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ORIGINAL PAPER

Synthesis and characterization of chitosan-based polyurethane elastomer dispersions

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Abstract A number of aqueous polyurethane dispersions were synthesized by the reaction of poly(ε-caprolactone) and isophorone diisocyanate, extended with different mass ratios of chitosan and dimethylol propionic acid. Their chemical structures were characterized by using FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and thermal properties were determined by TGA. Incorporation of chitosan into the polyurethane backbone improved thermal stability. The hydrophilicity of the prepared polymers was also examined by contact angle measurements. For all samples, the contact angles increased by increasing the amount of chitosan. The increased contact angle is ascribed to the decrease of the hydrophilicity of the polyurethanes, which is reduced by the increasing amount of chitosan with respect to dimethylol propionic acid chain extender.

Keywords Chitosan · Polyurethane · Polymerizations · Spectroscopy · Oligosaccharides · Dispersion

Introduction

In the past 30 years, substantial progress has been made on fundamental and applied research in chitosan technology. Chitosan (CS) is a polysaccharide obtained by deacetylation of chitin, which is the major constituent of the exoskeleton of crustaceous water animals, although this *N*-deacetylation is almost never complete. Chitosan is recommended as a functional material, and this natural polymer has excellent properties such as biocompatibility, biodegradability, non-toxicity, and adsorption properties, so it can be used in a wide range of applications, such as membranes [1], removal of metal ions from wastewater [2], drug delivery systems [3], biological applications [4, 5], tissue engineering [6], biosensors [7], scaffolds [8], and packaging [9].

Chitosan is structurally similar to cellulose and chitin (Fig. 1). Flash treatment of alkali-impregnated chitin at 140–190 °C has been reported to efficiently afford highly deacetylated chitosan over a short time period [10].

Water-based polyurethanes, on the other hand, have been implicated in environmental pollution and health issues [11]. These polyurethanes can be classified into ionic and nonionic types. Nonionic types contain a hydrophilic soft segment pendant group such as polyethylene oxide [12], whereas the ionic types contain anionic or cationic centers in the polymer chains. Conventional polyurethanes are insoluble in water and should contain ionic or nonionic hydrophilic segments in their structure to be dispersive in water [13, 14].

Combinations of these polymers may provide new materials with good physical and mechanical properties combined with bioactivity and degradability. In this research, following our previous study on chitin-based polyurethanes [15–17], chitosan-based water dispersion polyurethane [18] was prepared by the reaction of poly(ε-caprolactone)diol (PCL) and isophorone diisocyanate (IPDI) with different weight percent of chitosan and dimethylol propionic acid (DMPA) as chain extenders. The bulk structures and properties were characterized by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy as well as thermogravimetric analysis (TGA), the main focus being on the

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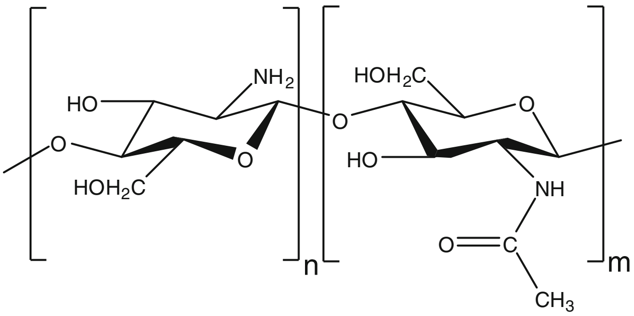


Fig. 1 Chemical structure of chitosan

effect of chitosan on the final structure and properties of the prepared polyurethanes.

Results and discussion

Chitosan-based water dispersible polyurethane elastomers were synthesized by the reaction of poly(ε-caprolactone)diol with isophorone diisocyanate, extended with different mass ratios of chitosan and dimethylol propionic acid. These ratios are described in percentage values throughout the manuscript where a '50% material' was prepared from such amounts of chitosan and DMPA that both materials contributed the same number of functional groups. The prepolymer method was applied for the synthesis of these elastomers. Termination with $NaHSO_3$ and salt formation between the carboxylic group of DMPA and triethylamine makes the polymer water dispersible. Chitosan used in this study was treated prior to use in the synthesis to achieve better solubility. The chemical structure of the polymers was characterized by FTIR and NMR spectroscopy, and polymer properties were examined by TGA and contact angle.

