



# Structures, properties and applications of the polyurethane ionomers

Piotr Król<sup>1,\*</sup> and Bożena Król<sup>1</sup>

<sup>1</sup>Department of Polymer and Biopolymer, Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszow, Poland

Received: 28 May 2019

Accepted: 22 August 2019

Published online:

3 September 2019

© The Author(s) 2019

## ABSTRACT

On the basis of the reports from 2010 to 2018, the chemical structure, production methods and applications of polyurethane ionomers were reviewed. The paper presents ionogenic reagents and counterions responsible for the incorporation of anionic and cationic groups into polyurethane chains and the resulting physicochemical properties of these polymers. The most important applications of synthesized ionomers as a waterborne polyurethane, elastomer materials, biomaterials and materials for special applications (electronics, nanocomposites) were presented.

## Abbreviations

PU	Polyurethane	MDEA	N-methyldiethanolamine
PUI	Polyurethane ionomer	NBDA	N-butyldiethanolamine
PUD	Polyurethane dispersion	BD	1,4-Butanediol
WPU	Waterborne polyurethane	TFBD	2,2,3,3-Tetrafluoro-1,4-butanediol
HMDI	4,4'-Methylene bis(cyclohexyl isocyanate)	HEMA	2-Hydroxyethyl methacrylate
MDI	4,4'-Methylenebis(phenyl isocyanate)	TEA	Triethylamine
HDI	1,6-Hexamethylene diisocyanate	EDA	Ethylenediamine
IPDI	Isophorone diisocyanate	DETA	Diethylenetriamine
PTMO	Polytetramethylene glycol	THF	Tetrahydrofurane
PCD	Polycarbonate diol	NMP	N-methylpyrrolidon
POG	Polyethylene glycol	DMF	Dimethylformamide
PPG	Polypropylene glycol	DBTL	Dibutyltin dilaurate
PCL	Poly( $\epsilon$ -caprolactone) diol	PAni	Polyaniline
PLA	Poly lactide diol	GO	Graphene oxide
PDMS	Poly(dimethylsiloxane)	FSE	Free surface energy
DMPA	2,2-Bis(hydroxymethyl)propionic acid	$T_g$	Glass transition temperature
DMBA	2,2-Bis(hydroxymethyl)butyric acid	DSC	Differential scanning calorimetry
		TGA	Thermogravimetric analysis
		AFM	Atomic force microscopy analysis

Address correspondence to E-mail: pkrol@prz.edu.pl

## Introduction

In a review article on linear polyurethanes published by us in 2007, we presented, among others, the basic structures and methods for the production of polyurethane ionomers (PUIs) [1]. Since then, there have been many interesting reports developing this topic in the scientific reports and patents [2]. This is related to the progress in the production of new types of polyurethanes with a controlled structure in which polar ionic groups affecting the phase structure of PU elastomers and determining their dielectric and mechanical relaxations, ionic conductivity and hydrophilicity are key factors [3]. Those groups allow forming dispersions and emulsions in water, which was previously considered as unfavorable and even hostile to the classical methods of polyurethane synthesis. Due to versatile application and excellent properties of ionomers, they were employed in a wide range of fields such as coating, adhesive, ink, building materials, automotive, textile and biomaterials [4–6].

In addition, the presence of ionic groups causes additional structural implications which, through modifications of supramolecular structures, affect the phase structure of polyurethanes changing their thermal and mechanical properties. This created new possibilities for using PPI in polymeric materials engineering. In recent years, the most important applications for ionomers have been noted in electronics and medicine [7, 8]. It is impossible to discuss all these issues in one paper; however, it should be analyzed on an ongoing basis, in order to promote new PUI applications. In this paper, using our experience in the field of PUI synthesis and application, we have attempted to present the latest achievements (since 2010) concerning the structures, properties and applications of this type of materials. It is impossible to refer to the initial works on this subject in the turn of the years 1970s and 1980s which initiated research on water-dispersible polyurethane ionomers for coating, laminating or special materials for medicine [9–11].

## Structures of the polyurethane ionomers

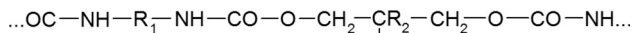
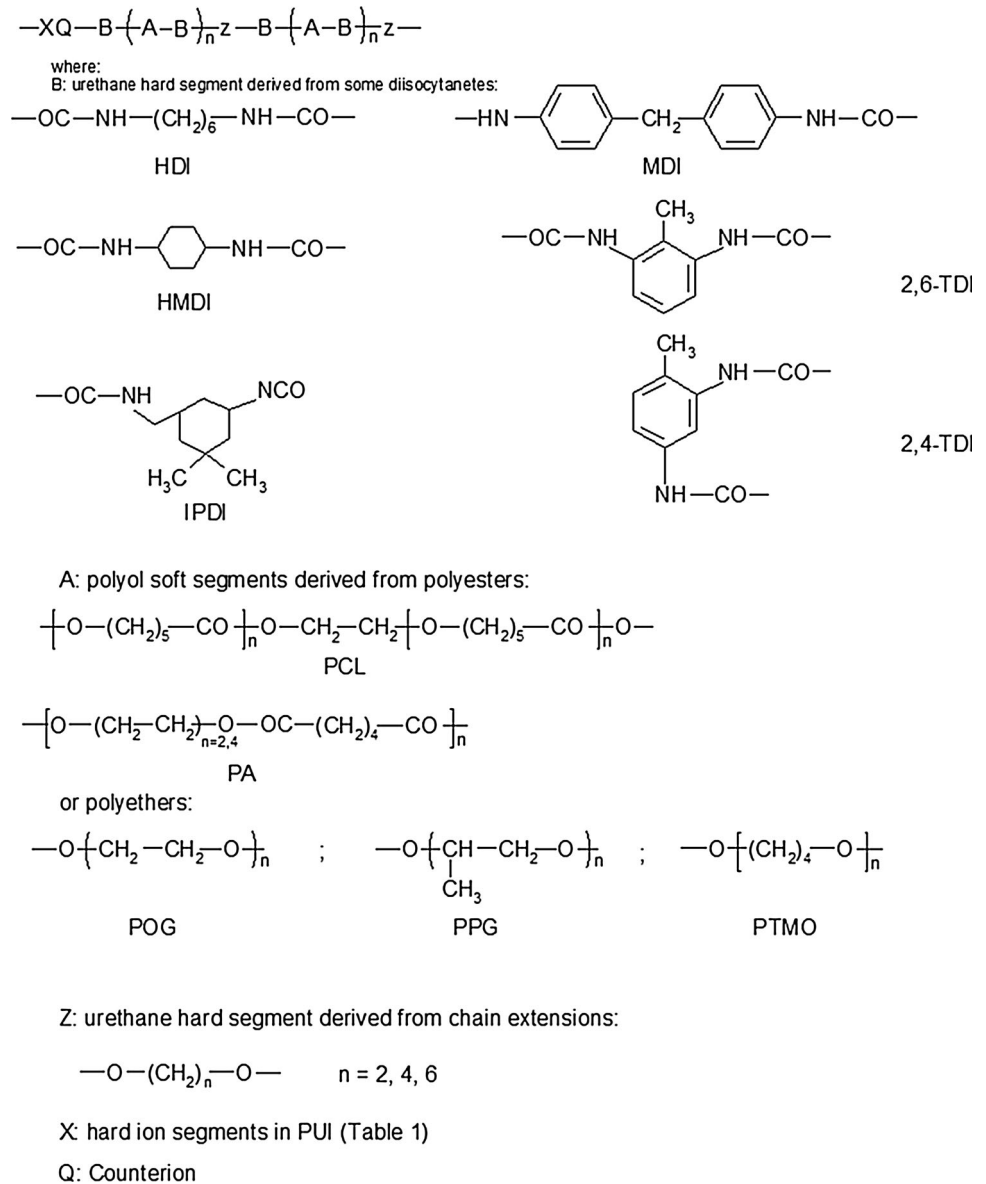
Among PUIs, polyurethane anionomers, polyurethane cationomers and polyurethane zwitterionomers should be distinguished. These polymers

