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Highly stretchable nanoalginate based polyurethane elastomers

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ABSTRACT

Highly stretchable elastomeric samples based on cationic polyurethane dispersions–sodium alginate nanoparticles (CPUD/SA) were prepared by the solution blending of sodium alginate and aqueous polyurethane dispersions. CPUDs were synthesized by step growth polymerization technique using N-methyldiethanolamine (MDEA) as a source of cationic emulsifier. The chemical structure and thermal–mechanical properties of these systems were characterized using FTIR and DMTA, respectively. The presence of nanoalginate particles including nanobead and nanorod particles were proved by SEM and EDX. It was observed that thermal properties of composites increased with increasing SA content. All prepared samples were known as thermoplastic-elastomers with high percentages of elongation. Excellent compatibility of prepared nanocomposites was proved by the DMTA data.

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1. Introduction

Polymeric nanoparticles have been in focus because of their clinical usages especially for therapeutics and carriers for delivery systems (Goycoolea, Lollo, Remuñá-López, Quaglia, & Alonso, 2009; Hu, Jiang, Ding, Ge, & Yuan, 2002; Pressly, Rossin, Hagooly, Fukukawa, & Messmore, 2007). Different methodologies including interfacial polymerization, emulsion polymerization, solvent evaporation, solvent deposition, thermally induced gelation process, nanoprecipitation, emulsification–diffusion and controlled gellification have been reported for synthesizing polymeric nanoparticles (Chen & Ma, 2004; Daemi & Barikani, 2012; Lee, Jeong, Shin, Kim, & Chang, 2005; Zhao, Carvajal, Won, & Harris, 2007).

Natural polysaccharides have been attracted as biopolymers due to their unique properties during last decades (Lee & Mooney, 2012; Pawar & Edgar, 2012; Travinskaya & Savelyev, 2006; Yang, Ren, & Xie, 2011; Zia, Bhatti, Barikani, Zuber, & Bhatti, 2009). Alginic acid and its carboxylic salts are important biopolymers with interesting features such as biocompatibility, biodegradability and the ability of gelation with multivalent cations (Arıca, Bayramoğlu, Yılmaz, Bektaş, & Genç, 2004; De-Bashan & Bashan, 2010; Opasanon, Muangman, & Namviriyachote, 2010). Alginates can be assumed as linear triblock copolymers which contain homopolymeric regions of guluronate (G-blocks) and mannuronate (M-blocks) that interspersed in blocks with two groups of 1–4-linked M and G residues (MG-blocks) (Scheme 1) (Li, Fang, Vreeker, & Appelqvist, 2007). These polymers can be used as micro and nano encapsulation agents and therefore have found different applications in drug delivery and control release systems (Ahmad, Pandey, Sharma, & Khuller, 2006; Finotelli, Silva, Sola-Penna, Rossi, & Farina, 2010).

On the other hand, polyurethanes (PUs) are interesting polymers with broad range of applications, which are synthesized from polyaddition reactions of isocyanate and hydroxyl groups (Chattopadhyay & Raju, 2007; Chattopadhyay & Webster, 2009; Lemos, Santos, Santos, Santos, & dos Santos, 2007; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008). These polymers have very good elasticity, high mechanical strength and abrasion resistance due to specific micro-phase structure formed between the hard and soft segments (Lu & Larock, 2008). Hard segments participate in high temperature properties, while soft segments affect on elastomeric properties of polymer at low temperatures (Cristiane, Santos, Delpech, & Coutinho, 2009; Ertema, Yilgor, Kosak, Wilkes, & Zhang, 2012). Traditional applications of solvent-based PUs encounter with some restrictions due to environmental regulations regarding volatile organic chemicals (VOCs) (Florian, Jena, Allauddin, Narayan, & Raju, 2010; Wynne, Fulmer, McCluskey, Mackey, & Buchanan, 2011). Conventional PUs are insoluble in water, therefore in order to disperse these polymers in water, hydrophilic groups (including ionic or non-ionic agents) must be added to their backbones (Liu, Xu, Liu, Cai, & Su, 2011). Presence of ionic groups in the structure of polyurethane affords interesting interactions between PUDs with important biopolymers and nanoparticles (Mao, Jiang, Luo, Liu, & Bao, 2009).

