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A simple approach for morphology tailoring of alginate particles by manipulation ionic nature of polyurethanes

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ARTICLE INFO

ABSTRACT

A number of different ionic aqueous polyurethane dispersions (PUDs) were synthesized based on NCO-terminated prepolymers. Two different anionic and cationic polyurethane samples were synthesized using dimethylol propionic acid and N-methyldiethanolamine emulsifiers, respectively. Then, proper amounts of PUDs and sodium alginate were mixed to obtain a number of aqueous polyurethane dispersions–sodium alginate (PUD/SA) elastomers. The chemical structure, thermal, morphological, thermo-mechanical and mechanical properties, and hydrophilicity content of the prepared samples were studied by FTIR, EDX, DSC, TGA, SEM, DMTA, tensile testing and contact angle techniques. The cationic polyurethanes and their blends with sodium alginate showed excellent miscibility and highly stretchable properties, while the samples containing anionic polyurethanes and alginate illustrated a poor compatibility and no significant miscibility. The morphology of alginate particles shifted from nanoparticles to microparticles by changing the nature of PUDs from cationic to anionic types. The final cationic elastomers not only showed better mechanical properties but also were formulated easier than anionic samples.

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1. Introduction

Polyurethanes (PUs) have found a broad range of commercial applications, because they can be processed by common processing techniques including casting, molding, injection and extrusion [1]. These high commodity polymers are synthesized through the convenient polyaddition polymerization reactions between isocyanate and hydroxyl functional groups [2]. The superior chemical and physical properties of polyurethanes arise from their biphasic nature [3]. Segmented polyurethanes, consisting of hard domains and soft segments have a broad range of applications in different industries [4]. Elastomeric behaviors and high temperature properties of polyurethanes are attributed to the soft segments and hard domains, respectively [5].

The environmental regulations and the considerable costs of solvents are two meaningful reasons for the possible replacement of traditional solvent-based PUs by those aqueous dispersions [6]. The creation of hydrophilic groups and addition of ionizable emulsifiers to the backbone of polymers are the two general methods for synthesis of aqueous polyurethane dispersions [7]. The chemical structure of ionizable emulsifiers determines the type and

properties of final polyurethane ionomer. Three types of PU ionomers can be synthesized as anionomer, cationomer and zwitterionomers according to the ionic charges of the functional groups on the polymer backbone [8]. The majority of the studies on PUDs have been focused on anionic polyurethane dispersions, while there are only few reports on the cationic PUs. The compounds dimethylol propionic acid and *N*-methyldiethanolamine are two prevalent emulsifiers which are used for preparation of anionic and cationic polyurethane ionomers, respectively [9]. Different applications reported for aqueous polyurethane dispersions in the related literature include adhesives, gloves, paints, elastomers, glass fiber sizing and automotive topcoats [10].

Alginate derived from brown algae is a random anionic linear biopolymer which is extremely in focus because of its excellent properties [11]. Unique chemical structure of alginate, combined with its biocompatibility and relatively low cost have made it an important polymer in pharmaceutical applications for example, wound dressings, drug delivery systems and cell encapsulation [12–14]. Some microorganisms and lyases degrade this biopolymer down to single components therefore, alginate can be assumed as a biodegradable polymer [15]. Alginate is a random polymer consisting of varying ratios of β-ʟ-guluronic acid (G) and β-ᴅ-mannuronic acid (M) monomers. The chemical structure of the alginate is formed by the sequences of three blocks including homogenous M and G homopolymers and heterogeneous MG blocks. The physical

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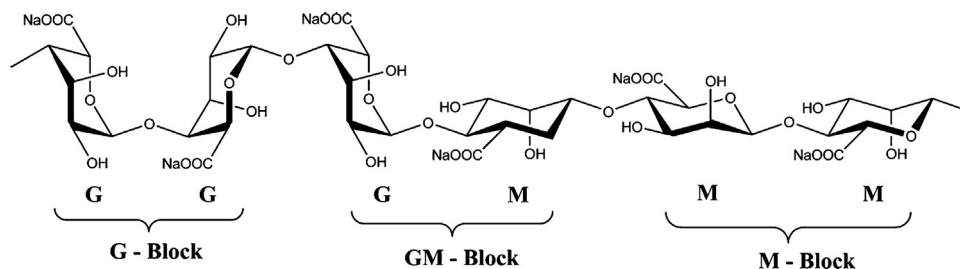
Scheme 1. Chemical structure of sodium alginate and its blocks.

and chemical properties of alginates are controlled by the amount and the sequence of mentioned blocks (Scheme 1) [16]. The salts of alginates with multivalent metals are insoluble in water, while those monovalent like sodium and ammonium alginate are soluble [17].

