyl acetate (3 × 70 mL) to remove unreacted initial compounds. The obtained IL (1-hexyl-3-methylimidazolium bromide) was dissolved in water (80 mL) followed by addition of tetrafluoroboric acid (20 mL). The mixture was stirred for 4 h. The formed bottom layer of obtained IL C_6C_1IM-BF_4 was extracted with methylene chloride (100 mL) and dried with sodium sulfate. The solution was filtered followed by solvent distillation. The obtained IL was dried in vacuum 1 mbar at 70–80°C for 12 h.

^{1}H NMR (400 MHz, DMSO-D_6): $\delta = 0.86$ (*t*, 3H, CH_3, $J = 7.2$ Hz), 1.258 (br. *s*, 6H, CH_2), 1.76 (*m*, 2H, CH_2), 3.84 (*s*, 3H, NCH_3), 4.14 (*t*, 2H, NCH_2, $J = 7.2$ Hz), 7.67–7.75 (*m*, 2H, NC(H)C(H)N), 9.06 [*s*, 1H, NC(H)N].



Scheme 1. Synthesis of 1-alkyl-3-methylimidazolium tetrafluoroborate ILs.

^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -147.3$.

1-Heptyl-3-methylimidazolium Tetrafluoroborate (C_7C_1IM-BF_4). The mixture of 1-methylimidazole (10 g, 0.12 mol) and 1-bromoheptane (25.1 g, 0.14 mol) was heated at 140°C with constant stirring under an argon atmosphere for 2 h. Further procedures were the same as those in the case of C_6C_1IM-BF_4.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (*m*, 3H, CH_3, $J = 7.2$ Hz), 1.26–1.31 (*m*, 8H, CH_2), 1.84 (*m*, 2H, CH_2), 3.94 (*s*, 3H, NCH_3), 4.16 (*t*, 2H, NCH_2, $J = 7.2$ Hz), 7.27–7.38 [*m*, 2H, NC(H)C(H)N], 8.76 [*s*, 1H, NC(H)N].

^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -151.7$.

1-Octyl-3-methylimidazolium Tetrafluoroborate (C_8C_1IM-BF_4). 1-Bromooctane (27 g, 0.14 mol) was added to the stirred 1-methylimidazole (10 g, 0.12 mol) under an argon atmosphere. The mixture was heated at 140°C for 2 h until the formation of goldish transparent phase was observed. The obtained viscous liquid was cooled to room temperature and washed with ethyl acetate-hexane mixture [3 : 1 (v/v), 3 × 70 mL]. Residual solvents were removed at reduced pressure and the obtained IL was dissolved in 120 mL of water. Tetrafluoroboric acid (20 mL) was added to the solution followed by stirring for 1 h. The formed water immiscible layer was extracted with methylene chloride (2 × 100 mL) and dried with sodium sulfate. The solvent was distilled off and IL was dried in vacuum 1 mbar at 70–80°C for 12 h.

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.86$ (*t*, 3H, CH_3, $J = 7.2$ Hz), 1.25–1.31 (*m*, 9H, CH_2), 1.86 (*m*, 3H, CH_2), 3.94 (*s*, 3H, NCH_3), 4.16 (*t*, 2H, NCH_2, $J = 7.2$ Hz), 7.27–7.38 [*m*, 2H, NC(H)C(H)N], 8.78 [*s*, 1H, NC(H)N].

^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -151.4$.

1-Dodecyl-3-methylimidazolium Tetrafluoroborate ($C_{12}C_1IM$-BF_4). The stirred mixture of 1-bromododecane (35 g, 0.14 mol) and 1-methylimidazole (10 g, 0.12 mol) was heated at 140°C for 2 h under an argon atmosphere. The obtained viscous liquid was cooled to room temperature and washed with hexane-ethyl acetate mixture [3 : 1 (v/v), 3 × 100 mL]. Residual solvents were removed at reduced pressure and IL was dissolved in 200 mL of water. Tetrafluoroboric acid (20 mL) was added to the solution followed by stirring for 1 h. The formed water immiscible layer was extracted with methylene chloride (2 × 100 mL) and dried with sodium sulfate. The solvent was distilled off and IL was dried in vacuum 1 mbar at 70–80°C for 12 h. The semi-solid product of light brown colour was obtained.