have a typical segment structure specific to PU elastomers. In the polymer chain, hard and soft segments are alternately arranged. Hard segments consist of urethane moiety which resulted from the reaction of diisocyanates or isocyanate prepolymers with small-molecule chain extenders as dioles or polyhydric alcohols in partially cross-linked structures. When amines are used as extenders, hard segments contain urea linkages. Soft segments are composed of long-chain polyols with molecular weights ranging from several hundreds to several thousands. In comparison with rigid segments, whose structures are derived from several most commonly used diisocyanates, the soft segments are more diverse due to both the polyols structure (polyethers, polyesters, oligomeric fatty acid derivatives) and their molecular weights. A typical structure of polyurethane chains is shown in Fig. 1. In PUI, the structure is more complex due to the presence of polar anionic or cationic segments incorporated by new urethane bonds formed by the reaction of low molecular weight compounds with ion-forming functional groups: usually carboxylic or sulfonic groups in anionomers (Fig. 2) or ammonium groups in cationomers (Fig. 3). To date, a significant number of ionic reagents with appropriate counterions have been described in the literature. In anionomers, the most popular ion segment is produced with the participation of DMPA, while in cationomers with MDEA. Other segment structures present in anionomers are shown in Fig. 4 and in Table 1, while in cationomers in Fig. 5 and in Table 2.

The significance of these structures for selected applications of PU ionomers will be discussed in the subsequent chapters of this paper.

There are also polyurethane zwitterions containing anionic  $-\text{SO}_3\text{H}$  groups derived, for example, from 1,3-propane sultone and cationic groups derived from diols based on derivatives of heterocyclic compounds such as imidazolium or pyridine. The PUI structure, the method of incorporating ionic segments into the chain and the counterions kind determine PUI properties, including ability to form dispersions in polar solvents, e.g., in water or ionic conductance of formed coatings. This is due to the fact that in PUI additional hydrogen bonds and electrostatic interactions are present. In addition to PU-bonded hydrogen bonds formed between  $-\text{NH}-$  groups as donors and  $\text{C}=\text{O}$  groups in urethane segments or O-atoms in polyether segments or  $\text{C}=\text{O}$  groups in polyesters as acceptors, there is additional interaction

**Figure 1** Structures of the polyurethane ionomers.

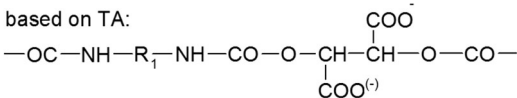


where:

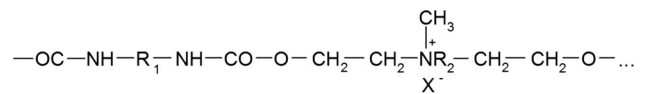
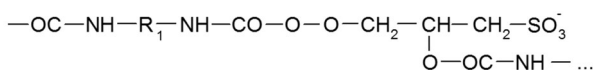
R<sub>1</sub>- structure from diisocyanate

R<sub>2</sub> = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> in DMPA or DMBA

based on TA:



based on 2-dihydroxypropylsulfonate:



where:

R<sub>1</sub>- structure from diisocyanate

R<sub>2</sub> :

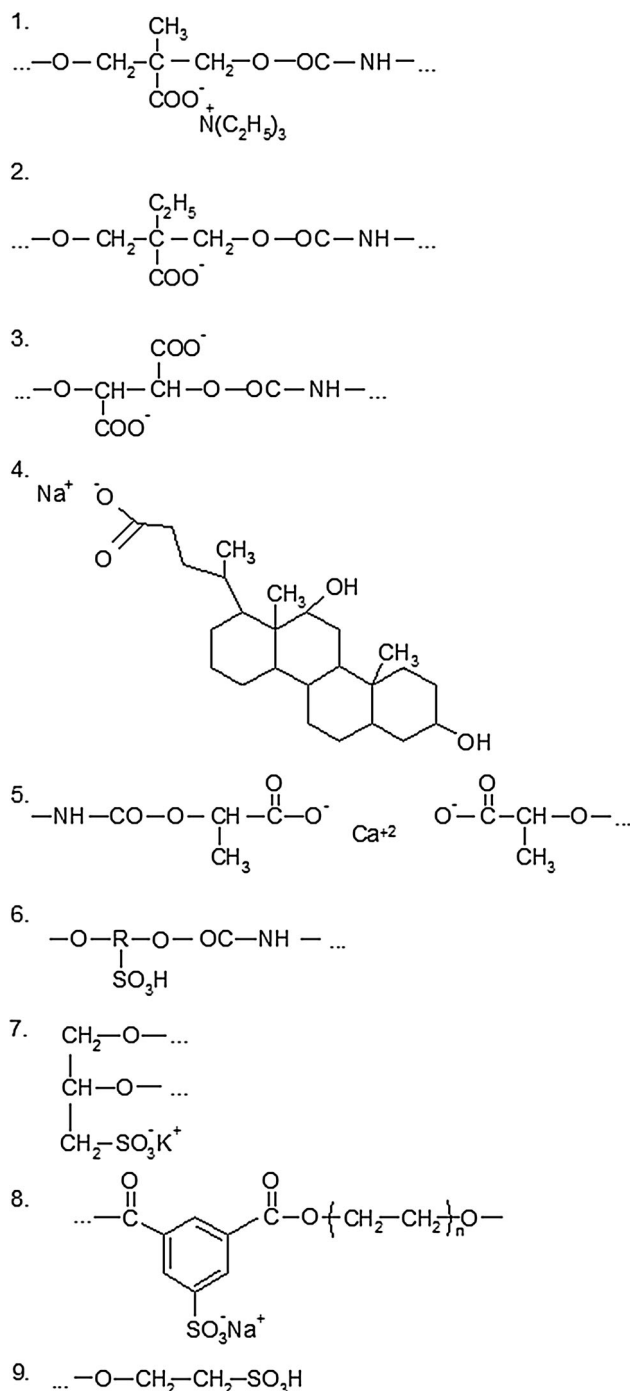
C<sub>n</sub>H<sub>2n+1</sub>    X = Br<sup>-</sup>, I<sup>-</sup>

H    X = R-COO<sup>-</sup>, Cl<sup>-</sup>

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup> in zwitterion

**Figure 3** Ionogenic segments of the polyurethane cationomers.

**Figure 2** Ionogenic segments of the polyurethane anionomers.



**Figure 4** Ionogenic segments in the polyurethane anionomers by Table 1.

involving ionic segments which may act as both donors and acceptors of additional hydrogen bonds. Ion segments also result in significant electrostatic interactions that strengthen the PU structure, contributing to the improvement in its thermal resistance and the increase in mechanical properties. An

increased tendency to create more ordered phases is not without significance, which can be observed in calorimetric and X-ray measurements [1].

## Waterborne polyurethane compositions

An important impulse for the development of waterborne polyurethanes was environmental requirements. The aim was to reduce the volatile organic compounds (VOCs) present in various varnishes, not only polyurethane, in favor of water systems. This topic is still widely presented in the literature and is the subject of numerous patent reports. It is impossible to omit it, especially since new interesting solutions have emerged in recent years.

The synthesis of PUI can be carried out as “prepolymer-ionomer” or “prepolymer mixing” process. These are multistage processes involving reaction of polyol with diisocyanate in the presence of a diol-containing acidic group (most often DMPA reagent in anionomers) or dihydroxy *N*-alkylammonium reagents (usually MDEA in cationomers), neutralizing the resulting urethane prepolymer terminated with  $\text{-NCO}$  groups with tertiary amine (in anionomers) or organic acid (in cationomers) and emulsifying the prepolymer-ionomer thus formed in water followed by reaction, for example, with 1,6-hexamethylenediamine. The disadvantage of this process is the need to dilute the viscous prepolymer-ionomer with acetone or THF. It is also possible prior to emulsifying the prepolymer in water to dilute the reaction mixture by adding a small amount of high boiling solvent (usually NMP is used for that purpose) before emulsifying it in water. Relatively slow reaction of free  $\text{-NCO}$  with water in such aqueous systems was confirmed by the same authors [48, 54].