Polyurethanes functionalized by polysaccharides are appropriate candidates for using as biomaterials. Moreover, alginate-based polyurethanes are probably more interesting options because alginates possess advantages like low cost and abundant. Because of the meaningful incompatibility between polyurethanes and alginates, new methods have been developed to increase their compatibility. Nevertheless, the previous researches only focused on the modification of chemical structure of the polyurethanes [18]. Here, we report the significant role of the emulsifiers and their types on the final properties of composites containing PUDs and alginates. Moreover, the effects of two different cationic and anionic emulsifiers (i.e. *N*-methyldiethanolamine and dimethylol propionic acid, respectively) were probed on the morphological, thermal and mechanical properties of alginate-based polyurethanes.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), *N*-methylpyrrolidone (NMP), *N*-methyldiethanolamine (MDEA), acetic acid (HOAc) and triethylamine (TEA) were purchased from Merck, Germany. MDEA, HOAc and TEA were used after dehydration with 4-Å molecular sieves for 1 week. Dimethylol propionic acid (DMPA) (Aldrich) was dried at 100 °C for 4 h before being used. Polytetramethylene glycol (PTMG) with a molecular weight 950–1000 was supplied by Arak petrochemical company and dried at 50 °C under vacuum for 24 h before use to ensure the removal of impurities that may interfere with the isocyanate reactions. Sodium alginate (SA) with molecular weight 5000–40,000 was supplied by Aldrich and used as delivered.

2.2. General procedure for synthesis of the CPUDs

All the aqueous polyurethane dispersions containing cationic or anionic emulsifiers were synthesized with the prepolymer mixing process (Scheme 2). A 20 g PTMG was placed in a 500-cm³ round-bottomed, four-necked flask equipped with a thermometer, mechanical stirrer, heating oil bath, dropping funnel, condenser with a drying tube, and an inlet and outlet of dry nitrogen and was degassed in vacuum at 60 °C for 15 min. The proper amount of IPDI was added dropwise to the system under mild stirring. The temperature was increased to 90 °C and the reaction was progressed until the theoretical NCO content was reached. The change in the NCO value was determined with the standard dibutylamine back-titration method (ASTM D 1638). Donating the hydrophilicity to the backbone of polyurethane was performed through the addition of a solution including MDEA in NMP. In chain extension step, 1,4-butanediol was added into the reactor and the reaction was continued for 15 min. In order to form the tertiary ammonium

groups, HOAc was charged into the reactor and the system was cooled to 65 °C. Finally, the required amount of deionized water was added dropwise into the mixture under very mild stirring conditions at room temperature (400 rpm). All the aqueous dispersions were prepared as 30 wt% solid content.

2.3. Synthesis of APUDs

A NCO-terminated prepolymer was obtained by the reaction of PTMG and IPDI through a polyaddition reaction. Anionic polyurethane dispersions were synthesized by insertion of DMPA as the anionic emulsifier into the prepolymer chain. The chain extension was completed using 1,4-butanediol. Eventually, the TEA was added to the reactor in order to form the carboxylate functional groups and disperse the polyurethane chains in aqueous media. The APUDs with 30 wt% solid content were obtained by addition deionized water to the mixture at room temperature.

### 2.4. Preparation of alginate-based anionic polyurethanes

The APUD/SA blends were prepared through the solution blending of the aqueous anionic polyurethane dispersions and sodium alginate. The prepared systems were cast into a Teflon plate at room temperature and followed by drying at 100 °C in oven for 24 h. The cured samples were stored for 1 week at room temperature for further measurements.

2.5. Preparation of alginate-based cationic polyurethanes

The alginate-based cationic polyurethane elastomers were prepared through blending of CPUDs and aqueous SA solution. It is necessary to add some milliliters chloroform to the mixture and replace the aqueous media of polymers by a mixture of water/chloroform during the addition of alginate solution to the CPUD to prevent gelation of the final blend in water. The prepared samples were cast by pouring the compositions onto a Teflon plate in the way same as APUD/SA blends.

