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Compatible compositions based on aqueous polyurethane dispersions and sodium alginate

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ABSTRACT

A series of aqueous polyurethane dispersions were synthesized by the reaction of polytetramethylene glycol and isophorone diisocyanate, extended with dimethylol propionic acid. Their chemical structures were characterized using FTIR, ^{1}H NMR, and ^{13}C NMR, and thermal properties were determined by DMTA. Then, a number of aqueous polyurethane dispersions–sodium alginate (PUD/SA) compositions were prepared by addition of sodium alginate solution with different concentrations into the aqueous polyurethane dispersion. Characterization of chemical structure and thermal properties of these blends were performed by FTIR, EDX and DMTA, respectively. The morphology of the alginate in polyurethane matrix was studied by SEM. The hydrophilicity of the prepared samples decreases by increasing the content of sodium alginate in blends. These observations were attributed to the increase of hydrophilicity of the blends as a consequence of addition of hydrophilic carboxylate, hydroxyl and ether functional groups of the alginate to them.

1. Introduction

Polyurethanes (PUs) have a broad spectrum of commercial applications in many market areas because of their excellent chemical and physical properties. These polymers are synthesized from polyaddition reactions of isocyanate and hydroxyl groups (Castagna, Fragiadakis, Lee, Choi, & Runt, 2011; Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008). Polyurethanes are formed from soft segments and hard domains. The soft segments refer to polymeric polyols, while hard segments are produced from reaction of diisocyanates with hydroxyl or amine chain extenders. Soft segments affect on elastomeric properties of polymer at low temperatures, while hard segments contribute to the high temperature properties such as dimensional stability, thermal resistance and physical crosslinking (Chen, Shieh, & Chui, 1997; Santos, Delpech, & Coutinho, 2009; Zia, Barikani, Bhatti, et al., 2008; Zia, Barikani, Zuber, et al., 2008). Traditional applications of solvent-based PUs encounter with some restrictions due to the environmental regulations and therefore aqueous polyurethane dispersions are proper substitutes for these polymers (Barikani, Honarkar, & Barikani, 2010; Florian, Jena, Allauddin, Ramanuj Narayan, & Raju, 2010). Conventional PUs are insoluble in water therefore hydrophilic groups must be added to their backbones in order to disperse of these polymers in water (Rosthauser & Nachtkamp, 1986). Aqueous polyurethane dispersions have found diverse applications in different industries like textile, adhesives, gloves, wood finishing, glass fiber sizing, automotive topcoats, films for packaging and other applications (Meng, Lee, Nah, & Lee, 2009; Sriram, Sundar, Dattathereyan, & Radhakrishnan, 2005). Aqueous polyurethane dispersions (PUD) are divided into two ionic and nonionic types based on applied emulsifiers. Ionic dispersing groups are usually molecules with low molecular weight, whereas those nonionic refer to polymeric polyols that have hydrophilic groups (Madbouly, Otaigbe, Nanda, & Wicks, 2005; Rahman & Kim, 2006).

On the other hand, alginates are important biological polymers which have been in focus intensely due to excellent biological and biomedical properties during recent decades (Pathak, Kim, Lee, Baek, & Paeng, 2008; Wanga et al., 2003). These polymers have two sources of bacteria and brown algae. Alginates with algae's sources show different structural and chemical properties with respect to their seasonal and growth conditions. Alginates are not degraded in the human gastric-intestinal tract, but some microorganisms and lyases can degrade alginates down to single components. Alginates lyases catalyze the depolymerization of alginates by splitting the 1–4 glycosidic linkages (Fenoradosoa et al., 2010). The structure of the alginate is formed from the sequence of two α-L-guluronic acid (G) and β-D-mannuronic acid (M) monomers (Fig. 1) (Aida, Yamagata, Watanabe, & Smith, 2010; Chandía, Matsuhiro, & Vásquez, 2001). Three different structures including homogenous M and G homopolymers and heterogeneous MG blocks are found in backbone of alginates. Amount and sequence of these blocks determine the properties and behaviors of polymer (Gomez, Lambrecht,