^{1}H NMR (300 MHz, DMSO-D_6): $\delta = 0.84$ (*t*, 3H, CH_3, $J = 7.2$ Hz), 1.25-1.31 (*m*, 16H, CH_2), 1.85 (*m*, 2H, CH_2), 3.84 (*s*, 3H, NCH_3), 4.14 (*t*, 2H, NCH_2, $J = 2$ Hz), 7.68–7.75 [*m*, 2H, NC(H)C(H)N)], 9.09 (*s*, 1H, NC(H)N).

^{19}F NMR (188 MHz, DMSO-D_6): $\delta = -148.2$.

Preparation of PC/IL Films

The composite PC/IL films were prepared by solvent casting from methylene chloride solution with polymer concentration 10 g/100 mL and IL content 1–5 wt % by weight of PC. The well mixed PC/IL solution was cast on a glass plate followed by solvent evaporation at 25°C to obtain the composite PC/IL film 50–60 μm thick. The samples were dried in vacuum 1 mbar at 80°C for 24 h.

Characterization

Thermal gravimetric analysis (TGA) data for ILs and composite PC/IL films were obtained using TGA Q500 thermogravimeter (TA Instruments). About 10 mg of each sample were heated from 30°C to 650°C with the heating rate of 10°C/min under a nitrogen atmosphere (flow rate was 90 mL/min).

Morphological characterization of PC/IL films was carried out by scanning electron microscopy (SEM) using a scanning electron microscope (Carl Zeiss EVO® 40 EP). The samples were being kept in a desiccator with P_2O_5 for 2 weeks to ensure that no water was present in the sample. The films were frozen in liquid N_2 and cryofractured to observe the cross-section of the samples. Both surfaces and the cross-section of the films were fixed on carbon scotch, then coated with carbon and observed using the accelerating voltage of 15 kV.

Water contact angle measurements (CAMs) for PC/IL films were determined using a goniometer Multiskop (Optrel, Germany) by the sessile drop method. The contact angle was estimated as the tangent normal to the water drop (3 μL) at the intersection between the sessile drop and the polymer surface by CAM software. All reported contact angles are the average of at least five measurements taken at different locations on the polymer surface.

Antimicrobial Properties of PC/IL Films

The microbiological investigations of the PC/IL films were carried out using a standard *Escherichia coli* strain GM 2163. The overnight culture was cultivated at 37°C in 5 mL of Luria-Bertani (LB) broth (composition per liter: 5 g yeast

Table I. TGA Data for 1-Alkyl-3-methylimidazolium Tetrafluoroborate ILs

IL	$T_{\Delta m=5\%}$ (°C)	$T_{\Delta m=10\%}$ (°C)	$T_{\Delta m=20\%}$ (°C)	$T_{\Delta m=50\%}$ (°C)
HexMIM-BF_4	367	408	426	453
HepMIM-BF_4	373	415	434	467
OMIM-BF_4	345	396	417	462
DMIM-BF_4	330	362	408	451

extract, 10 g tryptone, 10 g NaCl (pH 7.5))[31] sterilized by autoclaving on wet cycle 20 min at 15 psi to a concentration of 10^8 cell forming units (CFU) per ml (optical density of 0.2 at 620 nm). PC/IL films (55 mm in diameter) were sterilized before use. Fifty microliter of a bacteria suspension were spread over the polymer surface. The bacteria were incubated for 2 h whereupon they were transferred on the LB agar (containing 1 L of LB broth and 15 g of agar) by imprint method. Then, LB agar medium was incubated at 37°C for 24 h. The antimicrobial activity of PC/IL films was evaluated by the calculation number of living bacteria (N) taking into consideration the possible overlapping of the colonies according to the following equation:

$$N = N_{obs}\left(1 - \frac{q \cdot N_{obs}}{0.503 \cdot S}\right)^{-1},$$

where N_{obs} is the number of counted CFU, q is the colony area (cm^2), S is the print area (cm^2). The maximal part of the area occupied by non-overlapping colonies is equal to 0.503, as at random distribution of the discs fixed on the surface.[32] The neat PC film was used as a reference. The measurements were performed in triplicate for each polymer film.

RESULTS AND DISCUSSION

Thermal Stability of PC/IL Composites

The obtained TGA data for ILs are summarized in Table I. All synthesized 1-alkyl-3-methylimidazolium tetrafluoroborate ILs have the thermal decomposition points (which were defined as the temperature of 5% weight loss) in the range of 330–373°C under an air atmosphere that is in good agreement with the literature data.[25,28] Some decrease of the thermal stability of ILs with longer alkyl chains is observed.