2.6. Measurements

The IR spectra of synthesized APUs and their blend films were performed on a Bruker Equinox 55 FTIR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal (Ettlingen, Germany). The thermal properties of the prepared samples were studied by two Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). The DSC was recorded on a Stanton Redcroft STA-780 (London, UK). The dynamic mechanical analysis was performed with a Triton Tritic 2000 instrument at heating rate of 10 °C/min and frequency of 1 Hz over a temperature range of −100 to 100 °C. The dimensions of sample films were 20 mm × 10 mm × 1 mm for the DMTA measurements. TGA was recorded on a Polymer Lab TGA-1500 instrument (London) under a N_2 atmosphere from room temperature to 650 °C with a heating rate of 10 °C/min. Mechanical properties were
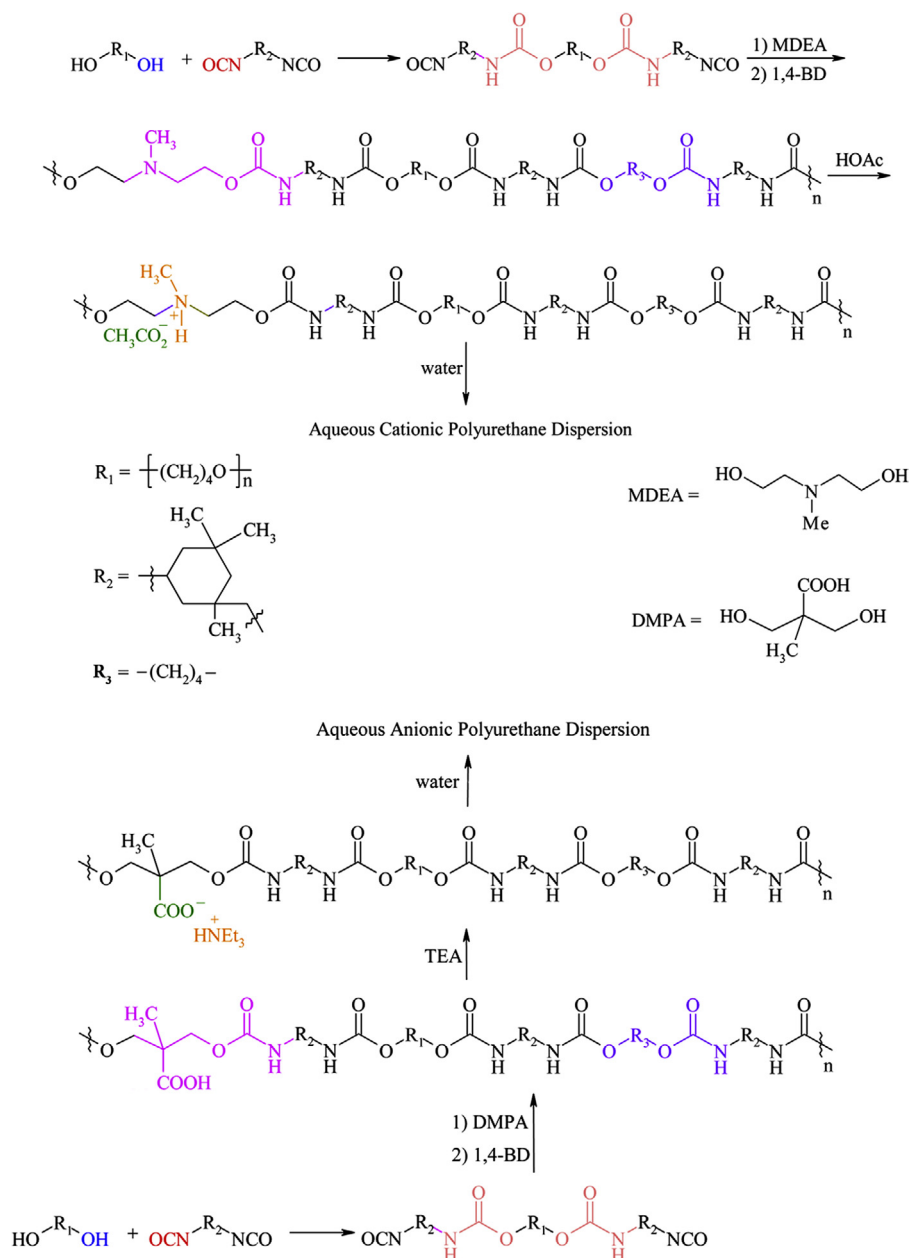
Scheme 2. Chemical procedures for synthesis of the aqueous ionic polyurethane dispersions.

examined by an Instron Universal Mechanical Test Machine (MTS System Corporation, Eden Prairie, MN) tensile tester model 10/M at a strain rate of 50 mm/min. The test specimens had dimensions of 50 mm × 5 mm × 0.5 mm. Scanning electronic microscopy (SEM) (Model Vega, Tescan Co., Czech Republic) was used to measure the size and shape of the alginate particles in polyurethane matrix. Characterization of alginate particles in the matrix of the polyurethane were performed using EDX method (Oxford instrument model INCA). The contact angle measurements were performed at room temperature by a G10 (Kruss, Germany) instrument via the sessile drop method.

3. Results and discussion

3.1. Molecular characterization

Two different cationic and anionic types of aqueous polyurethane dispersions were synthesized based on MDEA

and DMPA emulsifiers, respectively. The compositions of the synthesized polyurethane ionomers and their blends with SA have been summarized in Table 1.

Based on the electrical charges of polyurethane backbones, the two different aqueous/organic and aqueous media must be applied to prevent mixture gelation during the addition of alginate solution. The systems with block ratio 1:3:2 showed better physical, mechanical and curing properties than samples with other block ratios for both polyurethane ionomers. Therefore, final compositions of polyurethanes and alginates were formulated based on mentioned block ratio. Common PUDs extended with diamine chain extenders illustrate better properties than those diole compounds because of the more active hydrogen bonds and more chemical strength of urea bonds in comparison to the urethane linkages. However, for reduction of the prepared polyurethane's and alginate's tendency to the hydrogen bonding and a more reliable comparison between the responses of polyurethane ionomers, a common diol chain extender was incorporated to the backbone

Table 1
Feed composition of polyurethane ionomers with variable block ratios and their different formulations with sodium alginate.

Sample no.	Block ratio	PTMG (g)	IPDI (g)	DMPA (g)	MDEA (g)	TEA (g)	HOAc (g)	PU:SA (%)	Film property
1	1:3:1:1	20	13.34	2.68	–	2.02	–	–	Excellent
2	1:4:1:2	20	17.78	2.68	–	2.02	–	–	Semi-brittle
3	1:4:2:1	20	17.78	5.36	–	4.04	–	–	Sticky
4	1:3:1:1	20	13.34	–	2.38	–	1.20	–	Excellent
5	1:4:1:2	20	17.78	–	2.38	–	1.20	–	Semi-brittle
6	1:4:2:1	20	17.78	–	4.77	–	2.40	–	Sticky
7	1:3:1:1	20	13.34	2.68		2.02	–	99:1	Very weak
8	1:3:1:1	20	13.34	2.68		2.02	–	96:4	weak
9	1:3:1:1	20	13.34	–	2.38	–	1.20	99:1	Excellent
10	1:3:1:1	20	13.34	–	2.38	–	1.20	96:4	Excellent
11[a]	1:3:1:1	20	14.00	2.68	–	2.02	–	96:4	Desirable

[a] A specific formulation containing 5% excess IPDI relative to the polyurethane solid weight.

of polyurethanes. It is important noting that the liquid mixtures of anionic polyurethanes and sodium alginate have a large tendency to separate from each other, while the mixtures including cationic ionomer and alginate form significant stable dispersions in the presence of low molecular chlorinated hydrocarbons. Among the samples are listed in Table 1, all compositions of cationic PUDs and SA showed excellent miscibility and homogeneity, while the instability were declined by raising the SA content in compositions based on anionic ionomers. Thus, only the compositions containing 4% SA were analyzed and compared each other.