PUI synthesis can also be carried out in bulk as described in Ref. [32]. PUI was obtained by the reaction of poly(1,4-butylene adipate glycol), polyether diol-containing sulfonate groups, BD and IPDI with a few drops of DBTL catalyst at 50–60 °C. The mixture was quickly transferred from the flask to molds, and these molds were put in an oven at 110 °C. Hereafter, the temperature was gradually increased up to 160 °C. The reaction was completed in 4–5 h. Products were removed from the oven and cooled to room temperature. PUI was cut into small pellets. Then, acetone (twice the quantity of PU) was

**Table 1** Most frequent employed ion segments in polyurethane anionomers

Type of ionogenic segments	Structure by Fig. 4	References
2,2-Bis(hydroxymethyl)propionic acid (DMPA)	1	[4–6, 8, 12–26]
2,2-Bis(hydroxymethyl)butyric acid (DMBA)	2	[27]
Tartaric acid	3	[28]
Sodium deoxycholate (SD) 3 $\alpha$ , 12 $\alpha$ -dihydroxy-5 $\beta$ -cholanolic acid sodium salt	4	[29, 30]
Calcium L-lactate	5	[31]
Polyether diol-containing SO <sub>3</sub> H groups	6	[3, 32]
2-Dihydroxypropylsulfonate	7	[7]
Bis(2-hydroxyethyl)-5-sulfoisophthalate sodium (hard segment) and POG-based sulfonated polyol (soft segment)	8	[33]
2-Hydroxyethanesulfonic acid (isethionic acid)	9	[34]
Sulfonated NH group in urethane	–	[35]

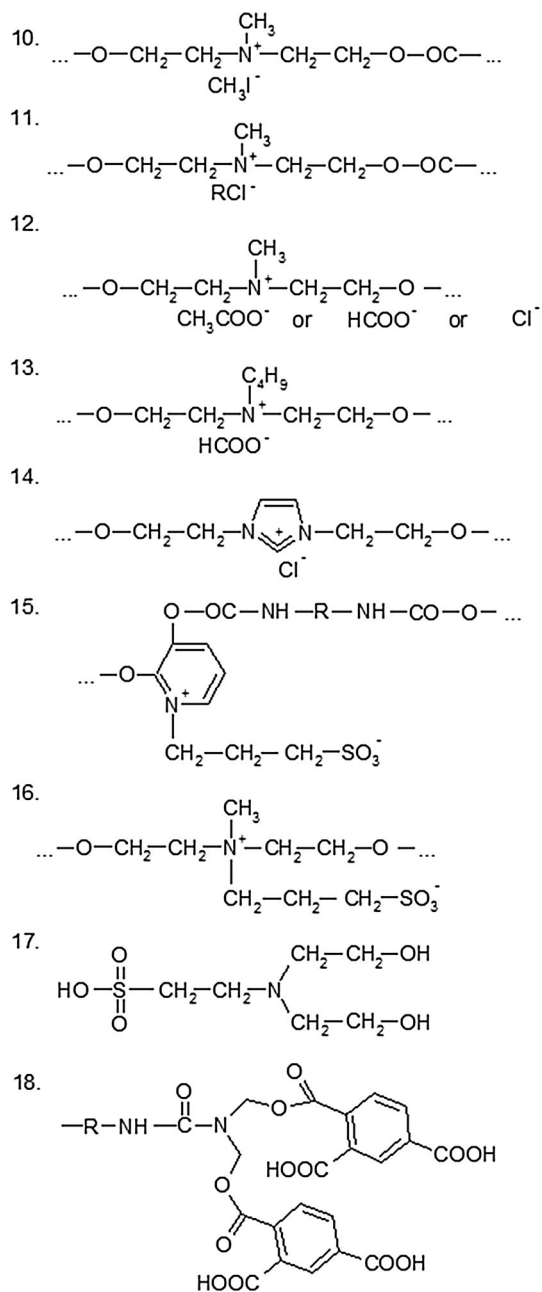
added to dissolve the solid polymer. When the pellets dissolved completely, specified quantity of water was added to disperse the polyurethanes ionomer solution. High solid content (around 50%) in PUDs was obtained after the acetone was evaporated.

Thus, both the type of raw materials and the polyaddition method determine the structure of the PUI. The type and amount of the introduced ionic reagent are also significant. It has been demonstrated that by synthesizing PU anionomer based on PCD, IPDI, DMPA reagents and TEA or EDA as counterions, by varying the amount of DMPA in the range of 4.5–10 wt%, we can modify the physicochemical properties of the dispersions as well as the morphology of the surface. It was the result of an increase in ionic interactions resulting in the increase in phase separation between hard and soft segments [26].

The results of model tests obtained on the basis of anionomer properties analysis based on PPG, IPDI and DMPA revealed that DMPA ionic reagent is crucial to obtain specific properties, such as solids content, viscosity, acid number and electrolytic stability of the PUDs [5]. It has also been demonstrated that the stability of PUDs increases with higher hydrophilic. It is a result of increasing zeta potential with increased DMPA/PPG molar ratio, which results in decrease in the average particle sizes and beginning of stabilization mechanism involving electrical double-layer formation. Crystallinity of the films was increased too with DMPA/PPG molar ratio due to the increase in interchain interactions through Coulombic interactions and hydrogen bonding. Consequently, crystalline melting temperature was

increased with the increase in DMPA/PPG molar ratio [14].

An important parameter that determines the application of coatings from PUI-based aqueous dispersions is their surface properties: wettability and free surface energy. Classical polyurethane coatings belong to hydrophilic materials, and the introduction of ionic segments further enhances these effects. FSE calculated by Owen–Wendt or by van Oss–Gooda methods on the basis of contact angle measurements with the use of standard liquids such as diiodomethane, formamide and water for common PU solvent-based PU coatings is 30–45 mJ/m<sup>2</sup>, while for coatings from PU cationomers 35–52 mJ/m<sup>2</sup> depending on polymer chain structure [44, 55]. In Ref. [23], an application of PUI coatings was reported for do covering of apolar polypropylene (PP). For this purpose in the first step, the PP samples were treated using oxygen and argon atmospheres. Afterward, a series of aqueous polyurethane–urea dispersions were synthesized as the novel polar coating for modified nonpolar polymers. The aqueous anionic polyurethane–urea dispersion (PUD) coating was synthesized in the reaction of the PTMO, IPDI and DMPA in NMP solution. Then, TEA was added to the mixture to neutralize the acid functional groups of DMPA. Finally, proper amount of deionized water was added dropwise into the system to obtain the PUD with 30 wt% solid content. In the final stage, the plasma-treated samples were coated by prepared PU anionomer. The results of *pull-off* analysis confirmed the significant role of the polyurethane as an extremely polar coating to create hydrogen bonding with



**Figure 5** Ionogenic segments in the polyurethane cationomers by Table 2.

functional groups on the surface of treated PP. The adhesion strength of PP increased from 0.04 to 0.61 MPa for neat and oxygen-based plasma-treated samples, respectively.

For many applications such as coatings for ceramic materials, textiles, paper or wood, it is necessary to increase the hydrophobicity of the coating. In the case of PUI, the increase in hydrophobicity can be achieved by several ways. The most effective method

is to introduce into the PU chains the segments containing fluorine atoms (e.g., TFBD). This monomer can be used both as a low molecular weight chain extension of isocyanate prepolymers and as an ingredient incorporated with the polyol system in the prepolymer synthesis step. FSE of the polyurethane cationomer coating which was synthesized in the reaction of MDI with POG 2000 or poly(tetrafluoroethyleneoxide-*co*-difluoromethylene oxide)  $\alpha,\omega$ -diisocyanate and MDEA as a result of the fluorine incorporated into cationomers (about 30 wt%) contributed to lower surface free energy values, down to about 15 mJ/m<sup>2</sup>. The introduction of Br<sup>-</sup> counterion from 1-bromobutane instead of the RCOO<sup>-</sup> derived from organic acid is also beneficial. That was achieved by gradual weakening of long-range interactions where dispersion interactions predominate [56]. Exact model tests showed that decrease in FSE by several mJ/m<sup>2</sup> for cationomer coatings can be also achieved by replacing MDEA by DMBA and by changing IPDI on MDI [44].