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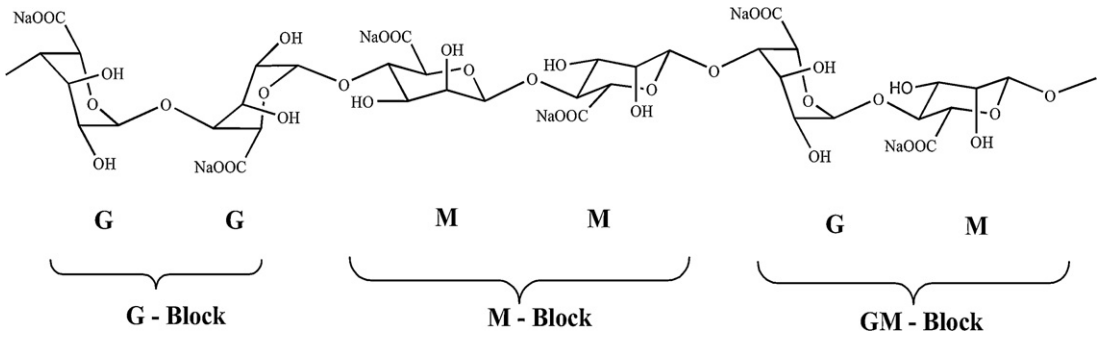

Fig. 1. Chemical structure of sodium alginate.

Lozano, Rinaudo, & Villar, 2009; Salomonsen, Jensen, Stenbæk, & Engelsen, 2008).

It has been observed that the rigidity of the chain blocks decrease as GG > MM > MG. Monovalent salts of alginate like sodium and ammonium alginate are soluble in water, while divalent Ca^{2+}, Sr^{2+} and Ba^{2+} and multivalent cations are insoluble in water due to the formation of complex structures with carboxylate and hydroxyl groups of alginates (Zhang, Yu, Zhao, Liu, & Guan, 2006). The ion-binding properties of alginate are generally related to formation of a complex and strong interactions between the functional groups of G-blocks and the divalent ion because of the specific stereo-structure of these blocks (Kaçar et al., 2002; Sinha & Khare, 2011).

Polyurethanes and alginates are two incompatible polymers with different glass transition temperatures. Therefore, developing of new procedures to produce compatible compositions of these polymers would be interesting. The aim of this research is preparation of compatible aqueous polyurethane dispersions–sodium alginate (PUD/SA) compositions and study of their compatibility by means of SEM, EDX and DMTA. It seems the presence of alginate can increase the biodegradability of the prepared blends.

2. Experimental

2.1. Chemicals

Polytetramethylene glycol (PTMG) with a molecular weight 1000 was supplied by Arak Petrochemical Company and dried at 50 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors that may interfere with the isocyanate reactions. Dimethylol propionic acid (DMPA) (Aldrich) was dried at 100 °C for 4 h before use. N-methylpyrrolidone (NMP), isophorone diisocyanate (IPDI) and triethylamine (TEA) were purchased from Merck, Germany. Sodium alginate (SA) with number-averaged molecular weight 12,000–40,000 was supplied by Aldrich and used as received.

2.2. Synthesis of PUD

A 500-cm^3 round-bottomed, four-necked flask equipped with a mechanical stirrer, heating oil bath, condenser, thermometer, dropping funnel, and N_2 inlet and outlet was used as reaction vessel. PTMG was charged into the reactor and the temperature of the oil bath was increased to 65 °C. Under mild stirring, proper amount of IPDI was added dropwise and the temperature was increased to 90 °C. It almost took 3 h to obtain NCO terminated prepolymer. Then a solution of DMPA in NMP was added and stirring continued for another 1 h. After that, in order to neutralize of carboxylic acid group, TEA 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 system at room temperature while the rate of stirring was increased vigorously to prevent gel formation. All the aqueous dispersions PUs were prepared as 30 wt% solid content. All the aqueous dispersions PUs were prepared as 30 wt% solid content. The scheme of polymer synthesis has been shown in Fig. 2 and the compositions of the synthesized polyurethanes have been summarized in Table 1.