The results of FTIR spectra for both cationic and anionic polyurethane elastomers, the powder of sodium alginate and the alginate-based polyurethanes are listed in Table 2. The FTIR spectrum of prepared polyurethanes extended by 1,4-butane diol overlaps with SA in some areas. The characterization of polyurethane chemical structures was performed by the disappearance of the isocyanate band at 2265 cm^{-1}. The appearance of stretching vibrations N–H, C=O and N–H for amide II band proved the formation of polyurethane samples with the proposed chemical structure. Both CPUD/SA and APUD/SA samples showed significant broad vibration bands at 3000–3500 cm^{-1} as compared to the neat polyurethane ionomers [19]. In addition, carbonyl band shifted to lower wavenumber in blend samples (Table 2, row 6).

The shift in carbonyl band and the broadening in mentioned region in IR spectra were ascribed to the hydrogen bonding between functional groups of both polymers. In addition, the appearance of uronic vibrational bands of alginate in anomeric region spectra of blends proved its presence in the matrix of the prepared polyurethanes. The minor contribution of alginate in the blends and significant overlapping of vibrational bands for both polymers are the firm reasons for disappearance of vibrational carboxylate bands in the blend spectra. These observations confirmed the claim toward the proper miscibility of the PUD ionomers and SA polymers.

3.2. DSC analysis

The effects of alginate on the phase separation of PUDs and their thermal properties were studied by the DSC technique. As an example, the DSC thermograms of both PU ionomers and their blends with sodium alginate are shown in Fig. 1.

All the PU ionomers and their blends with SA showed a transition at low temperatures around −33 to −29 °C. Based on the previous reports, this transition can be related to the glass transition of the soft segments [20,21]. This low T_g arises from the significant flexibility of C–C bond and its low barrier energy. The presence of sodium alginate in both cationic and anionic blends affords a negligible effect on the transition temperature of the soft segment. The interactions of polar functional groups of alginate and hard segments of both ionomers create the different transitions at higher temperatures. It is interesting to probe the significant differences

between anionic and cationic systems and their interactions with sodium alginate.

Both neat cationic and anionic polyurethanes showed transitions at −32.3 °C and −33 °C, respectively. These near temperatures confirmed that the comparable ionic emulsifiers with different electrical charges have no sensible effects on this transition. The findings of our recent studies have shown that the sodium alginate causes a small alteration on the T_g of soft segment due to its rigid chemical structure and dissimilar functional groups compared to the ether moieties of polyether diols. Therefore, the shift to the higher temperature values in the blend samples is expected. The minor temperature shift for cationic blend can be ascribed to the less effective hydrogen bonding between protons of tertiary ammonium functional groups and oxygen atoms of tetramethylene ether moieties of PTMG. The role of polyurethane ionic nature on the compatibility of prepared systems can be better explained by the transitions at room or higher temperatures. The blends containing anionic PUDs and SA are relatively incompatible. Therefore, a specific formulation containing 5% excess IPDI relative to the polyurethane solid weight was designed for better compatibility.
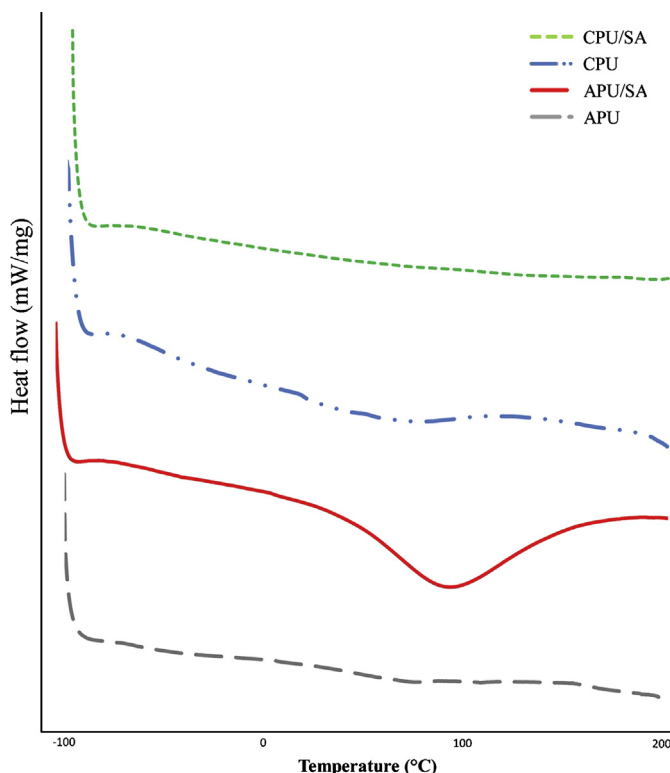

Fig. 1. DSC thermograms of ionic polyurethanes and their alginate based elastomers.