### Aqueous hybrid compositions based on the polyurethane ionics

The most important type of these products is urethane-acrylic polymers (PU-PA) dispersions synthesized mainly from PU anionomers. Incorporation of acrylic monomers into PUI chains is carried out in emulsion polymerization of acrylates in PUI aqueous dispersion. The hydrophilic-hydrophobic nature of PUI provides the possibility to form micelles, in which the elongation of polyacryl chains follows the free radical mechanism. Bonding of PU and PA chains can be achieved by extending the PUI prepolymer by HEMA. If unsaturated moieties are introduced in the structure of PUI, it can be cross-linked either by UV or through oxidative drying (self-cross-linking), which leads to improved mechanical strength and chemical resistance of films or coatings produced from such dispersions [57]. Multicomponent polymer dispersions made from PUI can be applied as adhesives, coatings and components of water-soluble varnishes [28]. In turn, article [16] describes sustainable WPU reinforced by poly(vinyl alcohol) (PVA). Composites were obtained by blending of PUI with 5 wt% PVA aqueous solutions. PUI was synthesized from castor oil, DMPA, MDI and TEA. The reinforcement effect was demonstrated

**Table 2** Most frequent ion segments in polyurethane cationomers and zwitterionomers

Type of ionogenic segments with counterion	Structure by Fig. 5	References
<i>N</i> -methyldiethanolamine (MDEA) + CH <sub>3</sub> I (as counter ion)	10	[36]
MDEA + RBr (R = C <sub><i>n</i></sub> H <sub>2<i>n</i>+1</sub> <i>n</i> = 2, 4, 6, 10)	11	[37]
MDEA + CH <sub>3</sub> COOH	12	[5, 38]
MDEA + HCOOH		[39–48]
MDEA + HCl		[49]
<i>N</i> -butyldiethanolamine + HCOOH	13	[41, 42]
1,3-Di(2-hydroxyethyl) imidazolium chloride	14	[50]
2,3-Dihydroxypyridine and 1,3-propane sultone, in PU zwitterionomer	15	[51]
MDEA + 1,3-propane sulfonate in PU zwitterionomer	16	[52]
<i>N,N</i> -bis(2-hydroxyethyl)-2-aminoethanesulfonic acid + ammonium counterion in zwitterionomer PU	17	[53]
MDEA + trimellitic anhydride + DMPA in zwitterionomer PU	18	[4]

by tensile test from the enhancement in Young's modulus and tensile strength. The UV/VIS spectra analysis suggested that the transparency of PVA was not influenced by incorporation of PU.

Interesting emulsifier for PUI compositions was obtained using DMPA or MDEA ionic reagents and sodium alginate (SA). Proper amounts of PUI and SA were mixed to obtain a number of aqueous PUI–SA elastomers. The cationic polyurethanes and their blends with sodium alginate showed excellent miscibility and higher elasticity, while the samples containing anionic polyurethanes and alginate proved poor compatibility and no significant miscibility. The morphology of alginate particles shifted nanoparticles to microparticles by changing the nature of PUI from cationic to anionic type. The final cationic elastomers not only showed better mechanical properties, but also were formulated easier than anionic samples. The hydrophilicity content of prepared polymers was examined by the measurement of formed contact angle between the surface of polymer samples and water drops. Due to the presence of hydrophilic functional groups in the backbone of alginate, it is expected that the hydrophilicity of blends should be higher compared to neat PUI. The values of measured contact angles confirmed the mentioned hypothesis. Difference in contact angle values between PUIs and their blends was attributed to the presence of carboxylate and hydroxyl groups of SA. In addition, all of the prepared samples were known as hydrophilic polymers because of contact angle values lower than 90° [6].

In turn, in the article [21], the two- or three-stage poly(urethane-dimethylsiloxane) anionomers (PU-

PDMS) synthesis processes were described with the use of IPDI and PTMO. PTMO was partially replaced by PDMS-diol, which has different chain structures. DMPA neutralized with TEA was used as the ionogenic component built into the polyurethane chain and EDA as the extender. The glass transition temperatures in the range of  $T_{g1} = -27$  to  $-30$  °C were ascribed to soft segments, transitions at  $T_{g2} = 52$ – $72$  °C, related to the phase transitions in hard segment domains. A particularly significant plasticizing effect was demonstrated by PDMS with two hydroxyl groups at one side of the chain.

The synthesis of waterborne polydimethylsiloxane–polyurethane cationomer composition was also successfully carried out. Different proportions of PDMS  $\alpha,\omega$ -diol modifier (0–7.3% by weight) were applied. DSC method was applied to the microstructural assessment of the obtained materials. A clear decrease in the degradation temperature with increased amount of incorporated PDMS indicates immiscibility part of the polysiloxane segments with soft segments derived from POG. Test results indicated that contact angle values rise with increasing content of the polysiloxane in the analyzed films [47].

### Application of polyurethane ionomers in elastomer materials

PU elastomers have already found a permanent place as construction materials in technical and medical applications. Among them, thermoplastic PU is the most important [58, 59]. Another major technological improvement in PU elastomers has risen from the

appearance of network-forming block copolymers. In this very active field of multiphase materials, telechelic polymers were crucial, especially in the synthesis of multiblock copolymers by step-growth processes. Hydroxyl-terminated, low molecular weight, aliphatic polyesters or polyethers have largely been used in the commercial production of thermoplastic polyurethane [60]. This is proven by the observed clear phase separations, as indicated by two areas of glass transition temperatures: in the range of negative Celsius temperatures associated with phase transitions within flexible segments and positive Celsius temperatures—with phase transitions within rigid segments. There is also crystalline phase which is visible in the wide-angle X-ray diffraction profiles. This phase is related to high Young's modulus (10 MPa) [33]. The large amount of polyurethane coatings based on the PUI described above exhibits features typical for elastomers [3, 6, 14, 26, 28, 32, 52, 61]. The effect of ionic group content on thermal, structural and shape memory properties of segmented polyurethane ionomers based on PCL, MDI, BD and DMPA neutralized with TEA was analyzed in detail in Ref. [15]. It was found that the ionomers with higher amount of ionic groups have relatively stronger tendency to crystallize. In addition,  $T_g$  of the soft segments had a large impact on the degree of phase separation, which was improved when the amount of ionization was higher than critical value. The difference in polarity of soft and hard phase upon ionization could be the driving force of increased phase separation. The results obtained from TGA analysis showed that the thermal stability of the ionomers was lower than that of the nonionomer sample. This phenomenon can be attributed to the reduction in hydrogen bond formation and decrease in cohesion in the hard domains of ionomers. In addition, ionic group content affected the shape recovery of the material, where this parameter rose with the increase in a number of ionic groups.

Chain extension of the polylactide diol (PLA)—prepared from lactide (LA) in the presence of MDEA as an initiator and Sn(Oct)<sub>2</sub> as a catalyst—with HDI has enabled the production of PLA-based poly(ester-urethane) elastomers with equally spaced tertiary amine groups. Treatment of the PU with iodomethane converted tertiary amine groups, which resulted in cationic ionomers. Hydrophilic and biodegradation properties of the coated elastomeric

PUI–PLA coatings were investigated. The thermal properties of the PU and PUI were similar. By contrast, the PUI exhibited higher tensile modulus than the starting PUs [36].