Physical and chemical interactions of PUDs with different polysaccharides have been reported in recent years. It is noteworthy to note that no report is available on cationic polyurethane/nanoalginate compositions in open scientific literature. It is a common procedure to obtain alginate nanoparticles

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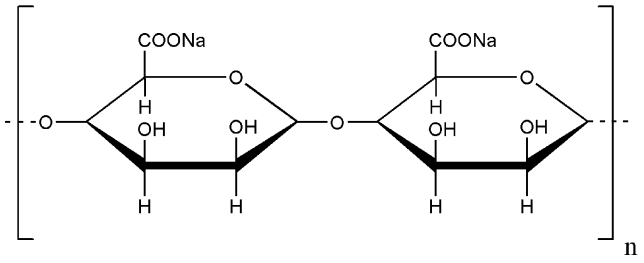


Scheme 1. Chemical structure of sodium alginate.

through the reaction of very dilute solutions of sodium alginate with a source of calcium cations, however we did not find any report about the composites of sodium alginate nanoparticles in the matrix of important polymers in the literatures, for example, polyurethanes. As part of our continuing efforts on the development of new methods for the preparation of carbohydrate based polyurethanes for example, starch (Barikani & Mohammadi, 2007), Chitin (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008; Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008), Chitosan (Barikani, Honarkar, & Barikani, 2010; Barikani, Honarkar, & Barikani, 2009) and cellulose (Daemi, Hatami, & Barikani, 2012), we have recently reported the preparation method of compatible composites based on anionic PUDs and sodium alginate (Daemi, Barikani, & Barmar, 2013). Because of the poor mechanical properties and brittle nature of sodium alginate and subsequent limitations for different applications of this polymer, preparation of stretchable composites containing sodium alginate is interesting. In continuation, the aim of this research is preparation of novel compatible elastomeric samples based on aqueous cationic polyurethane dispersions–sodium alginate nanoparticles (CPUD/SA) and study of physical, thermal, mechanical and morphological properties of these systems.

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. N-methyldiethanolamine (MDEA) (Merck) was dried at 100 °C for 4 h before use. N-Methylpyrrolidone (NMP), isophoronediisocyanate (IPDI) and acetic acid (HOAc) were purchased from Merck, Germany. Two different grades of sodium alginate (SA) with number-averaged molecular weights 5000–40,000 and 30,000–40,000 were obtained from Aldrich and used as received.

2.2. Synthesis of cationic aqueous polyurethane dispersions

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. Polytetramethylene ether glycol was placed into the reaction vessel and the temperature of the oil bath was increased to 65 °C. Under mild stirring, proper amount of isophoronediisocyanate was added dropwise and the temperature was increased to 90 °C. After 3 h, required amount of N-methyldiethanolamine in NMP was added and stirring continued for another 1 h. 1,4-Butanediol as a chain extender was added into the reactor in chain extension step. After that, in order to formation of quaternary ammonium groups from MDEA, acetic acid was added to the system at 65 °C. Finally, required amount of deionized water was added dropwise into the system at room temperature to obtain CPUDs with 30 wt.% solid content. From the different formulations of CPUDs based on block ratios 1:2:0.5: 0.5, 1:3:1:1, 1:3:2:1 and 1:3:1:2, the systems with mol ratio 1:3:1:1 showed the best physical and mechanical properties therefore, all aqueous polyurethane dispersions were synthesized based on this block ratio. A schematic illustration of the chemical route for synthesis cationic polyurethane is shown in Scheme 2.

2.3. Preparation of compatible CPUD/sodium alginate elastomers

The CPUD/sodium alginate elastomers were prepared through blending of CPUDs and aqueous SA solution. It is necessary to replace the aqueous media of polymers by a mixture of water/chloroform media during the addition of alginate solution to the CPUD to prevent gelation of the final composite in water. Three different samples of PUD/SA were synthesized with 99:1%, 98:2% and 96:4% w/w concentrations. The blended films were cast by pouring the compositions onto a teflon plate at room temperature followed by drying at 100 °C in oven for 24 h.