Table 2
FTIR data for both polyurethane ionomers and their blends.

Vibration (cm^{-1})	SA	CPUD	CPUD/SA	APUD	APUD/SA
ν(OH)	3400[a]	–	*[b]	–	*
ν(NH)	–	3319	3325	3322	3320
ν_{NCO}	–	–	–	–	–
ν(CH)$_{sym\ str}$	2920 2851	2945 2859 2795	2941 2856 2795	2948 2866	2945 2860 2794
ν(C=O)$_{urethane}$	–	1714	1710	1724	1719
ν(NH)$_{Amide\ II}$	–	1538	1541	1532	1540
ν(CH)$_{asym\ str}$	1463 1421	1463 1365 1305	1462 1365 1305	1462 1364 1306	1463 1364 1304
ν(COO$^-$)$_{asym}$	1649	–	*	*	*
ν(COO$^-$)$_{sym}$	1460	–	*	*	*
ν(OCO)$_{asym}$	1107	1111	1112	1105	1100

[a] The maximum intensity of the broad peak.
[b] The vibrational carboxylate bands were disappeared because of the minor contribution of the alginate.

The excess IPDI affords a significant broad endothermic peak contrasted to the neat anionic polyurethane sample. This broad peak can be related to the formation of the urea and allophanate linkages which are accompanied with better compatibility and miscibility of the SA and APUD mixtures.

Furthermore, these linkages cause the microcrystalline domains between polymer chains and the subsequent entanglements of polymeric chains between both polymers. In contrast to the ionic polyurethanes, the cationic elastomers containing SA showed a different behavior to the thermal response at room and higher temperatures.

Both the effective hydrogen bonding obtained by active protons of tertiary ammonium groups and the strong ionic attraction between dissimilar electrical charges of carboxylate and tertiary ammonium functional groups cause a selective interaction between the alginate and heteroatoms of polyurethane backbone. These interactions contributed to the subsequent disappearance of melting temperature of soft segments. This intimate interaction may be described by a complex chemical structure which is formed by hydrogen bonding (Scheme 3). However, both stronger electrostatic interactions of SA and CPUs and more entanglement between the polymeric chains of cationic ionomers and SA guaranty the formation of more compatible systems.

3.3. DMTA studies

The dynamic mechanical thermal analysis was utilized for studying the viscoelastic properties of the prepared samples. The DMTA is served for obtaining some useful information regarding polymers including, the types of transitions and their values, the mechanical behavior versus the temperature, the quantity of damping and the miscibility of blends. The latter property can be shown by the comparison of the transition temperature shift of neat polymer and its blend. The storage modulus (E') versus temperature curves of the PU ionomers and other samples are shown in Fig. 2.

The common polyurethanes with superior phase separation show a transition at low temperatures, which is an important characteristic of soft segment, while this transition was concealed in our samples because of the low molecular weight of PTMG and the interfere of emulsifiers in the phase separation of polyurethane segments.

The cationic polyurethane samples containing SA demonstrated excellent compatibility and miscibility as the result of the opposite electrical charges and the significant hydrogen bonding. The transition temperature of the soft segment of cationic polyurethane appeared at 20 °C, approximately near to the melting temperature of the neat PTMG. Based on the less effective hydrogen bonding of PTMG moieties in comparison to the hard segments of CPUs with functional groups of SA, it is expected that the transition temperature of alginate based cationic polyurethanes to be the same as neat cationic polyurethane. The results of DMTA and the

appearance of soft segment transition temperate of alginate based-CPUs at 20 °C confirmed the proposed scheme for potential hydrogen bonds between SA and CPUs (Scheme 3).

In contrast, the neat anionic PU sample and its blend with SA showed sensible different transition temperatures. This difference can be assigned to the both similar negative electrical charges of both continuous and dispersed phases, and the more effective hydrogen bonding compared to the cationic ones.