### Application of polyurethane ionomers as biomaterials

Polyurethane biomaterials play significant role in biomedical applications due to their mechanical and thermal properties. They are nonimmunogenic, chemically resistant in the environment of physiological fluids, nontoxic and sometimes even biocidal [8, 62]. Polyurethanes are extremely versatile, and therefore, their hydrophobicity/hydrophilicity, biocompatibility, biodegradability and ability to conjugate with proteins, drugs or biologically active substances can be successfully tailored by the introduction of various functional groups for diverse biomedical applications [63, 64]. This statement also applies to ionomers. For this reason, sodium deoxycholate as low molar mass chain extender was presented to prepare special polyurethane ionomers usable as biomedical devices. These polyurethane ionomers have identical hard segment containing bile salt moiety, with different soft-segment moieties. POG soft segment promotes stronger ionic interactions and solvation capacity of ions, and also higher ionic conductivity in these polyurethane ionomers [29]. Sodium deoxycholate-based poly(ester-ether)-urethane ionomers have also been obtained for the development of biomedical materials. The synthesized biocidal polyurethanes are effective in inactivation of examined bacteria strains: *Staphylococcus aureus*, *Sarcina lutea*, *Escherichia coli* and *Pseudomonas aeruginosa* [30, 65].

It has to be underlined that fluorinated waterborne shape memory poly(urethane-urea) (PUU) anionomers for potential medical implant application were also synthesized from PCL, perfluoropolyether (PFPE) diol, DMPA, IPDI, EDA and DETA. The effect of PFPE content in the soft segment, degree of cross-linking of the molecular structure and the properties of these PUU films were studied. The experimental results showed that switching temperature of PUU could be fine-tuned by PFPE mass percentage and EDA/DETA ratio in the range between 33 and 44 °C, covering the range of body temperature. Through the introduction of cross-linked structure, the strain



recovery rate could be retained above 90%, effectively compensating for the negative effect on shape memory performance brought by PFPE segments. This property is beneficial for applications as elastomeric device biomaterials [18].

The use of PU ionomers as biomaterials for the reconstruction of bone tissue is noteworthy. A calcium-containing monomer, namely calcium lactate, was used for the synthesis of calcium-containing polyurethane intended for use in biomedical applications. Ether-based PU was prepared using PTMO, HDI and calcium lactate. Their properties were compared with those of a control polyurethane sample without any metal. Because of ionic clustering in calcium lactate-incorporated ionic polyurethane, the mechanical properties and storage modulus were enhanced compared with those of nonionic polyurethane. An evaluation of blood–material interactions revealed that the material is biocompatible and it does not induce hemolysis [31].

Two types of polyurethane ionomers with different contents of carboxyl groups have been prepared and then used for hydrothermal synthesis of hydroxyapatite–polyurethane composites. Prior to composite preparation, polyurethane ionomers were subjected to hydrothermal treatment in order to verify the stability of polymeric structures in conditions of 20 atm pressure and 140 °C temperature. Compatibility of polyurethane ionomers and hydroxyapatite-based composites with mesenchymal stem cells has been assessed. Preliminary results of the *in vitro* tests showed positive effect on proliferation of mesenchymal stem cells on the surface of hydrothermally treated polymers and composites. The biological properties found make it possible to use these composites as bone replacement materials [66].

### Special applications of PU ionomers

In this chapter, attention has been paid to the less widespread applications of the PUIs described above. The chemical structure, diversity of hydrogen interactions and strong electrostatic interactions as well as the resulting phase-related fixation observed in polyurethane ionomers have created new possibilities of using these polymers as special materials in electronics and catalysis [3, 34, 38]. It was proved that the presence of charges trapped in functional groups

can be used to produce polymers with increased electrical conductivity.

Polyurethane carboxylate ionomers based on POG 600 with sodium and various ammonium, phosphonium and imidazolium cations are synthesized for systematic comparison of different cationic counterions. Generally, larger cations act as plasticizers, lowering  $T_g$  because of weaker Coulombic force for ion associations (acting as physical cross-links).  $T_g$  can be reduced from 47 to  $-6$  °C when replacing  $\text{Na}^+$  cation with large ether oxygen-containing ammonium without changing polymer composition, and the lower  $T_g$  can enhance ionic conductivity by five orders of magnitude. Ionic conductivity has a stronger correlation with segmental relaxation, suggesting that counterion motion is coupled to the POG local motions. Sodium counterions are mostly trapped by para-phenylene diisocyanate (PDI)–carboxylate–pPDI segments, whereas the larger counterions are less trapped. Cation species and methoxyalkyl tails were found to impact both conducting ion concentration and their mobility but  $T_g$  and  $R$ -relaxation time are the key factors for ionic conductivity at a given temperature [27].

Introduction of PANi which is able to transmit current increases the conductivity of composites based on sulfonate anionomer (PUSA) and para toluene sulfonic acid (PTSA). PANi has become one of the most studied conducting polymers due to the fact that it can be readily synthesized. HCl-doped PANi was synthesized by chemical oxidative polymerization of aniline in HCl, which was converted to PANi–emeraldine salt (EB) by treatment with  $\text{NH}_4\text{OH}$ . PTSA doped by PANi was synthesized from EB–PANi by redoping with PTSA solution. PUSA was synthesized from MDI, PPG 1000, BD and 2-dihydroxypropylsulfonate diol (SDOL). The composite was prepared by mixing of the solutions of two polymer components in DMF and then solution casting. The conductivity was found to increase by 100 times with concomitant decrease in percolation threshold when polyurethane was replaced by PUSA in the composite for the same amount of PANi. The composite film was thermally stable up to 300 °C [7].

New aqueous cationomeric polyurethane dispersions with PANi were synthesized by three-step reaction process. IPDI reacted with polyols, namely PPG 400, 1000 and 2000, to form prepolymers which were chain extended with MDEA. Quaternization and self-emulsification with deionized water resulted

in PUDs. Synthesized PUDs were used for blending with 2, 4 and 6 wt% of PANi–water dispersions to form new conductive composites. The obtained conductivity was in the range from  $1.2 \times 10^{-5}$  to  $3.7 \times 10^{-5}$  S/cm. These composites were evaluated for their corrosion protection abilities on mild steel panels by standard accelerated tests [49].

PU cationomers based on imidazolium diol and ionic liquid (IL) as chain extender of PU have also been obtained. It is important that casting of PU solutions with various contents of IL forms novel membranes. Thermal study reveals that IL-containing PU membranes exhibit a constant soft-segment  $T_g$  at  $-81$  °C; however, the  $T_g$  of imidazolium hard segments systematically shifts to lower temperatures with increasing IL content. This suggests that IL preferentially locates into the imidazolium ionic hard domains, which is also evident in small-angle X-ray scattering. Moreover, dielectric relaxation spectroscopy demonstrates increased ionic conductivity of PU membranes by five orders of magnitude upon incorporation of 30 wt% IL. IL-free HMDI cationomer membrane exhibited a low ionic conductivity on the order of  $10^{-11}$  S  $\text{cm}^{-1}$  at 20 °C which was significantly enhanced by five orders of magnitude upon incorporation of 30 wt% IL. Moreover, ionic conductivity of membranes with IL strongly depended on temperature. In the case of membrane with 30 wt% IL, ionic conductivity increased from the order of  $10^{-10}$  to the order of  $10^{-5}$  S  $\text{cm}^{-1}$  as temperature increased from  $-10$  to 100 °C [50]. The introduction of carbon nanotubes additionally increases the electrical conductivity of polyurethane coatings and independently contributes to the increase in thermal and mechanical properties, as demonstrated in few papers [13, 46].

Anionic waterborne polyurethane (aWPU) from IPDI, PTMO, DMPA, TEA and BD was synthesized. Cationic WPU (cWPU) was also prepared using MDEA and HCl instead of DMPA and TEA. Since the graphene oxide (GO) is anionic due to the  $-\text{COOH}$  group, GO and a WPU are compatible because of the repulsive forces between identical ionic charges. Thus, cationic surfactant-treated GO/aWPU to increase the compatibility was synthesized. cWPU/GO, where attractive forces act between anionic GO and cationic WPU, was also prepared. The thermal stability, glass transition temperature and mechanical properties of these nanocomposites were investigated. The thermal stability of the WPU was

enhanced after incorporation of GO nanosheets. The  $T_g$  of the hard segment of WPU was increased by the incorporation of GO. These results are attributed to the fine dispersion of GO in WPU and strong interfacial interactions between GO and WPU. Enhanced dispersion and interfacial interaction lead to better mechanical properties. Tensile strength, initial modulus and elongation at break of WPU/GO nanocomposites were increased with the incorporation of GO nanosheets. WPU/GO nanocomposites with enhanced stiffness and toughness can be prepared by a simple method (anion–cation matching) [13].