TGA curves obtained for PC/IL composites under a nitrogen atmosphere are presented in Figure 1. As one can see, the pure PC shows no weight loss up to 400°C and starts to degrade at the temperature close to 436°C in a single step with the maximum weight loss rate occurs at 501°C (Figure 1). However, PC/IL composites have considerably lowered thermal degradation points showing two-step degradation process for all studied ILs [Figure 1(a) and Table II]. The first step occurs at about 300–350°C and the second one—close to 400°C. The decomposition step at about 300–350°C can be attributed to the PC chemical degradation caused by the products of IL initial thermal degradation.[33] Under an air atmosphere PC/IL samples start to decompose in the similar temperature range (not shown). Thus, one can conclude that the degradation of PC/IL composites does not proceed by thermo-oxidative

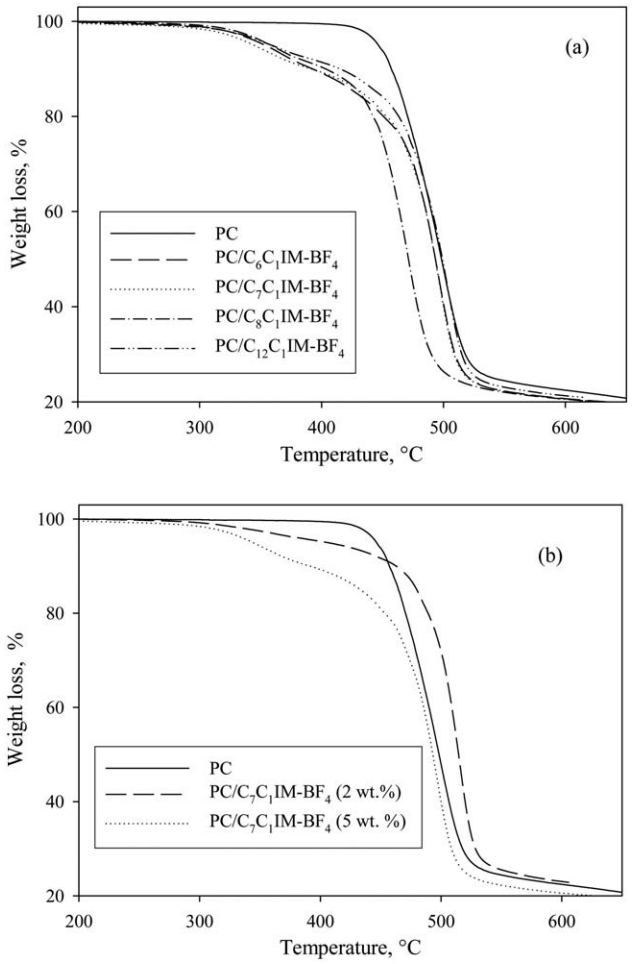


Figure 1. TGA curves of PC/IL composites under a nitrogen atmosphere: (a) as a function of IL and (b) as a function of IL content for C_7C_1IM-BF_4.

mechanism. Moreover, there is a little difference between thermal degradation points of PC samples containing ILs with various alkyl chains (Table II).

The influence of the IL content on the thermal stability of the PC/IL composite has been also investigated using C_7C_1IM-BF_4 [Figure 1(b)]. In the case of PC containing 2 wt % of IL, the first step at about 320°C is less pronounced and the thermal decomposition point is shifted by ~60°C to a higher temperature region in comparison with PC containing 5% of IL [Figure 1(b) and Table II].

The obtained TGA data indicate that PC/IL composites have good thermal stability for the melt processing, especially at low IL content.