3.4. SEM and EDX analysis

The morphological aspects of the samples including the distribution of SA particles and the characterization of both polyurethane and alginate polymers were studied by SEM and EDX methods, respectively. Thanks to the relatively similar elemental compositions of both SA and PU samples and the restrictions regarding the characterization techniques such as, the different solvents of each polymer and the following limitation for applying the NMR spectroscopy, the EDX method was utilized for the characterization of alginate particles in the polyurethane bulk [18a]. The characterization of sodium alginate particles in the microstructure was performed by the distinct Na peak, the most valuable element in the chemical structure of SA. Based on the Na peak from EDX data, the nano- or microparticles of sodium alginate were readily distinguished from the bulk of the polyurethanes (Additional data are provided as supplementary information). The SEM analysis showed the importance of the electrical nature of polyurethane on its properties and interactions with sodium alginate. The SEM images indicated that sodium alginate can be dispersed as the nanoparticles with proper distribution on the polyurethane
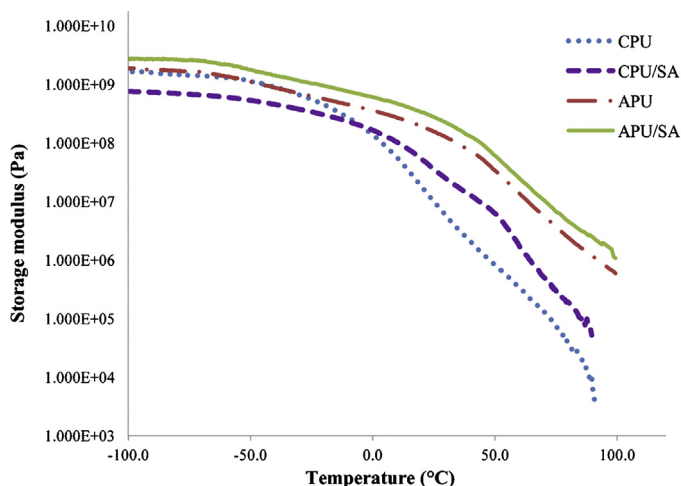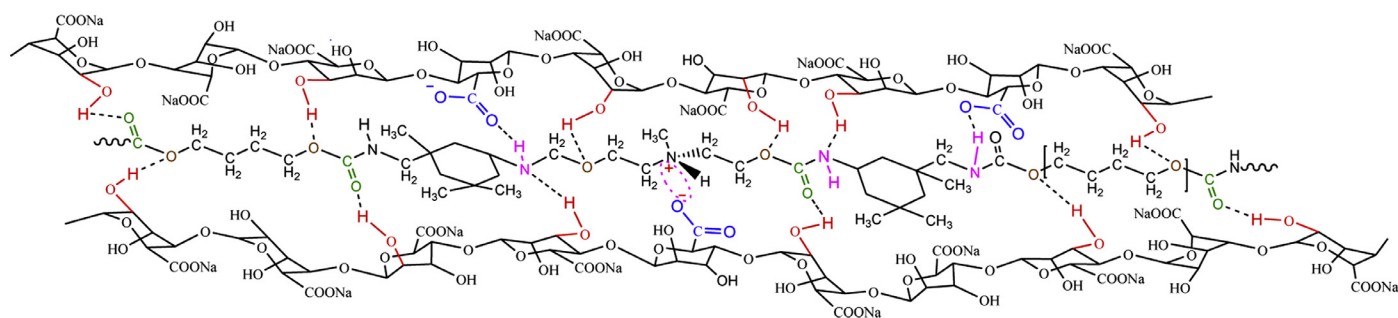

Fig. 2. Mechanical thermal analysis of PU ionomers and their composites.

Scheme 3. Plausible hydrogen bonds between cationic polyurethane and sodium alginate and the formation of tertiary ammonium carboxylate polymeric salts.
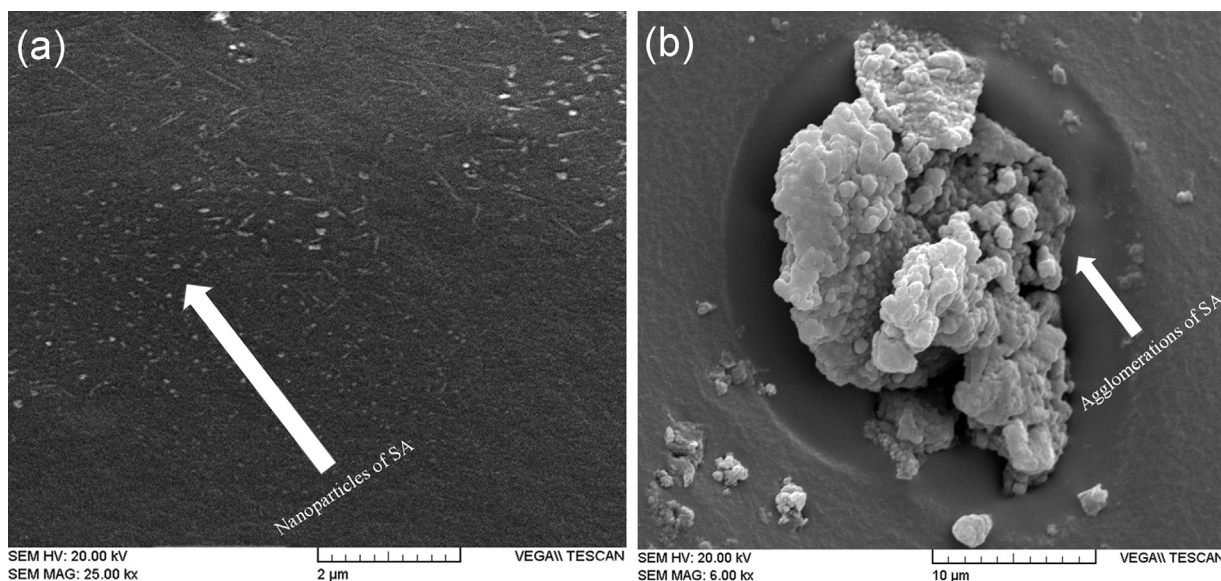

Fig. 3. Morphology of the alginate particles in the matrices of polyurethane ionomers: (a) alginate nanoparticles in cationic polyurethane, (b) microparticles of SA in the anionic polyurethane.

bulk, because of the intense coulombic forces between anionic carboxylate of alginate and cationic tertiary ammonium groups of polyurethane. Polymeric tertiary ammonium carboxylate salts which are produced from the electrostatic interactions between cationic polyurethane and polyanionic alginate can be detected as nanobead or nanorod particles based on the molecular weight of SA chains (Fig. 3a) [18a].

In contrast, the morphology of sodium alginate particles were transformed to the micro-agglomerations for the alginate-based anionic polyurethane samples (Fig. 3b). The appearance of SA agglomerations can be explained by the serious repulsive interactions of the similar negative charges of carboxylate ions in both polyurethane and alginate polymers and more tendencies for the creation of hydrogen bonding between similar polymeric chains.