The electrical properties of polymer films obtained from polyurethane cationomers with 0–2 wt% graphene admixture were studied. The cationomers were synthesized in the reaction of MDI isocyanate, PCL 2000, MDEA and HCOOH. The studies showed that polymer film obtained from waterborne cationomer polyurethane is characterized with lower volume resistivity on the level of  $6.0 \times 10^8$   $\Omega$  m than in the cases of layers obtained from polyurethane and polyurethane anionomer synthesized from the same diisocyanates and similar polyols. Also, these cationomers have higher values of the real part of permittivity  $\epsilon'$  (capacity) and imaginary part of permittivity  $\epsilon''$  (dielectric losses), which can be explained by the high polarity and the phase structure. In the relaxation phenomena in the tested material, there are probably dominant interactions of the *dipole–dipole* type; therefore, a strong frequency dispersion of constants  $\epsilon'$  and  $\epsilon''$  especially in the range of  $10^{-4}$ – $10^{-1}$  Hz and significant increase in relaxation time (with the increase in graphene contents) especially at low frequency are observed. The admixture of graphene in the amount of 0.5–2 wt% results in the increase in conductivity, and percolation threshold is set on the level of approx. 1 wt%. The values of constants  $\epsilon'$  and  $\epsilon''$  clearly grow with the increase in graphene amount with the similar shape of frequency dispersion curves as for PU without admixture. A significant decrease in the resistivity of coatings obtained from PU cationomers modified with graphene was found. It turns out that the functionalization of graphene in THF by ultrasound can be an equally effective method for the permanent incorporation of graphene particles into the PU matrix and for obtaining conductive material, alternatively for the use of oxide graphene [46].

PU ionomers may also be used to obtain enhanced dyes. Chemical attachment of small molecular fluorescent dye onto a polymer matrix to afford a fluorescent polymer dye has attracted a great deal of attention during the past few years due to the unique properties and potential optical applications. A waterborne polyurethane-based fluorescent dye 4-amino-*N*-cyclohexyl-1,8-naphthalimide (WPU-ACN) was synthesized by attaching ACN dye into polyurethane chains according to a prepolymer-ionomer process. The structure of WPU-ACN was confirmed by means of Fourier transform infrared spectroscopy and UV–visible absorption. The improved thermal stability of WPU-ACN could be attributed to the incorporation of naphthalimide units in the preformed urethane groups. The fluorescence intensity of WPU-ACN was dramatically enhanced compared to ACN. It was found that the fluorescence intensity of WPU-ACN increased with increasing temperature and the fluorescence spectra of WPU-ACN showed a positive solvatochromic effect. In addition, the fluorescence of WPU-ACN emulsion was very stable not only for long-term storage, but also for fluorescence quenching [22].

A series of novel dye-incorporated WPU and WPU/clay nanocomposites with ionic groups at the chain ends was synthesized by the in situ method. For this, 4-(2-pyridyl azo) resorcinol (azo-dye) was used in the polymer structure. By changing the particle size and clay content of dispersed polymer, the color change of the resulting dispersions from pale cherry to dark cherry with different color shadows was observed. The effect of organically modified montmorillonite (OMMT) on the properties of water-based polyurethane colored coatings was studied. For this, a dye-incorporated polyurethane anionomer containing 3 mol% of DMPA as a matrix polymer was synthesized. Cloisite 30B WPU nanocomposites containing various amounts of OMMT were prepared by the in situ method. These polymers were thermally stable and processable. Their  $T_g$  was about 20–30 °C, and their  $T_{10\%}$  was between 310 and 345 °C. In addition, these water-dispersed polymers can be spray coated on the glass, metal or wood surface easily and show relatively good scratch resistance [25].

Other materials that deserve attention are phase change materials (PCMs) used for the storage of thermal energy. They are an important class of modern materials which substantially contribute to

the efficient use and conservation of waste heat and solar energy. Many different groups of materials have been investigated during the technical evolution of PCMs, including inorganic systems (salt and salt hydrates), organic compounds such as paraffins or fatty acids and polymeric materials, e.g., POG [67]. For thermal energy storage, the linear PU ionomers as solid–solid thermoplastic PCMs also were synthesized. POGs with 6000 and 10000 average molecular weight were used as latent heat storage materials, and MDI, MDEA and 1,3-propanesulfonate (PS) as supporting materials. The change in phase enthalpies of PU ionomers was 142.5 and 152.3 J/g, respectively, which were much close to the highest reported value of the branched PUPCM or the cross-linked PUPCM. The results of FTIR spectroscopy and AFM suggested a high degree of phase separation that existed in PUI. Additionally, the thermal resistance of PUIs was improved by the introduction of ionic groups. It was evidenced that the energy effects observed in PUI based on this type of polyols can be relatively large, and the released heat can be used to heat small rooms [52].

The *core–shell* structure of the PUI formed by polar ion and urethane segments and apolar groups derived from polyols can be used to create special nanocapsules in which biocide can be trapped. Depending on the environmental conditions, they can undergo controlled degradation and release occluded substances to the environment. An example is 4,5-dichloro-2-octyl-4-isothiazolin-3-one (DCOIT) pesticide—an off-white solid with a moderately sweet, pungent odor. It is the active ingredient in a series of biocide formulations. Self-assembly coated DCOIT nanocapsules were synthesized by block ionomer solution, in which the solution was prepared by polymerization of POG/IPDI/DMPA in DMF. The physicochemical properties of the block ionomer and the particle size, morphology and optical properties of the DCOIT nanocapsules were characterized with particle size analyzer, transmission electron microscopy (TEM) and UV–Vis spectrometer. The results of this study showed that the block polyurethane and DCOIT nanocapsules were prepared successfully. As the ratio of wall/core varied from 1:1 to 2:1, the release rate of the DCOIT from nanocapsules was fast at first and then experienced a deceleration stage; after that, it increased sharply. The deceleration stage became shorter as the ratio decreased [17]. In this case, the increased

biodegradability of the polar PU anionomer plays an important role. In this respect, the usefulness of composites obtained from PU ionomers modified with substances of natural origin should also be considered.

Polyurethane-based hydrogels were synthesized by PUI polymerization in emulsion, which were prepared from the liquefied bagasse. The polyurethane ionomer in emulsion was highly microphase-separated owing to the hydrophobic interaction of the lignin in liquefied bagasse. The data of the swelling ratio showed that the hydrogels were sensitive to pH and ionic strength. The hydrogel swelled at pH 9.0 and deswelled at pH 4.0 reversibly. The results of DSC analysis revealed that the freezing water in the swollen hydrogels was all free water. The adsorption experiment of the hydrogels for Cu(II) ion suggests that the hydrogels can be used as adsorbent for the removal of heavy metal ions from aqueous solutions [68].

The novel soluble alginate-based PU in organic solvents was synthesized by the reaction of NCO-terminated prepolymers and tributylammonium alginate (TBA-Alg). Alginate is a naturally occurring biopolymer with a broad range of unique features, e.g., biodegradability, biocompatibility, nontoxicity and nonimmunogenicity. Sodium alginate was added to a mixture of HCl ethanol and stirred overnight at 4 °C. The solid fracture, alginic acid, was separated by filtration under vacuum with a coarse filter paper. Then, the alginic acid was purified by washing with ethanol and acetone and dried. In the next step, dried alginic acid was dispersed in water and neutralized by tributylamine under controlled delivery conditions to obtain the TBA-alginate, a soluble form of alginate in polar aprotic organic solvents. Then, the IPDI diisocyanate and PTMO were mixed to obtain a NCO-terminated prepolymer. Afterward, initiated by DMPA, chain extension of prepolymer was performed and continued with the TBA-Alg solution [69].