2.3. Preparation of PUD/SA compositions

The PUD/SA blends were prepared through solution blending of aqueous polyurethane dispersions and aqueous sodium alginate solutions. Two different samples of PUD/SA blends were synthesized with 99.6:0.4% and 99:1% concentrations. The blend films were cast into a Teflon plate at room temperature followed by drying at 100 °C in oven for 24 h. The cured samples were stored for 1 week at room temperature for further characterization and measurements.

2.4. Measurements

The IR spectra of the blend films were performed on a Bruker-Equinox 55 FTIR spectrometer (Ettlingen, Germany) with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. The ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO)-d_6 solution using a Bruker Avance 400 MHz Spectrometer (Germany). Chemical shifts (δ) were reported in ppm by using tetramethylsilane (TMS) as a standard. The dynamic mechanical measurement (DMTA) was performed with a Triton Tritic 2000 instrument over a temperature range of −100 to 100 °C at heating rate of 10 °C/min and frequency of 1 Hz. The dimensions of sample films were 20 mm × 10 mm × 1 mm for the DMTA measurements. Scanning electronic microscopy (SEM) (Model Vega, Tescan Co., Cheque) was used to measure the size and shape of the alginate in polyurethane matrix. Contact angle measurements were performed at room temperature by a G10 (Kruss, Hamburg, Germany) instrument via the sessile drop method.

3. Results and discussion

3.1. Molecular characterization

Aqueous polyurethane dispersions based on IPDI, PTMG, DMPA and TEA were prepared by prepolymer mixing process and then

Table 1
Feed composition of polyurethanes with variable block ratios.

Sample no.	Block ratio	IPDI (g)	PTMG (g)	DMPA (g)	TEA (g)	Film property
WBPU1	1:2:1	8.89	20	2.68	2.02	Very weak
WBPU2	1:3:2	13.33	20	5.36	4.04	Excellent
WBPU3	1:4:3	17.78	20	8.04	6.06	Brittle

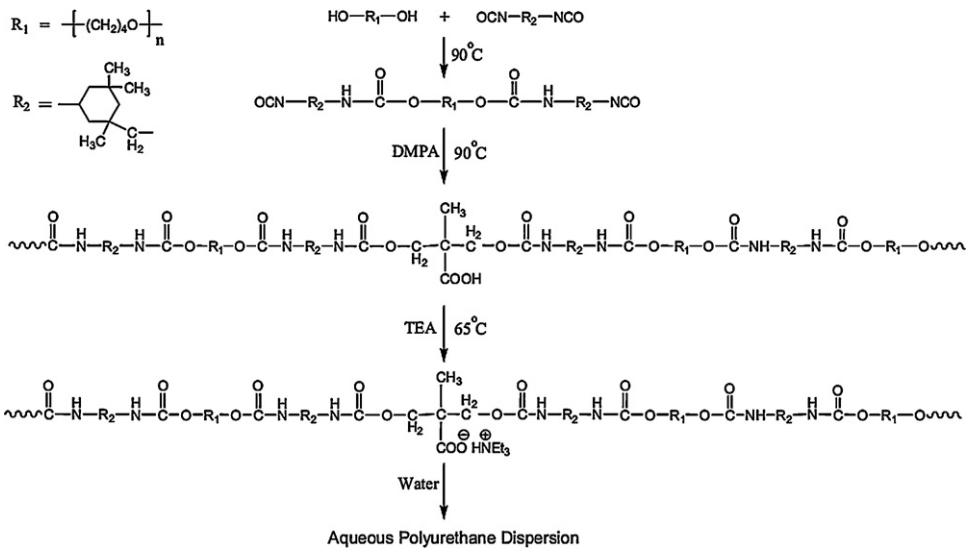

Fig. 2. Chemical procedure for synthesis of the aqueous polyurethane dispersions.

mixed with sodium alginate aqueous solutions to prepare PUD/SA blends. The polyurethanes with block ratio 1:3:2 showed better properties than ones with other block ratios, therefore preparation of PUD/SA blends and characterizations of them were performed based on this block ratio. DMPA was used as both emulsifier and chain extender in this work, while conventional aqueous polyurethane dispersions are usually extended by diamine or diol chain extenders.