The significant repulsion between SA and APU samples and the strange morphology of SA agglomerations is comparable to the previous reports regarding the formation of SA microparticles in the matrix of polyurethanes extended by DMPA [18b]. In the previous study, the better distribution and the lower dimensions of SA particles raised from more contents of DMPA as a coupling agent between SA and PU chains, while the portion of DMPA in present polyurethanes was less than previous researches and the particle sizes were significantly raised. Generally, the ionic nature of the polyurethane chains and the contents of ionic emulsifiers play an important role on the interactions, morphologies and the properties of polyurethanes and their blends with carbohydrates, such as alginates (Scheme 4).

3.5. Mechanical properties

Beside the excellent features of sodium alginate and its derivatives, their poor mechanical properties is an open challenge for scientists [22]. Recently, Sun et al. [22b] and Daemi et al. [18a] reported two important researches regarding the extremely stretchable alginate systems based on ionically crosslinked alginates in the presence of crosslinked polyacrylamide and cationic polyurethanes, respectively. Here, this study discloses the novel elastomeric polyurethanes based on SA which can be stretched more than 20 times of their original length without rupture in the wet state. Both dried anionic and cationic PU samples were significantly stretched more than 11 times of their original length (Fig. 4 and Table 3).

Therefore, the elongation at break dropped to 11 times equated with the neat PU, while the mechanical strength was increased. The

Table 3
Mechanical properties of the PU ionomers and their alginate based samples.

Sample number	Sample	Tensile strength (MPa)	Elongation at break (%)
1	Neat CPUD	20.06	1300[a]
2	CPUD/SA	21.12	1150[a]
3	Neat APUD	23.44	1220
4	APUD/SA	26.66	530

[a] These data have excellent conformity with our previous results [18a].

Scheme 4. Proposed mechanism for illustration of the effects of the emulsifier nature on properties of alginate based polyurethane: (a) Interactions of anionic polyurethane and sodium alginate and the formation of SA agglomerations, (b) The formation of nanoalginate particles in the matrix of cationic polyurethane.

lower elongation and higher strength, which be resulted of the SA presence, can be assigned to the interruption of PUs phase separation because of the hydrogen bonding with alginate and the rigid nature of the uronic residues of this biopolymer.

In contrast to the cationic PUs, the ionic samples containing SA showed no proper mechanical properties. It seems that the microparticles of SA can readily initiate and propagate the cracks through the tested sample therefore, the value of the

Table 4
Thermal stability and dynamic mechanical analysis data of PU ionomers and their micro- or nanocomposites.

Number	Sample	T_{onset}[a] (°C)	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	T_g[b] (°C)	tan δ[c]
1	SA	27.2	122.3	226.5	272.6	–	–
2	Neat APU	28.7	284.6	315.4	364.1	31.3	0.73
3	APU:SA 96: 4%	28.5	271.8	310.3	356.4	35.5	0.45
4	Neat CPU [18a]	28.8	260.4	284.7	335.4	26.6	0.87
5	CPU:SA 96: 4% [18a]	28.2	248.7	283.1	340.9	30.1	0.54

[a] T_{onset}: Initial decomposition temperature; T_{10}: Temperature of 10% weight loss (from TGA); T_{20}: Temperature of 20% weight loss (from TGA); T_{50}: Temperature of 50% weight loss (from TGA); T_g: glass-transition temperature.
[b] The central point of the maximum in the tan δ peak was used for measurement of T_g.
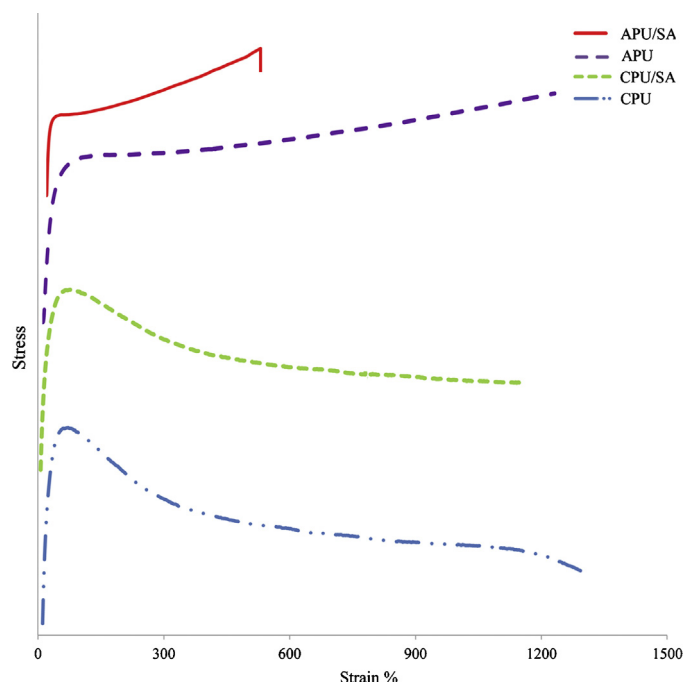[c] Altitude of the tan δ peak.

Fig. 4. Meaningful difference is obvious between CPUD/SA and APUD/SA samples based on mechanical analysis data.

Fig. 5. TGA thermograms of polyurethane ionomers and their composite samples.

strain is intensely decreased as compared to the similar cationic samples.