## Conclusions

In recent years, significant interest in polyurethane ionomers has been observed. The use of new compounds allowing the introduction of ionic segments into polyurethane chains is described in great detail. In this respect, new possibilities of the synthesis of

PU cationomers were achieved using hydroxy derivatives of heterocyclic compounds as pyridine and imidazole, which together with sulfonated polyols. This allowed obtaining new PU zwitterionomers. Among the numerous applications of the PUI, the focus of attention—apart from improving the manufacturing technology of WPU as an ecological paints and coatings—was devoted to the development of materials for electronics as coatings with increased electrical conductivity and for biomedical applications. Their hydrophobicity/hydrophilicity, biocompatibility, biodegradability and conjugation with proteins, drugs or biologically active species can be successfully tailored by the introduction of different functional groups for various biomedical applications. It is worth noting that in Espacenet patent base for phrases “*waterborne polyurethane*” and “*aqueous polyurethane*” covering the years 2010–2018, over 1638 and 1266 results were obtained, respectively. However, this issue would require a separate critical analysis.

## Funding

Funding was provided by Rzeszow University of Technology (Grant No. U-DS.CS.18.001).

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

- [1] Król P (2007) Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane

- elastomers, copolymers and ionomers. *Prog Mater Sci* 52:915–1015
- [2] Jaudouin O, Robin J-J, Lopez-Cuesta PD, Imbert C (2012) Ionomer-based polyurethanes: a comparative study of properties and applications. *Polym Int* 61:495–510
- [3] Wang SW, Colby RH (2018) Linear viscoelasticity and cation conduction in polyurethane sulfonate ionomers with ion in the soft segment-single phase systems. *Macromolecules* 51:2757–2766
- [4] Bullermann J, Spohnholz R, Friebe S, Tunga ST (2014) Synthesis and characterization of polyurethane ionomers with trimellitic anhydride and dimethylol propionic acid for waterborne self-emulsifying dispersions. *J Appl Polym Sci* 52:680–690
- [5] Zhou X, Fang C, Chen J, Li S, Li Y, Lei W (2016) Correlation of raw materials and waterborne polyurethane properties by sequence similarity analysis. *J Mater Sci Technol* 32:687–694
- [6] Daemi H, Barikani M, Barmar M (2014) A simple approach for morphology tailoring of alginate particles by manipulation ionic nature of polyurethanes. *Int J Biol Macromol* 66:212–220
- [7] Deka R, Bora MM, Upadhyaya M, Dilip Kumar Kakati DK (2015) Conductive composites from polyaniline and polyurethane sulphonate anionomer. *J Appl Polym Sci* 132:41600
- [8] Francolini I, D'Illario L, Guaglianone E, Donelli G, Martinnelli A, Piozzi A (2010) Polyurethane anionomers containing metal ions with antimicrobial properties: thermal, mechanical and biological characterization. *Acta Biomater* 6:3482–3490
- [9] Dieterich D, Keberle W, Witth H (1970) Polyurethane ionomers, a new class of block polymers. *Angew Chem Int Ed Eng* 9:40–50
- [10] Neumaier HH (1974) Aqueous dispersions of polyurethane ionomers for coating and laminating. *J Coat Fabr* 3:181–193
- [11] Lelah MD, Pierce JA, Lambrecht LK, Cooper SL (1985) Polyether–urethane ionomers: surface property/ex vivo blood compatibility relationships. *J Colloid Interface Sci* 104:422–439
- [12] Tai NL, Adhikari R, Shanks R, Hakkey P, Adhikari B (2018) Flexible starch-polyurethane films: effect mixed macrodiol polyurethane ionomers on physicochemical characteristics and hydrophobicity. *Carbohydr Polym* 197:312–335
- [13] Kim HJ, Han J, Son Y (2017) Mechanical properties, thermal stability, and glass transition behaviors of a waterborne polyurethane/graphene oxide nanocomposite. *Mater Trans* 58:892–897
- [14] Senevirathna SR, Amarasinghe S, Karunaratne V, Koneswaran M, Laleen K (2017) The effect of change of ionomer/polyol molar ratio on dispersion stability and crystalline structure of films produced from hydrophilic polyurethanes. *J Appl Polym Sci* 134:44475
- [15] Montaz M, Barikani M, Razawi-Nouri M (2015) Effect of ionic group content on thermal and structural properties of polycaprolactone-based shape memory polyurethane ionomers. *Iran Polym* 24:505–513
- [16] Xu CL, Zeng J-B, WY-Z (2014) Sustainable waterborne polyurethane ionomer reinforced poly(vinyl alcohol) composite films. *Compos Sci Technol* 96:109–115
- [17] Shao Q-H, Chen J, Hu J-Q, Wang F, Tu W-P (2014) Synthesis, characterization and release properties of DCOIT nanocapsules encapsulated by block ionomers. *J Funct Mater* 45:06020–06024
- [18] Wang Z, Hou Z, Wang Y (2013) Fluorinated waterborne shape memory polyurethane urea for potential implant application. *J Appl Polym Sci* 127:710–716
- [19] Zhu H-J, Hu J-Q, Tu W-P, Wang F (2012) Synthesis and characterization of PEG-IPDI-DMPA block ionomers and their solution behavior in water phase. *J Funct Mater* 42(5):942–946
- [20] Król P, Pielichowska K, Byczyński Ł (2010) Thermal degradation kinetics of polyurethane–siloxane anionomers. *Thermochim Acta* 507:91–98
- [21] Byczyński Ł, Król P (2013) Synthesis, thermal and performance properties of poly(urethane-dimethylsiloxane) anionomers. Part I. Structural studies. *Polim (Pol)* 58:188–193
- [22] Hu X, Zhang X, Liub J, Daia J (2014) Synthesis, characterization and fluorescence performance of a waterborne polyurethane-based fluorescent dye 4-amino-*N*-cyclohexyl-1,8-naphthalimide, WPU-ACN. *Polym Int* 63:453–458
- [23] Chashmehjahanbina MR, Daemib H, Barikanib M, Salimia A (2014) Noteworthy impacts of polyurethane-urea ionomers as the efficient polar coatings on adhesion strength of plasma treated polypropylene. *Appl Surf Sci* 317:688–695
- [24] Zhao W, Zhang G, Jiang L, Lua T, Huang X, Shen J (2011) Novel polyurethane ionomer nanoparticles displayed a good biosensor effect. *Coll Surf B Biointerfaces* 88:78–84
- [25] Rafiemanzelat F, Adli V, Mallakpour S (2015) Effective preparation of clay/waterborne azo-containing polyurethane nanocomposite dispersions incorporated anionic groups in the chain termini. *Des Monomer Polym* 18:303–314
- [26] Cakić SM, Spírková M, Risti IS, B-Simendi JK, Cincović M, Poreba R (2013) The waterborne polyurethane dispersions based on polycarbonate diol: effect of ionic content. *Mater Chem Phys* 138:277–285
- [27] Wang S-W, Liu W, Colby RH (2011) Counterion dynamics in polyurethane-carboxylate ionomers with ionic liquid counterions. *Chem Mater* 23:1862–1873