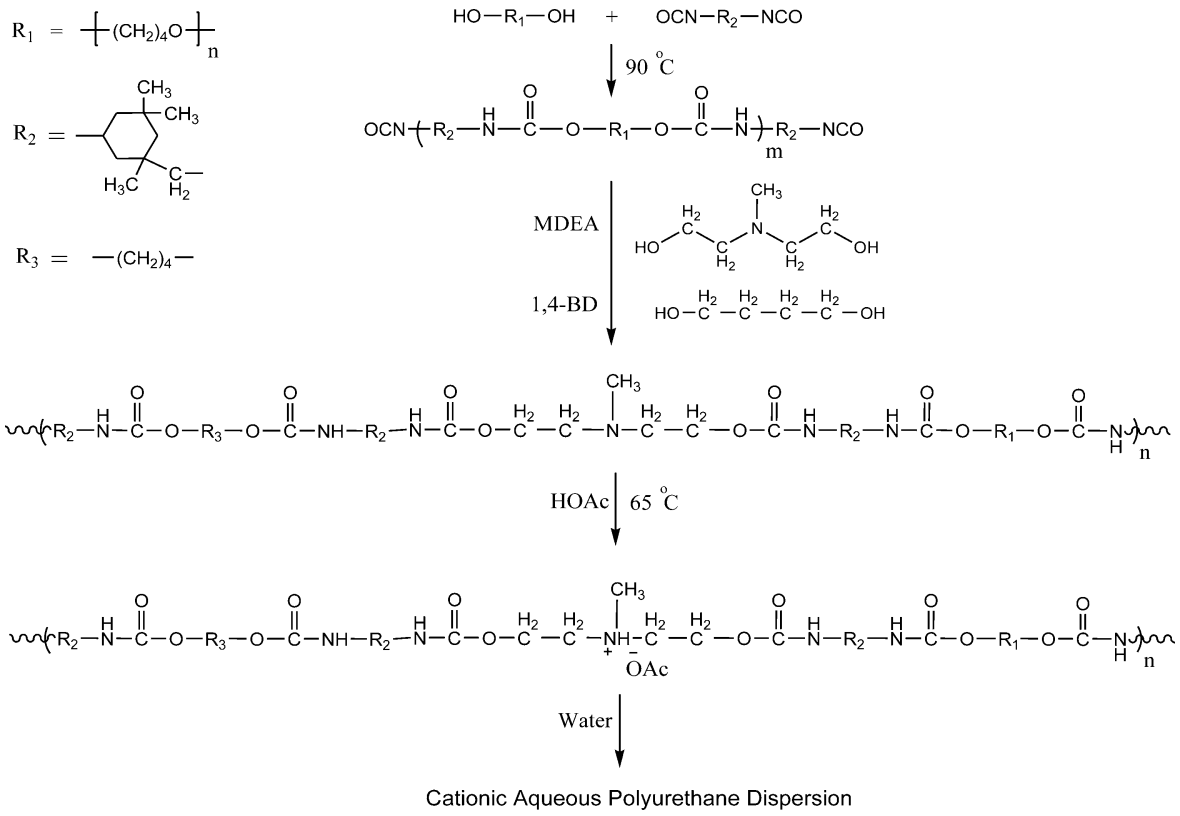
2.4. Measurements

Chemical characterization of blend films was done by the IR spectra, which performed on a Bruker-Equinox 55 FTIR spectrometer (Ettlingen, Germany) with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. 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. Thermogravimetric analysis (TGA) was recorded on a Polymer Lab TGA-1500 instrument (London) under a N_2 atmosphere from room temperature to 600 °C with a heating rate of 10 °C/min. Scanning electronic microscopy (SEM) (Model Vega, Tescan Co., Cheque) was used to measure the size and shape of the alginate nanoparticles in polyurethane matrix. Characterization of alginate nanoparticles in the matrix of the polyurethane were done with using EDX method and by Oxford instrument model INCA. The films of CPUD and its samples with sodium alginate were prepared by casting the solution samples in a mold for the measurement of tensile properties. After evaporation of water at 70 °C for 24 h, the films were further dried at 100 °C under a vacuum for another 12 h. Stress–strain measurements were performed on an Instron Mechanical Testing instrument (MTS System Corporation, Eden Prairie, MN) tensile tester model 10/M at a strain rate of 50 mm/min. Tensile tests were conducted using atensile tester, attaching a constant-temperature heating chamber. The test specimens had dimensions of 50 mm × 5 mm × 0.5 mm. Contact angle measurements were performed at room temperature by a G10 (Kruss, Hamburg, Germany) instrument via the sessile drop method. This measurement was done by placing the drops of water 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.