The Fourier transform infrared (FTIR) spectra of the polyurethane, sodium alginate and blend of PUD/SA were recorded and compared. FTIR spectra of polyurethane elastomer, sodium alginate and blend PUD/SA with mass ratio 99:1 are shown in Fig. 3. FTIR spectrum of polyurethane extended by dimethylol propionic acid was performed to verify the disappearance of the NCO at 2265 cm^{-1} (Fig. 3a). Prepared polyurethanes were characterized with stretching vibrations N—H at 3322 cm^{-1}, C=O at 1713 cm^{-1} and N—H for amide II band at 1537 cm^{-1}. The C—H asymmetric and symmetric stretching vibrations of alkyl groups were appeared at 2944, 2859 and 2795 cm^{-1}. The absorption bands at 1463, 1365, and 1306 cm^{-1} were assigned to CH_2 bending vibration, C—H bending symmetric vibration and CH_2 wagging, respectively. C—O—C stretching vibrations of polyol were observed at 1000–1150 range. On the other hand, spectrum of sodium alginate which in some areas has overlapping with PU is shown in Fig. 3b. Stretching vibrations of O—H bonds of alginate were appeared in the range of 3000–3600 cm^{-1}. Asymmetric and symmetric stretching vibrations of aliphatic C—H were observed at 2920 and 2851 cm^{-1}, respectively. Observed bands in 1649 and 1460 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of carboxylate salt ion, respectively. The bands at 1107 and 935 were attributed to the C—O stretching vibration of pyranosyl ring and the C—O stretching with contributions from C—C—H and C—O—H deformation (Campos-Vallette et al., 2009; Leal, Matsuhiro, Rossi, & Caruso, 2008). Finally, blend PUD/SA showed a broad band at 3000–3500 cm^{-1} (Fig. 3c). In addition, C=O band shifted to lower wavenumber 1711 cm^{-1} in blend sample. The broadening in mentioned region and the shift in carbonyl band in IR spectrum were attributed to the hydrogen bonding between O—H groups of alginate and ether, urethane and carboxylate groups of polyurethane and N—H bonds of urethane and ether and carboxylate groups of alginate. These variations proved our claim toward proper miscibility of PUD and SA polymers.

NMR spectra of prepared aqueous polyurethane dispersions extended with DMPA are shown in Fig. 4. The ^1H NMR spectrum of synthesized polyurethane sample supported the proposed structures (Fig. 4a). Observed peaks at 0.82–0.93 ppm were attributed to methyl groups of the isophorone diisocyanate structure in the polyurethane backbone. Methyl group of DMPA and some methylene groups of IPDI were appeared at 0.93–1.04 ppm. Methylene groups of polytetramethylene glycol and ethyl groups of triethylamine salt were observed at 1.42–1.47 ppm. CH_2—O protons of repeating units of PTMG were appeared at 3.27 ppm. Observed peaks at 3.86 and 3.97 ppm were assigned to urethane CH_2 groups of PTMG and DMPA, respectively. Weak peaks appearing at 6.88–7.09 ppm were attributed to *cis* and *trans* conformers of urethane NH groups.

The presence of carbonyl groups of urethane bonds with peaks at 156–158 ppm in ^{13}C NMR spectrum proved the formation of polyurethane polymer structure (Fig. 4b). Methyl group of DMPA and methylene groups of PTMG CH_2—C were observed at 18 and 27 ppm, respectively. Methyl side chain, methylene groups and other carbons of IPDI ring were appeared at 24–45 ppm. Ethyl groups of triethylammonium and methylene groups of IPDI that are linked to urethane bond were observed at 47 and 55 ppm respectively. The observed peaks at the 64 and 65 ppm were assigned to CH_2—O of DMPA in the polyurethane backbone. The peaks at 70 and 71 were assigned to CH_2 groups of PTMG that are attached to urethane bonds. Carbonyl (C=O) groups of the carboxylates of DMPA were observed at 175 ppm.