3.6. TGA analysis

The scrutiny of thermal stability of prepared samples was performed by applying the TGA technique. The thermal properties of samples were measured and reported for different percentages of weight loss, especially at 10% weight loss, that is a common norm for thermal stability (Table 4).

It has been reported that the polyurethane systems which are synthesized from aliphatic isocyanates and alcohols have the greatest thermal stability compared to other polyurethane systems [23]. Fig. 5 shows that all of the PU samples and their blends initiate to degrade at temperatures higher than 250 °C and have well correlation with previous reports.

Subramani et al. reported that chain extenders promote both the molecular weight and the thermal stability of PUDs [24]. In addition, it seems the thermal degradation of ionic PUs containing IPDI and DMPA progresses based on the retropolymerization reaction of PUDs [25]. The initial weight loss for SA was apparently less than polyurethane samples because of the presence of significant absorbed water on hydrophilic functional groups in the backbone of alginates. The alginate began to decompose at below 100 °C, but the rapid degradation was observed at 216–270 °C. The
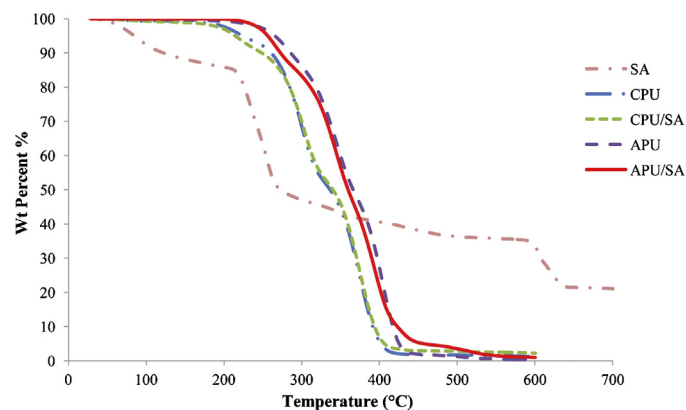
initial degradation may be ascribed to the vaporization of moisture, while the latter was attributed to the biopolymer degradation [26]. It is obvious from Fig. 5 that the early degradation stage of both cationic and anionic polyurethanes occurs at 190 °C and 220 °C, respectively. This study proposes that the higher temperature of the initial stage for anionic PUs may be related to the diffusion of the hard domains into the soft segments therefore, the rupture of the weakest bond, C–NH, occurs at relatively higher temperatures.

The early stage of degradation for both PU blends containing SA was observed at lower temperatures compared to their neat resources. The presence of significant amounts of absorbed water and thermally unstable carboxylate functional groups in the chemical structure of the sodium alginate affords the lower thermal stability of blends at temperatures below 400 °C. Because of the higher thermal resistance of anionic PUs, the APU/SA blends showed better thermal properties compared to the alginate-based cationic PUs. The raise of thermal stability with increasing alginate content at elevated temperatures was assigned to the more stable of the uronic acid monomers.

3.7. Contact angle

The hydrophilicity content of the prepared polymers was examined by the measurement of the formed contact angle between the surface of polymer samples and water drops. This test was performed by placing the drops of water on three different areas of the surface of the polymers by using a microsyringe. The hydrophilicity contents of samples were reported based on the mean value of these measurements (Table 5). Because of the presence of hydrophilic functional groups in the backbone of alginate, it is expected that the hydrophilicity of blends should be higher than neat polyurethane ionomers. The values of measured contact angles confirmed the mentioned hypothesis. The decreases of contact angle between polyurethane ionomers and their blends were attributed to the presence of carboxylate and hydroxyl groups of SA. In addition,

Table 5
Contact angles of neat PU ionomers and their blends with alginate salt.

Sample Number	Sample	Contact Angle (°)
1	Neat CPU	75 ± 2
2	CPU/SA	60 ± 2
3	Neat APU	76 ± 1
4	APU/SA	64 ± 4

all of the prepared samples were known as hydrophilic polymers because of their lower contact angle than 90°.

4. Conclusion

The different ionic polyurethane dispersions were synthesized based on two well-known ionic emulsifiers, i.e. *N*-methyldiethanolamine and dimethylol propionic acid. The polyurethane ionomers were prepared by the reaction of IPDI and PTMG, and the formation of NCO-terminated prepolymer. All of the PU ionomers were extended by 1,4-butanediol. Both anionic and cationic polyurethanes were characterized by different techniques and used for the subsequent reactions. A series of the alginate-based polyurethanes were formulated by solution blending of the polyurethane dispersions and sodium alginate. The effects of the emulsifier types were studied on the final properties of the prepared compositions. The nanocomposite elastomers of cationic PUs and SA showed excellent miscibility, while the anionic ones were appeared as the relatively incompatible ingredients. The FTIR and EDX procedures confirmed the SA presence in the macro- and microstructure of the polyurethane bulk, respectively. Based on the SEM images, the sodium alginate was homogeneously dispersed as the nanoparticles on the bulk of cationic polyurethanes, while agglomerations of SA were significant on those anionic elastomers. Furthermore, the thermal stability of alginate-based polyurethanes increased with raising the alginate content for both blends. The cationic blends illustrated the excellent mechanical properties with high elongation at break, while the elongation was significantly dropped for APU/SA samples because of the immiscibility of the SA and APUs.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijbiomac.2014.02.029.

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