3. Results and discussion

3.1. Molecular characterization

The Fourier transform infrared (FTIR) spectra of the polyurethane, sodium alginate and blend of CPUD/nanoalginate samples were recorded and compared. Synthesized polyurethanes were characterized with the disappearance of the NCO vibration at 2265 cm^{-1} and the presence of stretching vibrations of N—H at 3319 cm^{-1}, C=O at 1714 cm^{-1} and N—H for Amide II band at



Scheme 2. Chemical procedure for synthesis of the aqueous cationic polyurethane dispersions.

1538 cm^{-1} (Fig. 1a). The asymmetric and symmetric stretching vibrations of aliphatic groups were appeared at 2945, 2859 and 2795 cm^{-1}. The absorption bands at 1463, 1365, and 1305 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. 1b. Observed bands in 1649 and 1460 cm^{-1} were attributed to asymmetric and symmetric stretching vibrations of carboxylate group, respectively. Finally, CPUD/SA elastomer showed significant broad vibration band at 3000–3500 cm^{-1}. In addition, carbonyl band shifted to lower wave number 1701 cm^{-1} in blend sample (Fig. 1c). The Broadening in mentioned region and the shift in carbonyl band in IR spectrum were related to the hydrogen bonding between functional groups of both polymers. In addition, the appearance of uronic vibrational bands of alginate in blend sample on the anomeric region spectrum proves the presence of the alginate in the matrix of the prepared polyurethane.

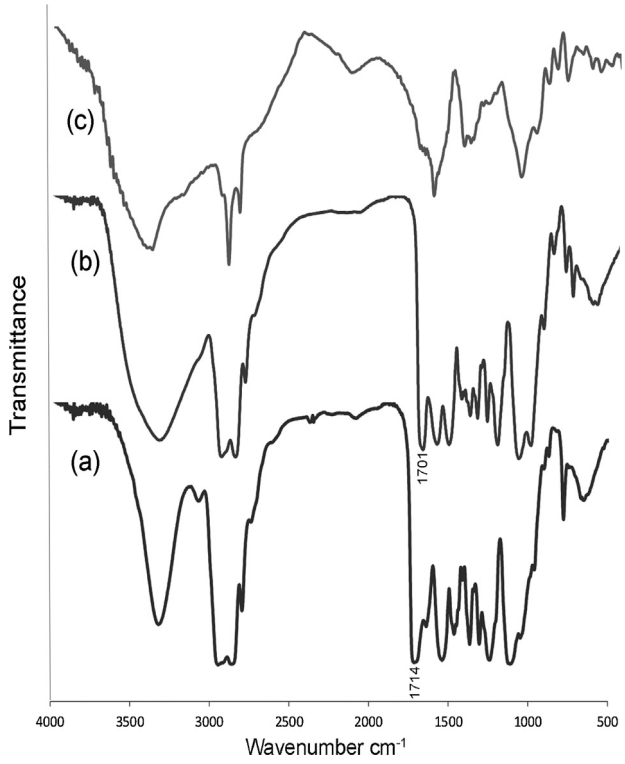


Fig. 1. FTIR spectra of (a) neat cationic PU; (b) CPUD/SA composite with 96:4 weight ratio; and (c) sodium alginate.