3.2. DMTA studies

The viscoelastic properties of prepared samples were studied by dynamic mechanical thermal analysis. DMTA can show miscibility of a blend by comparison the transition temperature shift of neat polymer and its blend. Different types of transitions and relaxations which are related to the structure and morphology of polymer sample can be detected by means of DMTA measurements. Storage modulus (E') versus temperature curves of PU samples is shown in Fig. 5. It is obvious from Fig. 5 that both 99.6:0.4% and 99:1% blends of PUD/SA show no significant difference with neat PU sample. This observation shows excellent miscibility of these polymers with together. It is important to note that this miscibility has not been reported so far (Yun, Yoo, & Kim, 2007). Presence of

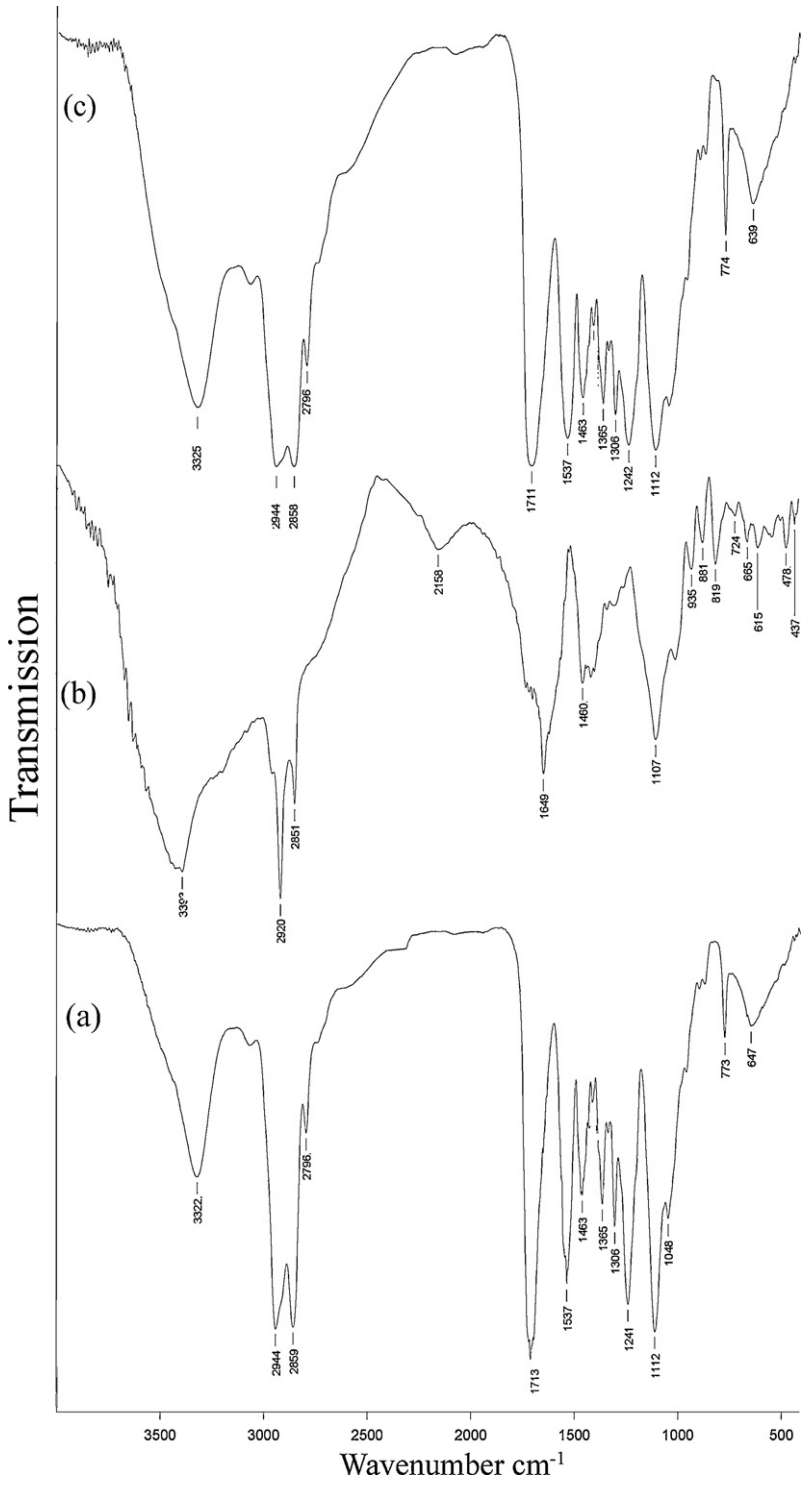

Fig. 3. FTIR spectra of (a) neat PU, (b) sodium alginate and (c) blend PUD/SA with 99:1 weight ratio.