Morphology and Surface Properties of PC/IL Films

Morphological aspects were studied by SEM measurements to evaluate homogeneity of PC–IL composites. Figure 2 shows SEM images of both surface and the cross-section for the composite PC/C_7C_1IM-BF_4 films with different IL content. The neat PC film demonstrates a relatively smooth surface without any pin-pore existed, and no cavities in the cross-sectional view [Figure 2(a)]. The similar morphology presented in Figure 2(b,c)

Table II. TGA Data for PC/IL Composites Containing 5 wt % of ILs

	$T_{\Delta m=5\%}$ (°C)		$T_{\Delta m=10\%}$ (°C)		$T_{\Delta m=20\%}$ (°C)		$T_{\Delta m=50\%}$ (°C)	
PC composition	Air	Argon	Air	Argon	Air	Argon	Air	Argon
Neat PC	410	446	440	457	460	470	480	498
PC/C_6C_1IM-BF_4	362	353	374	392	398	451	445	493
PC/C_7C_1IM-BF_4[a]	387	406	412	463	432	489	464	515
PC/C_7C_1IM-BF_4	353	344	368	391	410	453	464	493
PC/C_8C_1IM-BF_4	357	358	371	403	388	442	430	471
PC/$C_{12}C_1$IM-BF_4	361	359	393	415	426	463	483	499

[a] IL content 2 wt %.

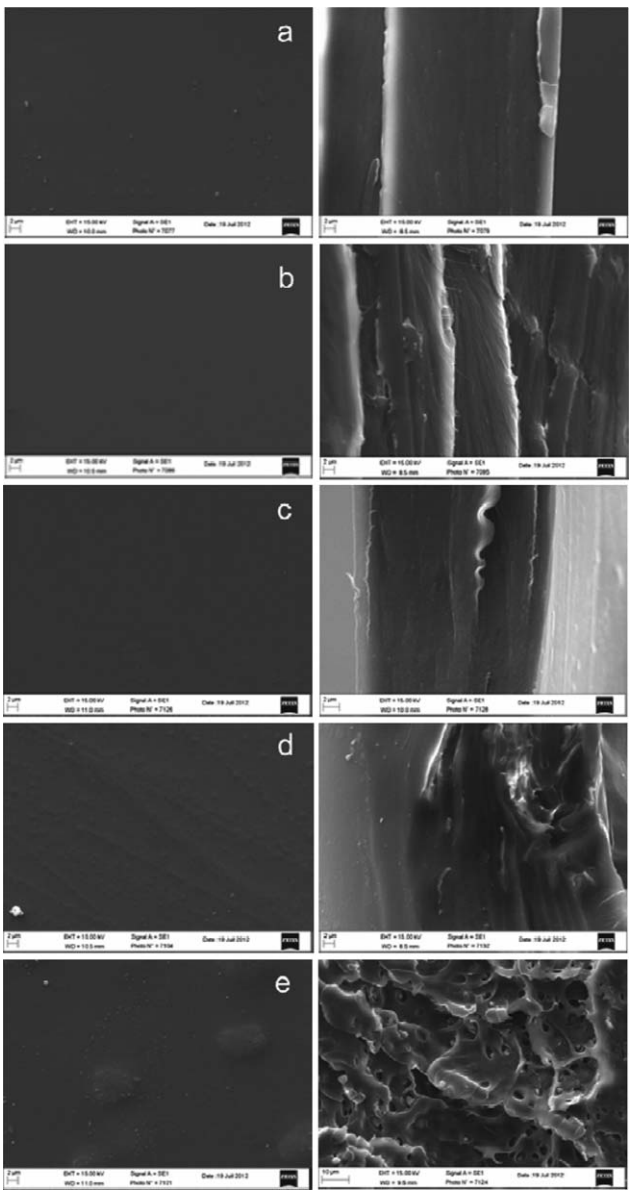


Figure 2. SEM images of both surface and cross-section of PC/C_7C_1IM-BF_4 films with the different content of IL: (a) neat PC, (b) 2 wt % of C_7C_1IM-BF_4, (c) 3 wt % of C_7C_1IM-BF_4, (d) 4 wt % of C_7C_1IM-BF_4, (e) 5 wt % of C_7C_1IM-BF_4.

testifies to the good dissolution of IL in PC matrix at low IL content of 2 and 3 wt %. However, with the further increase of the IL content in the polymer film, a coarse aspect can be seen that becomes more obvious when the IL concentration increases. In addition some particle-like substances can be observed on the surface (Figure 2(d,e)]. As it can be seen, starting from 4% of IL in the composite film, more distribution of IL entrapments is present and IL tends to aggregate. More aggregations appear with increasing of the IL content. The same morphological features were observed for the other studied ILs. There were many rugged cavities in the cross-sectional view for the composite film with 5% of IL that indicates the phase separation (Figure 2(e)].