3.2. SEM and EDX analysis

The presence of sodium alginate nanoparticles in microstructure were proved by the distinct peak of the Na from EDX data, while the bulk of CPUD did not show this peak (Fig. 2). The SEM images of the cationic polyurethane/nanoalginate with molecular weight of SA 5000–40,000 compositions indicated two interesting nanobead and nanorod particles (Fig. 3a). These two different morphologies of nanoparticles directed us to study the effects of alginate molecular weight on the properties of these particles. Further investigations on molecular weight of sodium alginate confirmed our prediction about the intimate interactions between ionic groups of both alginate and polyurethane polymers. Broadness in molecular weight of SA was appeared as two fascinating different bead and rod-like morphologies (Fig. 3). Alginate chains with low molecular weight because of the lower carboxylate group contents were appeared as the nanobeads, while higher molecular weight ones were detected by nanorod structures. In addition, the presence and agglomeration

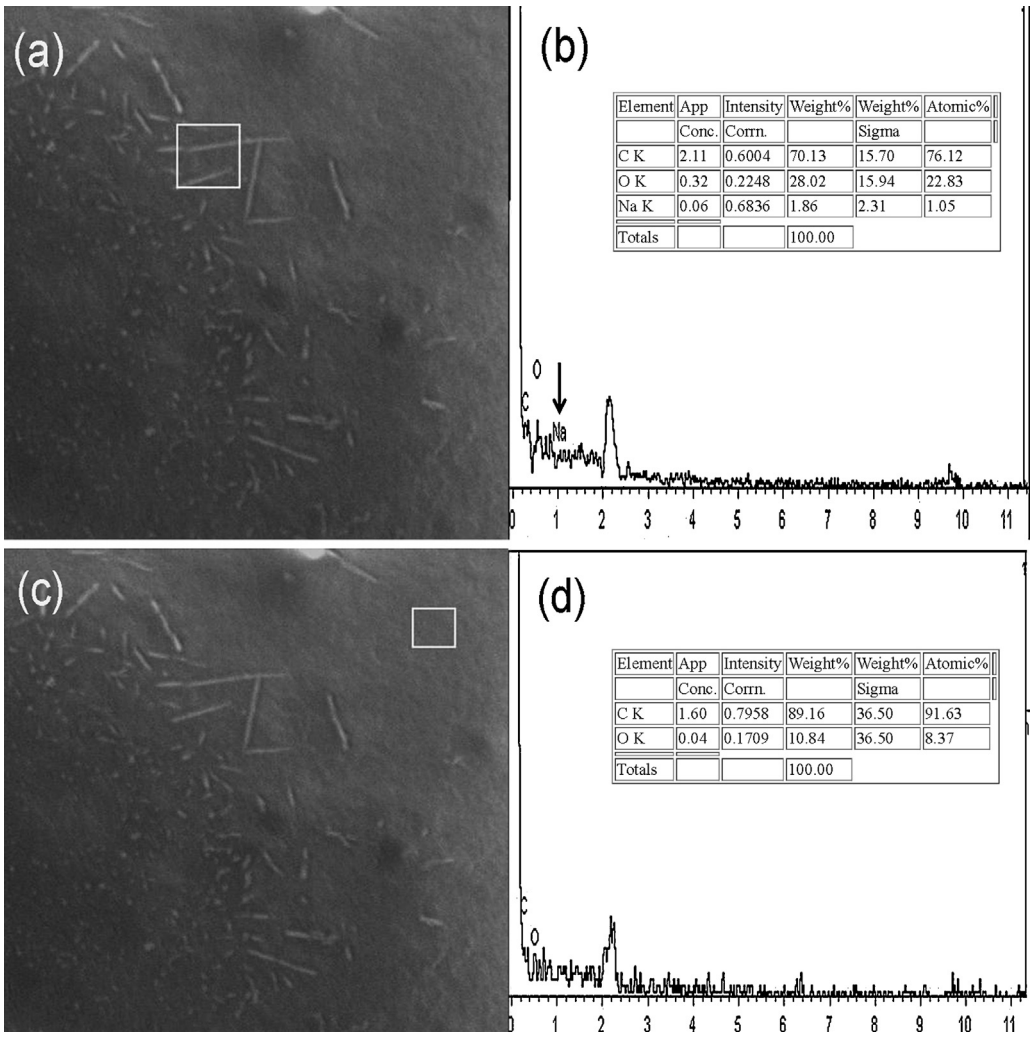


Fig. 2. The presence of sodium peak from EDX date in nanocomposite (a and b) and its absence in polyurethane bulk (c and d).