hydrophilic and ionic groups in both PU and SA polymers afford good Columbic interactions and hydrogen bonding between functional groups of these polymers. On the other hand, it is obvious from Fig. 5 that increasing in alginate contents in the blend results to decrease of miscibility. This issue arises from decreasing of hard segment content of PU in the blends that affords decreasing of the hydrogen bonding between urethane groups of hard segments and SA polymers. Polyurethanes usually show one transition at low temperatures which is attributed to the glass transition temperature of soft segment (i.e. PTMG), however this transition was not observed at our samples due to interfere of DMPA in phase separation of soft and hard segments. It has been reported that transitions of hard segments can be affected by the contents of DMPA in the backbone of the polymer. The melting temperature of the soft segment appears same as previous reports (Rahman & Kim, 2007), approximately at 20 °C. The melting temperature of the

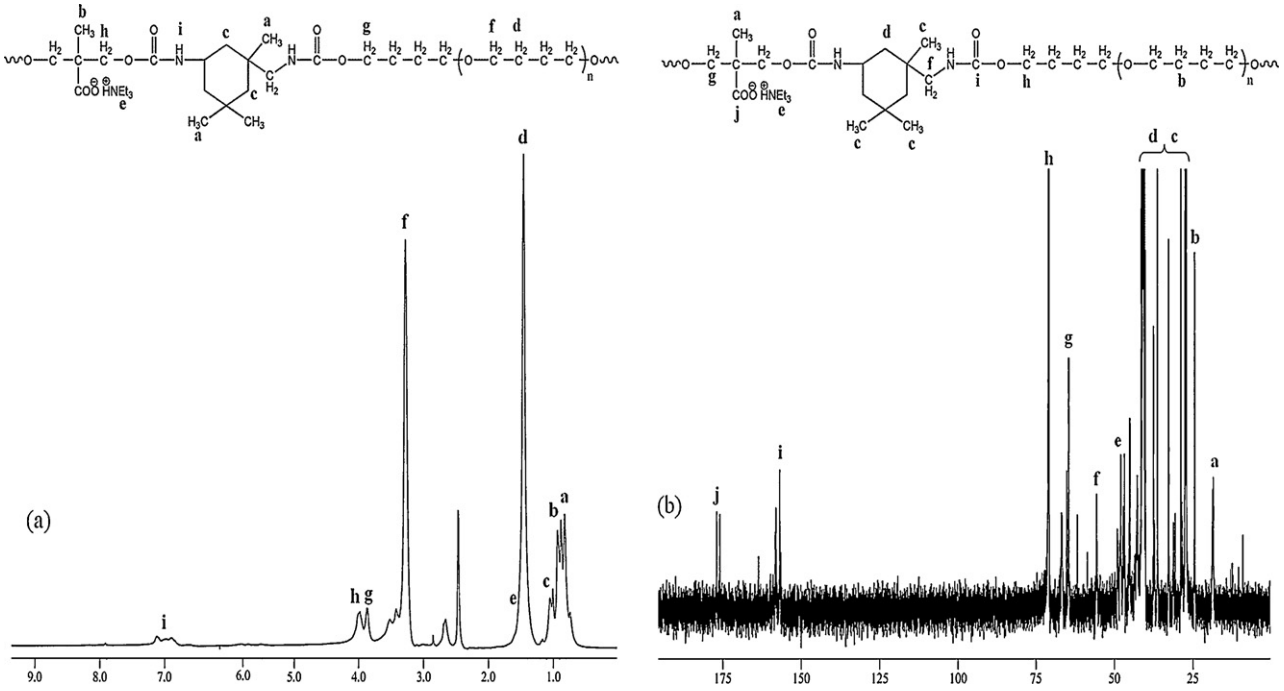

Fig. 4. (a) ^{1}H NMR spectrum of polyurethane extended with DMPA. (b) ^{13}C NMR spectrum of polyurethane extended with DMPA.

soft segment of all prepared samples were relatively identical that proved our claim to prepare of compatible compositions of aqueous polyurethane dispersions and sodium alginate (Fig. 6).