Water contact angle values of PC/IL films are presented in Table III. It can be seen that PC surface become more hydrophilic when modified with 5% of C_6C_1IM-BF_4 and C_7C_1IM-BF_4 IL. An increase of the contact angle was observed for polymeric films containing ILs with longer alkyl radicals which make PC surface more hydrophobic.

Antimicrobial Activity of PC/IL Films

The results of microbiological investigations of PC films containing ILs are presented in Figures 3 and 4 and Table IV. Figure 3 contains photos of LB agar surface on which bacteria *E. coli* were transferred and cultivated after 2 h contact with PC/IL films surfaces.

Continuous growth of bacterial colonies on all over nutrient medium was observed after contact with neat PC films [Figure 3(a)]. The marginal decrease of bacterial colonies number took place when used PC films containing 2 wt % of IL [Figure 3(b) and Table IV]. Further increase of IL content in PC films led to more pronounced antimicrobial effect. Thus, the noticeable depression of bacterial culture growth was detected after its contact with polymeric films

Table III. Water Contact Angle of PC Films Containing 5 wt % of ILs

Sample	Water contact angle θ, (°)
Neat PC	76 ± 1
PC/C_6C_1IM-BF_4	65 ± 2
PC/C_7C_1IM-BF_4	72 ± 2
PC/C_8C_1IM-BF_4	78 ± 2
PC/$C_{12}C_1$IM-BF_4	82 ± 2

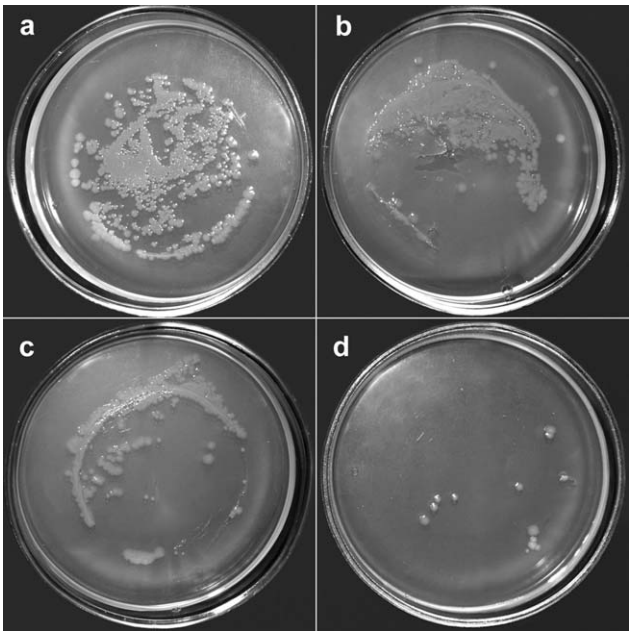


Figure 3. Bacterial colonies (*E. coli*) grown on LB agar after 2 h contact with PC/IL films: (a) neat PC, and PC/C_7C_1IM-BF_4 films with IL content 2 wt % (b); 3 wt % (c); 4 wt % (d).

comprising 3% of IL [Figure 3(c)]. For such PC/IL compositions the total number of viable colonies on agar surface was only 9–13% from control value (Table IV). The growth of only single colonies was observed on the agar medium when the test culture contacted with PC films containing 4% of IL [Figure 3(d)]. Finally, addition of 5% of IL into PC films fully inhibited growth of tested microorganism [Figure 4(b) and Table IV].

The obtained results are in good agreement with the data reported for antimicrobial activity of other imidazolium-based IL, particularly, water soluble 1-butyl-3-methylimidazolium tetrafluoroborate, as well as water insoluble 1-butyl-3-methyl imidazolium hexafluorophosphate.[20] Thus, it was found that both ILs have substantial inhibitory effects on the growth of *E. coli* bacteria. The minimal inhibitory concentrations of the said ILs on *E. coli* growth was between 0.7 and 1% (v/v), whereas no further bacterial growth was observed in the presence of 4% (v/v) of IL.[20] Although 1-butyl-3-methyl imidazolium hexafluorophosphate is water immiscible, thorough shaking of the culture ensured direct contact of the bacterial