of quaternary ammonium groups along to the polyurethane chain and their interactions with high molecular weight alginate chains may explain the peculiar nanorod structures. The intense coulombic forces between anionic and cationic groups of polymers, which correspond with carboxylate groups of alginate and quaternary ammonium ones in polyurethane afford excellent interactions of both polymers. In fact, the electrostatic interactions between quaternary ammonium groups of cationic polyurethane and

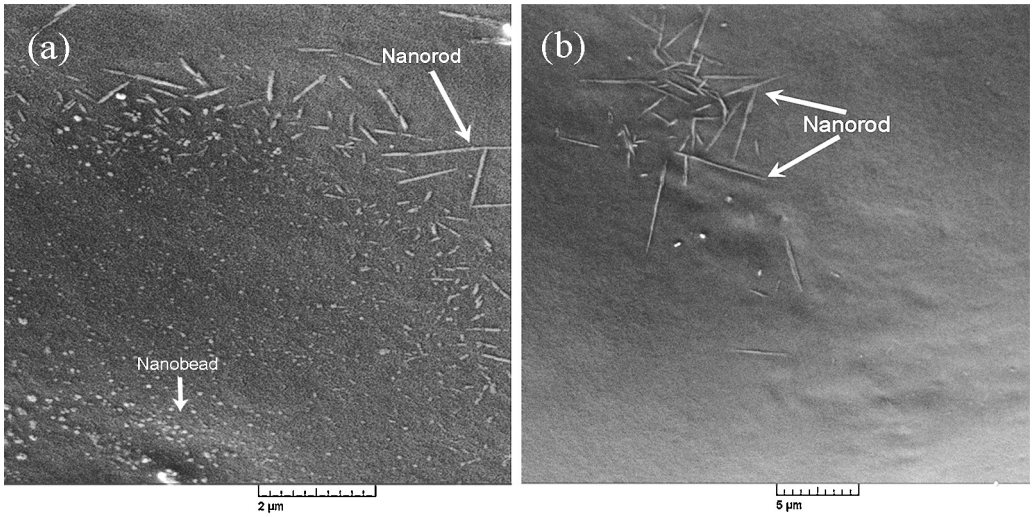


Fig. 3. Morphology of nanoalginate particles in polyurethane matrix: (a) nanobead and nanorod particles in SA with molecular weight 5000–40,000 and (b) nanorod particles in SA with molecular weight 30,000–40,000.

Table 1
Thermal stability and dynamic mechanical analysis data of PU and nanocomposites.

Number	Sample	T_{onset} (°C)	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	T_g (°C)[a]	tan δ[b]
1	SA	27.24	122	226	272	–	–
2	Neat CPUD	28.84	260	284	335	26	0.87
3	CPUD:SA 99:1%	28.8	238	270	318	27	0.73
4	CPUD:SA 98:2%	28.43	247	276	324	29	0.58
5	CPUD:SA 96:4%	28.23	248	283	340	30	0.54

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.
[a] The central point of the maximum of the tan δ peak was used.
[b] Altitude of the tan δ peak.

carboxylate groups of the polyanionic alginate cause a polymeric quaternary ammonium carboxylate salt which can be appeared as nanoparticles on the surface of bulk polyurethane. For proving our claim, sodium alginate with molecular weights 30,000–40,000 was blended with CPUD. SEM images of these elastomers were emerged as nanorod particles with similar size and morphology (Fig. 3b).