3.3. SEM and EDX images

The study of morphological aspects of the samples and characterization of both alginate and polyurethane polymers were performed by SEM and EDX methods, respectively. The SEM images of the anionic polyurethane/sodium alginate compositions indicated that sodium alginate was interspersed as agglomerations in a matrix of polyurethane. It is obvious from Fig. 7a that the size of alginate particles differs from nanometer to micrometer particles because of the different molecular weight of alginate chains. The main reason for agglomeration of alginate was attributed to the similar negative charge of carboxylate ions in both alginate and polyurethane polymers and their repulsive interactions. The presence of sodium alginate in polyurethane matrix was proved by the peak of the Na from EDX data (Fig. 7b and c).

3.4. Contact angle

Measurement of the formed contact angle between water drops and the surface of the polymer samples shows the hydrophilicity content of samples. The drops of water were placed on three different areas of the surface of samples by using a microsyringe. The mean value of these measurements was calculated and reported as hydrophilicity content of samples. The results showed that contact angle of PUD films without sodium alginate was 79°, while with addition of SA, contact angle of blendes decreased. These results prove that hydrophilicity of polyurethane films raise significantly with addition of SA content (Table 2). Presence of carboxylate and

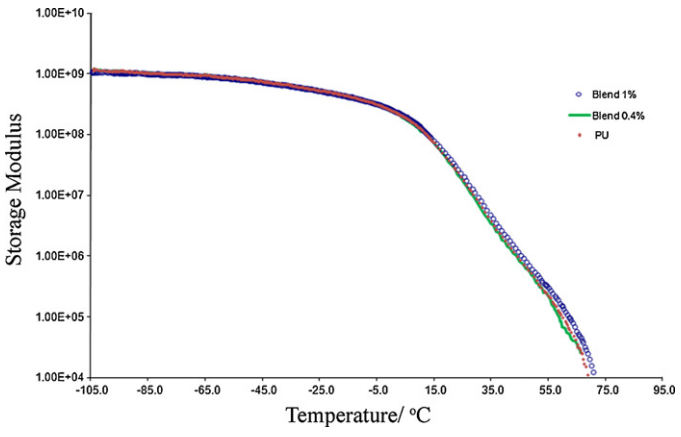

Fig. 5. Storage modulus versus temperature curves of neat PU and its blend samples.

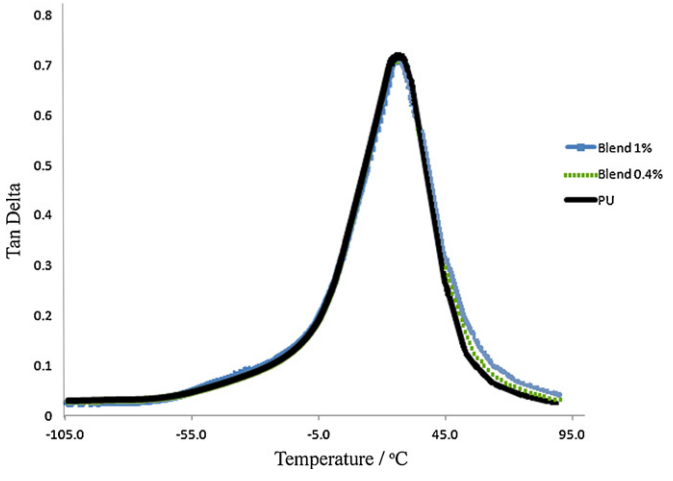

Fig. 6. Dynamic mechanical properties (tan δ) of neat PU and blend samples as a function of sodium alginate content.