IR spectroscopy

The Fourier transform infrared (FTIR) spectra of the chitosan before and after the depolymerization were recorded and compared. No obvious change in functional group absorption means that only cleavage of 1,4-*β*-D-glucoside bonds occurred and chitosan with lower molecular weight is formed due to oxidation [19, 20]. The viscosity average molecular weight of chitosan was measured by viscometry and found to be 3.5×10^5 and 2.9×10^4 before and after the treatment, respectively. For determination of molecular weight the well-known Mark–Houwink equation was used:

$$[\eta] = KM^{\alpha} \tag{1}$$

In Eq. 1 η is the intrinsic viscosity, M is molecular weight, K and α are constants. These constants were $K = 1.81 \times 10^{-3}\ \text{cm}^3\ \text{g}^{-1}$ and $\alpha = 0.93$. The intrinsic viscosity of chitosan samples (before and after treatment) was measured with an Ubbelohde viscometer in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at 25 °C.

FTIR spectra of polyurethane extended by chitosan and DMPA with 0, 25, 75, and 100% chitosan with respect to DMPA are also shown in Fig. 2. The N–H stretching vibration bands appeared at 3,330 cm^{-1}. The C–H symmetric and asymmetric stretching vibrations of CH_2 groups were observed at 2,940 and 2,865 cm^{-1}, respectively. The absorption bands at 1,722, 1,658, and 1,544 cm^{-1} are due to C=O stretching and N–H deformations.

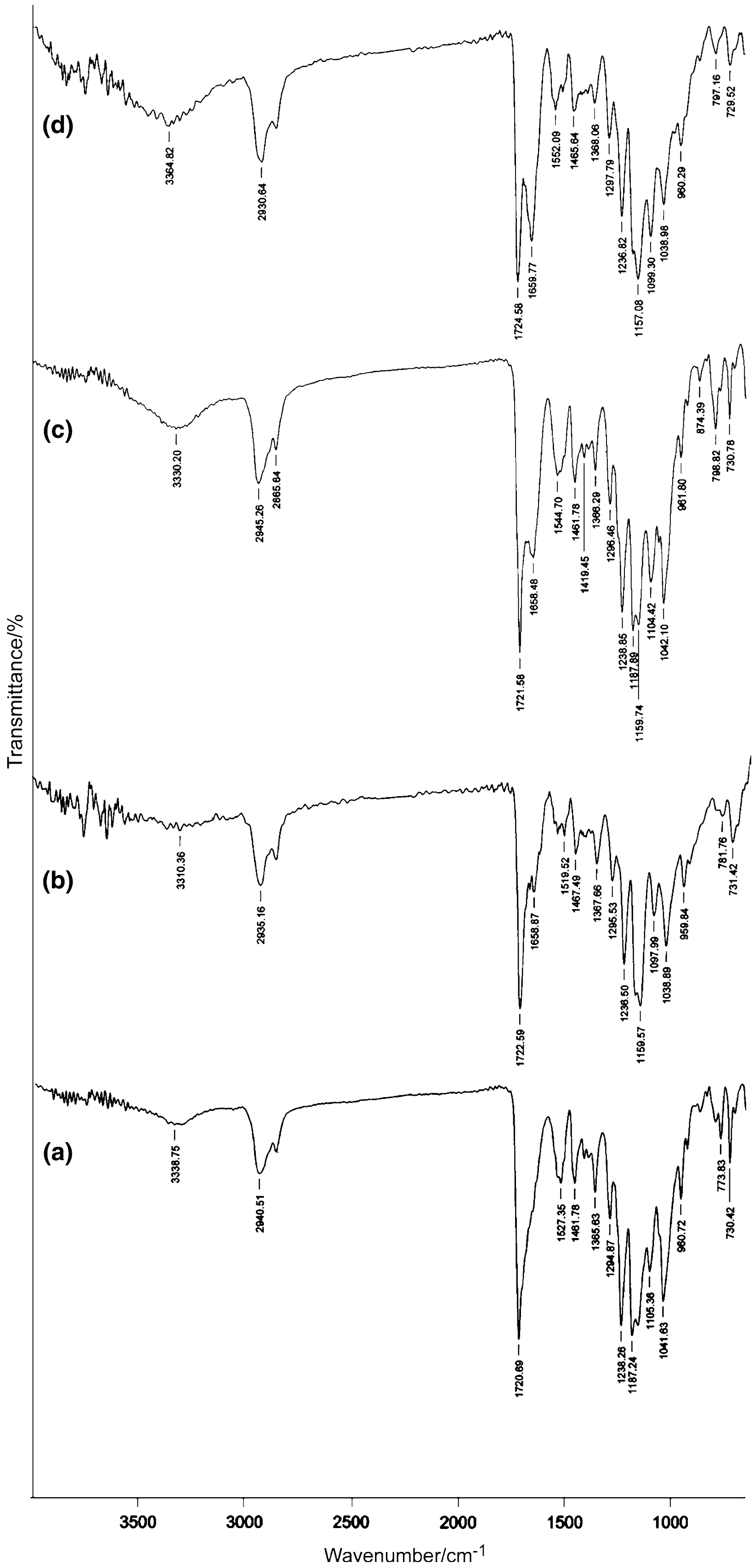
The absorption bands at 1,458, 1,360, and 1,302 cm^{-1} were attributed to CH_2 bending vibration, C–H bending vibration, and CH_2 wagging, respectively. C–O–C stretching at 1,038–1,238 cm^{-1} was also observed which is attributed to the polyol C–O–C bond and ring and bridge C–O–C vibrations of chitosan–ether-type absorption.