3.3. TGA analysis

The thermal stability of the prepared compositions and original sodium alginate were evaluated by the TGA technique. The thermal decomposition of all samples were evaluated at different percentages of weight loss (i.e., 10, 20, and 50%), and the results are presented in Table 1. The most valuable norm for thermal stability, that is, at 10% weight loss, was found in the range 235–260 °C. The lower decomposition temperature range at 10%–50% weight loss for blends in comparison to the neat polyurethane was related to the presence of absorbed water and thermally unstable COO^- groups in the structure of sodium alginate. It is obvious from Table 1 that thermal stability of the samples increases with increasing alginate content in the blends. This was due to the higher thermal stability of the ring structures of alginate in comparison to polyurethane structure, because the molecular chain of alginate is composed of quite thermally stable uronic acid monomers.

3.4. DMTA studies

Dynamic mechanical properties of polyurethane and its nanocomposite elastomers with sodium alginate were studied by dynamic mechanical thermal analysis. 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. Tan delta (tan δ) versus temperature curves of elastomeric samples is shown in Fig. 4. The maximum in tan δ is usually used as the definition of T_g. The cationic polyurethane showed a transition at 26 °C, while other samples were characterized with transitions which were too close to the transition temperature of the later sample. It is obvious from Fig. 4 that all of PUD/SA samples show no significant difference with neat PU sample. This observation shows excellent miscibility of these polymers with together. This miscibility comes from the different electrostatic charges of both cationic polyurethane and anionic alginate and hydrogen bonding between the donor and acceptor functional groups of both polymers. It is important to note that this excellent miscibility has not been reported so far. In addition, it is apparent from Fig. 4 that with increasing alginate content, the transition temperature of the soft segment remains constant. This excellent miscibility comes from the dissimilar electrical charges and is comparable to our previous report. The relatively identical melting temperature of the soft segment of all prepared samples proves our claim to prepare of compatible elastomers of cationic polyurethane dispersions and sodium alginate.

3.5. Mechanical property studies

Recently, Sun et al. reported the extremely stretchable and tough hydrogels based on ionically crosslinked alginate, and covalently crosslinked polyacrylamide (Sun, Zhao, Illeperuma, Chaudhuri, & Oh, 2012). Here, we introduced the elastomeric sample based on cationic polyurethane and sodium alginate which can be stretched to >11 times its original length without rupture (Fig. 5). The sample neat PU showed a significantly higher elongation and lower tensile strength than all of the other samples (Table 2). This behavior was attributed due to the not interfered structure of the neat polyurethane. In addition, it may also be related to higher hard-segment contents for the neat polyurethane compared to the other samples. In addition, it is important to note that the prepared elastomer is stretched about 100 times to the neat sodium alginate. These results proved the formation of elastomeric samples containing sodium alginate with extremely brilliant mechanical properties. Comparison of the mechanical properties data of prepared samples showed that elastomers containing sodium alginate had higher mechanical strengths than neat cationic polyurethane. The higher strengths and lower elongations of samples containing sodium alginate may be implied to the brittle nature of the uronic residues of alginate structure and the hydrogen bonds between the functional groups of the alginate and polyurethane segments. This hydrogen bonding disturbs the microstructure of the soft and hard segments of the polyurethane and therefore, the phase separation of these segments decreases because of the presence of alginate chains. Greater amounts of the sodium alginate in the matrix of the polyurethane produce a lower elongation with higher mechanical strength. These observations can be explained by decrease of phase separation of polyurethane segments in the presence of greater amounts of sodium alginate.

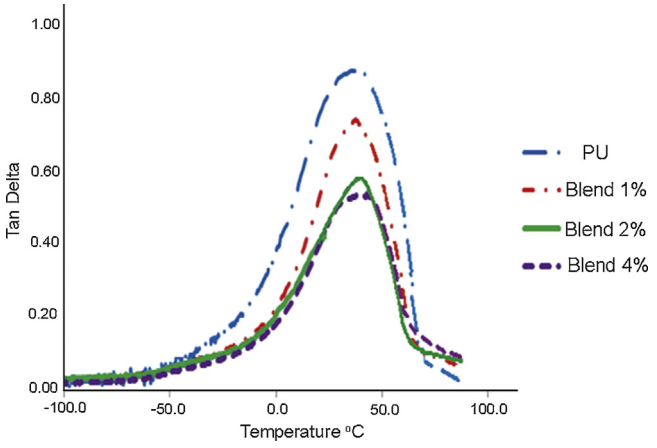


Fig. 4. Dynamic mechanical properties (tan δ) of neat PU and blend samples as a function of sodium alginate content.