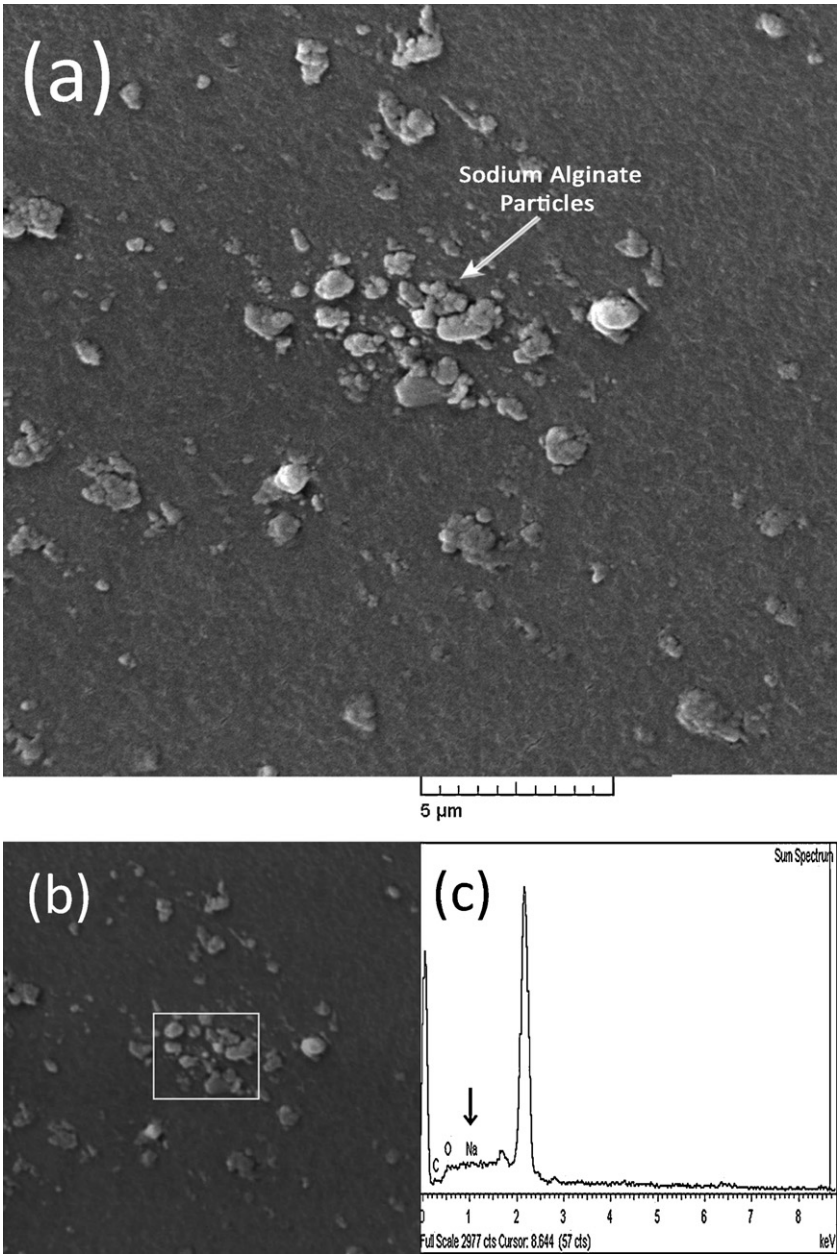

Fig. 7. Morphology (a) and characterization (b and c) of alginate in polyurethane matrix.

Table 2
Contact angles of neat PUD and its compositions with alginate salts.

Sample	Contact angle (°)
Neat polyurethane	79
Blend 99.6:0.4%	75
Blend 99:1%	71

hydroxyl groups of SA affords hydrophilicity of compositions raised with increasing SA content.

4. Conclusion

Solution blends of sodium alginates solutions and aqueous polyurethane dispersions were prepared based on PTMG and IPDI extended with DMPA. Proposed structure of synthesized polyurethane was confirmed by FTIR, ^{1}H NMR and ^{13}C NMR spectrometric methods. Both storage modulus and tan δ versus temperature showed identical glass transition for neat PUD and its blends with sodium alginate. The SEM and EDX showed the presence of alginate and its distribution as agglomerations in polyurethane matrix. It was observed that contact angle decreased with increasing sodium alginate content. This decrease in contact angle is ascribed to the increase of the hydrophilicity of the blends, which is attributed to hydrophilic groups of alginate.

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