- [28] Bahadur A, Schoaib M, Saeed A, Iqbal S (2016) FT-IR spectroscopic and thermal study of waterborne polyurethane-acrylate leather coating using tartaric acid as an ionomer. *e-Polymers* 16:463–474
- [29] Filip D, Asandulesa M, Macocinschi D, Aflori M, Vlad S (2016) Molecular dynamics, conductivity and morphology of sodium deoxycholate-based poly(ester ether)urethane ionomer biomaterials. *J Mater Sci* 51:8516–8528
- [30] Filip D, Macocinschi D, Paslaru E, Tuchilus CG, Vlad S (2016) Surface characterization and antimicrobial properties of sodium deoxycholate-based poly(ester ether) urethane ionomer biomaterials. *React Funct Polym* 102:70–81
- [31] Nair PA, Ramesh P (2012) Synthesis and characterization of calcium-containing polyurethane using calcium lactate as a chain extender. *Polym J* 44:1009–1014
- [32] He L, Sun D (2013) Synthesis of high-solid content sulfonate-type polyurethane dispersion by pellet process. *J Appl Polym Sci* 127:2823–2831
- [33] Gao R, Zhang M, Dixit N, Moore RB, Long TE (2012) Influence of ionic charge placement on performance of poly(ethylene glycol)-based sulfonated polyurethanes. *Polymer* 53:1203–1211
- [34] Bottino A, Capannelli G, Comite A, Costa C (2011) Synthesis and characterisation of polyurethane proton exchange membranes. *J Fuel Cell Sci Technol* 8(5):051011
- [35] Banerjee S, Mishra A, Singh MM, Maili B, Ray B, Maili P (2011) Highly efficient polyurethane ionomer corrosion inhibitor: the effect of chain structure. *RSC Adv* 1:199–210
- [36] Nakayama Y, Inaba T, Toda Y, Tanaka R, Cai Z, Shiono T, Shirahama H, Tsutsumi C (2013) Synthesis and properties of cationic ionomers from poly(ester-urethane)s based on polylactide. *J Polym Sci, Part A: Polym Chem* 51:4423–4428
- [37] Król B, Król P (2009) Synthesis and characterisation of coating polyurethane cationomers containing quaternary ammonium alkyl groups derived from built-in alkyl bromides. *Colloid Polym Sci* 287:189–201
- [38] Daemi H, Rad RR, Barikani M, Adib M (2013) Catalytic activity of aqueous cationic polyurethane dispersions: a novel feature of polyurethanes. *Appl Catal A Gen* 468:10–17
- [39] Król B, Król P (2010) Coatings materials obtained from polyurethane cationomers modified with functionalized silsequioxanes. *Polim (Pol)* 55:440–451
- [40] Król P, Król B, Pielichowska K, Pikus S (2011) Comparison of phase structures and surface free energy values for the coating synthesised from linear polyurethanes and from waterborne polyurethane cationomers. *Colloid Polym Sci* 289:11757–11767
- [41] Król P, Król B (2012) Waterborne cationomer polyurethane coatings with improved hydrophobicity. *Colloid Polym Sci* 290:879–893
- [42] Pielichowska K, Król P, Król B, Pagacz J (2012) TOPEM DSC study of glass transition region of polyurethane cationomers. *Thermochim Acta* 545:187–193
- [43] Król P, Król B (2012) Waterborne polyurethane cationomers synthesised from 4,4'-methylene(bis phenyl isocyanate) or isophorone isocyanate, polyesters and N-methyl or N-butyl diethanolamine—analysis the structure and selected properties of the obtained coatings. *Polim (Pol)* 57:799–811
- [44] Król P, Król B, Lechowicz J (2014) Modelling the surface free energy parameters of polyurethane coats—part 2. Waterborne coats obtained from cationomer polyurethanes. *Colloid Polym Sci* 292:1051–1059
- [45] Król P, Król B, Pielichowska ŠM (2014) Composites prepared from the waterborne polyurethane cationomers-modified graphene. Part I. Synthesis, structure, and physicochemical properties. *Colloid Polym Sci* 293:421–431
- [46] Król P, Król B, Zenker M, Subocz J (2015) Composites prepared from the waterborne polyurethane cationomers-modified graphene. Part II. Electrical properties of the polyurethane films. *Colloid Polym Sci* 293:2941–2947
- [47] Król B, Pielichowska K, Król P, Chmielarz P (2017) Polyurethane cationomers modified by polysiloxane. *Polym Adv Technol* 28:1366–1374
- [48] Król B, Pielichowska K, Król P, Kędzierski M (2019) Polyurethane cationomer films as ecological membranes for building industry. *Prog Org Coat* 130:83–92
- [49] Gurunathan T, Rao CRK, Narayan R, Raju KVS (2013) Synthesis, characterization and corrosion evaluation on new cationomeric polyurethane water dispersions and their polyaniline composites. *Prog Org Coat* 76:639–647
- [50] Gao R, Zhang M, Wang S-W MR, Colby RH, Long TE (2013) Polyurethanes containing an imidazolium diol-based ionic-liquid chain extender for incorporation of ionic-liquid electrolytes. *Macromol Chem Phys* 214:1027–1036
- [51] Ramesh S, Radhakrishnan G (1996) Polyurethane zwitterionomers using 2,3-dihydropyridine. *Eur Polym J* 32:993–998
- [52] Chen K, Liu R, Zou C, Shao Q, Lan Y, Cai X, Zhai L (2014) Linear polyurethane ionomers as solid–solid phase change materials for thermal energy storage. *Sol Energy Mater Sol Cells* 130:466–473
- [53] Zander ZK, Wang F, Becker ML, Weiss RA (2016) Ionomer for tunable softening of thermoplastic polyurethane. *Macromolecules* 49:926–934
- [54] Kozakiewicz J (2015) Developments in aqueous polyurethane and polyurethane-acrylic dispersion technology Part I. Polyurethane dispersions. *Polim (Pol)* 60:525–535

- [55] Król P, Król B, Lechowicz J (2013) Modelling the surface free energy parameters of polyurethane coats—part 1. Solvent base coats obtained from linear polyurethane elastomers. *Colloid Polym Sci* 291:1031–1047
- [56] Król B, Król P, Pikus S, Chmielarz P, Skrzypiec K (2010) Synthesis and characterisation of coating polyurethane cationomers containing fluorine built-in hard urethane segments. *Colloid Polym Sci* 288:1255–1269
- [57] Kozakiewicz J (2016) Developments in aqueous polyurethane and polyurethane-acrylic dispersion technology Part II. Polyurethane-acrylic dispersions and modification of polyurethane and polyurethane-acrylic dispersions. *Polimery* 61:79–156
- [58] Akram N, Zia KM, Sattar R, Tabassum S, Saeed M (2019) Thermomechanical investigation of hydroxyl-terminated polybutadiene-based linear polyurethane elastomers. *J Appl Polym Sci* 136:47289
- [59] Ye S-H, Chen Y, Mao Z, Gu X, Shankarraman V, Hong Y, Ahanov V, Wagner WR (2018) Biodegradable zwitterions polymer coatings for magnesium alloy stents. *Langmuir* 35:1421–1429
- [60] Jérôme R (1989) Halato-telechelic polymers: a new class of ionomers. *Telechelic polymers: synthesis and applications*. Department of Macromolecular Chemistry, University of Liege, Liege, pp 261–288
- [61] Wang Y-J, Jeng U-S, Hsu S-H (2018) Biodegradable water-based polyurethane shape memory elastomer for bone tissue engineering. *ACS Biomater Sci Eng* 4:1397–1406
- [62] Liu H-L, Dai SA, Fu K-Y, Hsu S (2010) Antibacterial properties of silver nanoparticles in three different sizes and their nanocomposites with a new waterborne polyurethanes. *Int J Nanomed* 5:1017–1028
- [63] Filip D, Macocinschi D, Paslaru E, Munteanu BS, Dumitriu RP, Lungu M, Vasile C (2014) Polyurethane biocompatible silver bionanocomposites for biomedical applications. *J Nanoparticle Res* 16:2710
- [64] Buruiana T, Melinte V, Chibac A, Matiut S, Synthesis BS (2012) Evaluation and preliminary antibacterial testing of hybrid composites based on urethane oligomethacrylates and Ag nanocomposites. *J Biomater Sci Polym Ed* 23:955–972
- [65] Filip D, Macocinschi D, Vlad S, Lisa G, Mariana Cristea M, Zaltariov MF (2016) Structure–property relationship of sodium deoxycholate based poly(ester ether)urethane ionomers for biomedical applications. *J Appl Polym Sci* 133:42921
- [66] Piticescu RM, Popescu LM, Buruiana T (2012) Composites containing hydroxyapatite and polyurethane ionomers as bone substitution materials. *Dig J Nanomater Biostruct* 7:477–485
- [67] Pielichowska K, Pielichowski K (2014) Phase change materials for thermal energy storage. *Prog Mater Sci* 65:67–123
- [68] Zhiyuan O, Fangeng C (2010) Synthesis of polyurethane-based hydrogels from liquefied bagasse. *J Biobased Mater Bioenergy* 4:346–352
- [69] Daemi H, Barakani M (2014) Molecular engineering of manipulated alginate—based polyurethanes. *Carbohydr Polym* 112:638–647

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.