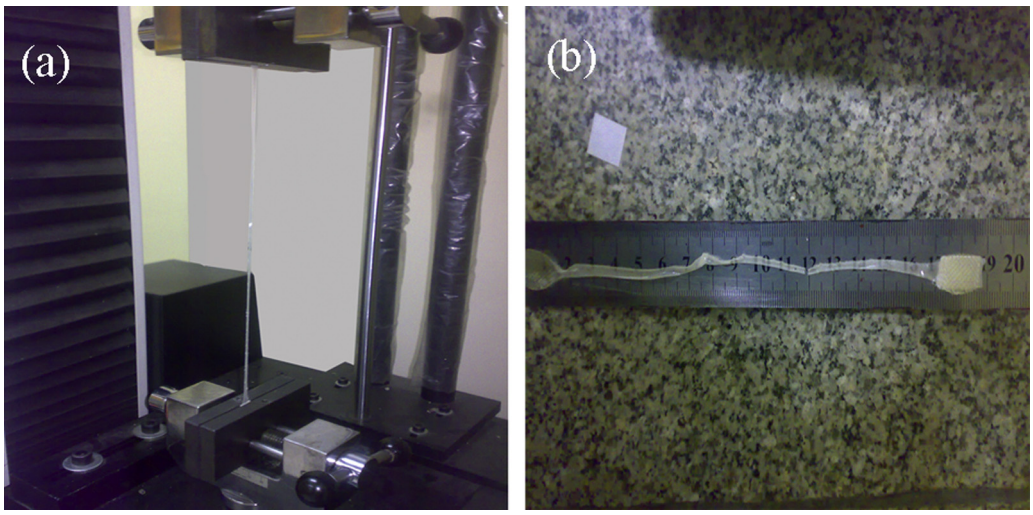


Fig. 5. Mechanical properties of elastomeric sample containing 4% sodium alginate: (a) excellent elongation before the break, (b) rapid recovery of the stretched samples after the rupture.

Table 2
Mechanical property data of the PU samples.

Sample number	Sample	Tensile strength (MPa)	Elongation at break (%)
1	Neat CPUD	20.06	1300
2	CPUD:SA 99:1%	21.12	1260
3	CPUD:SA 98:2%	23.44	1190
4	CPUD:SA 96:4%	26.66	1100
5	SA	–	10

Table 3
Contact angles of neat PUD and its elastomers with alginate salt.

Sample number	Sample	Contact angle (deg)
1	Neat CPUD	75 ± 2
2	CPUD:SA 99:1%	69 ± 2
3	CPUD:SA 98:2%	66 ± 1
4	CPUD:SA 96:4%	60 ± 2

3.6. 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 results showed that contact angle of CPUD films without sodium alginate was 75°, while with addition of SA, contact angle of elastomers decreased to 60° for the sample containing 4% alginate (Table 3). These results prove that hydrophilicity of polyurethane films raise significantly with addition of SA content because of the presence of hydrophilic carboxylate and hydroxyl groups of sodium alginate structure.

4. Conclusion

Compatible aqueous cationic polyurethane dispersions–sodium alginate nanoparticles elastomers were prepared by solution blending of cationic polyurethane dispersions based on PTMG and IPDI extended with MDEA and 1,4-BD chain extenders and sodium alginate. Neat CPUD and its nanocomposite elastomers with sodium alginate showed excellent miscibility with attention to the DMTA and FTIR results. The SEM and EDX showed the presence of sodium alginate nanoparticles in polyurethane bulk. The prepared composites indicated two interesting nanobead and nanorod morphologies in respect of different molecular weights of sodium alginate samples. In addition, the thermal stability of samples increases with increasing alginate content in the elastomers because of the presence quite thermally stable uronic residues. All prepares samples were known as thermoplastic-elastomers with high elongation percentages.

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