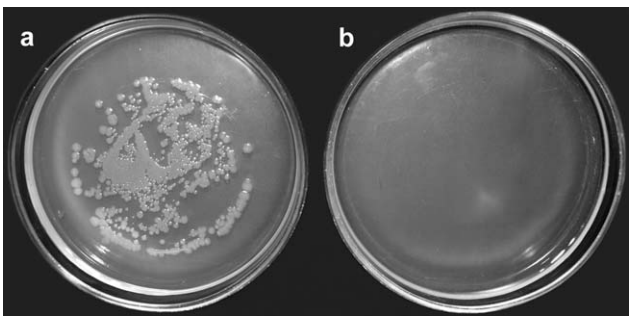


Figure 4. Bacterial colonies (*E. coli*) grown in LB agar after 2 h contact with (a) neat PC and (b) PC/$C_{12}C_1$IM-BF_4 film with IL content 5 wt %.

Table IV. Number of Colony Forming Units Grown in LB Agar After 2 hours Contact with PC/IL Films

	IL content in PC film (wt %)				
Sample	0	2	3	4	5
PC/C_6C_1IM-BF_4	720.32	280.45	98.67	6.57	0
PC/C_7C_1IM-BF_4	720.32	242.66	86.35	9.38	0
PC/C_8C_1IM-BF_4	720.32	310.75	65.24	5.05	0
PC/$C_{12}C_1$IM-BF_4	720.32	290.47	72.15	8.85	0

cells and IL. It should also be noted that polyesters (PET, PBT) internally modified with imidazolim ILs showed pronounced antibacterial activity at low ILs content (2%).[23,24] Such approaches are reported as more effective that blending to obtain more stable polymer composite.[23,24] However, an external modification of PC with ILs is more simple and low-cost method to impart antimicrobial properties that is important from the practical point of view.

On the whole, PC compositions, containing equal content of different ILs, showed similar inhibitory effect on *E. coli* growth (Table IV), although pronounced alkyl chain effect of imidazolium cation of ILs on their antimicrobial activity has been reported.[17–19] Probably, it can be explained by different surface properties of PC/IL films as well as different release rates of ILs into agar medium. Thus, it can be supposed that the more active but more hydrophobic IL, comprising longer alkyl chains have lower release rate from PC film than IL with shorter alkyl radicals. Moreover, the presence of ILs produced the changes in the surface properties of the composite film such as its wettability (Table III). As one can see, longer the alkyl chain of imidazolium cation is, more hydrophobic surface, i.e., higher water contact angle, is. In general, hydrophobic surfaces are considered less resistant to bacterial adhesion than hydrophilic, providing more favorable sites for colonization.[34] In any case, the best results were obtained with the higher IL content in the PC film (4 and 5%), showing high antibacterial efficacy of the PC films with imidazolium-based ILs against *E. coli* bacteria.

CONCLUSIONS

Water immiscible 1-alkyl-3-methylimidazolium tetrafluoroborate ILs (where alkyl is hexyl-, heptyl-, octyl-, and dodecyl-) were synthesized by the alkylation of 1-methylimidazole with corresponding bromoalkane followed by the anion metathesis with tetrafluoroboric acid. The thermal decomposition temperature of all studied ILs is significantly above 300°C, which is the melt processing temperature of PC. The composite PC/IL films were prepared by solvent casting and characterized in terms of their morphology, thermal stability, and antimicrobial activity against *E, coli* bacteria. SEM images of the PC/IL films have shown their homogeneity in the case of IL content from 2 to 4 wt %. However, for the PC/IL film with 5% of IL the phase separation, caused by IL aggregation, was observed. The PC/IL compositions were found to have reduced thermal decomposition points in comparison with neat PC, but still above 300°C.

The polymer films based on PC and ILs shown high activity against *E. coli* bacteria with a clear dependence on the IL content. PC films containing 3% of IL have substantial inhibitory effect of the bacteria growth reducing the number of survival bacteria colonies on at least one order of magnitude. The composite PC/IL films with 5% of IL after only 2 h of contact killed 100% of the bacteria showing excellent antimicrobial efficacy compared with neat PC.

Thus, it can be supposed that 1-alkyl-3-methylimidazolium tetrafluoroborate ILs are promising antimicrobial additives for PC resins, combining low cost, low water solubility and good thermal stability. Such biocides are suitable for the obtaining of solvent cast PC-based films or coatings. However, it is necessary to investigate the chemical stability of PC under the influence of ILs at the melt processing conditions. Therefore, rheological investigations of PC containing different ILs will be performed in the future to determine their processability by common forming methods.

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