On extending the prepolymer with different proportions of chitosan/DMPA, the FTIR spectra showed a very strong peak at about 1,722 cm^{-1}, which was assigned to C=O stretching of soft segment and urethane bonds. Another new peak was also observed at about 1,658 cm^{-1}, which was assignable to chitosan–HN–C=O bonds. The intensity of hydrogen-bonded C=O increased as the chitosan content increased (1,658 cm^{-1}), suggesting the formation of new hydrogen bonds between chitosan and polyurethane (PU). Moreover, with increasing chitosan content, the peak of urethane carbonyl groups at around 1,722 cm^{-1} (WPU1: 1,720 cm^{-1}; WPU2: 1,722 cm^{-1}; WPU4: 1,721 cm^{-1}; WPU5: 1,724 cm^{-1}) slightly decreased, while the peak at 1,658 cm^{-1} for amide I increased. This implies stronger interchain interactions between chitosan and PU in chitosan-based PU than in DMPA-based PU. The intensity of N–H stretching vibration bands appearing at 3,330–3,360 cm^{-1} also increased slightly with increasing chitosan content in polyurethane. It was considered that the increase of the absorbance of NH and CO bands could only be explained by the presence of chitosan on the polyurethane backbone.

NMR spectroscopy

The NMR spectrum of polyurethane extended with 50:50 chitosan/DMPA is shown in Fig. 3. The ^{1}H NMR spectra of final synthesized polyurethane samples were in accordance with the proposed structures (Fig. 3a). Methyl groups of the isophorone diisocyanate structure in the polymer backbone were observed at 0.83–0.94 ppm. Central methylene groups of polycaprolactone were observed at 1.26–1.29 ppm. The ethyl groups of triethylamine and some other methylene groups were observed at 1.45–1.53 ppm. Peaks for CH_3CO–, CH_2O–, and

Fig. 2 FTIR spectra of the synthesized polymers: **a** 0%, **b** 25%, **c** 75%, **d** 100% chitosan as a chain extender



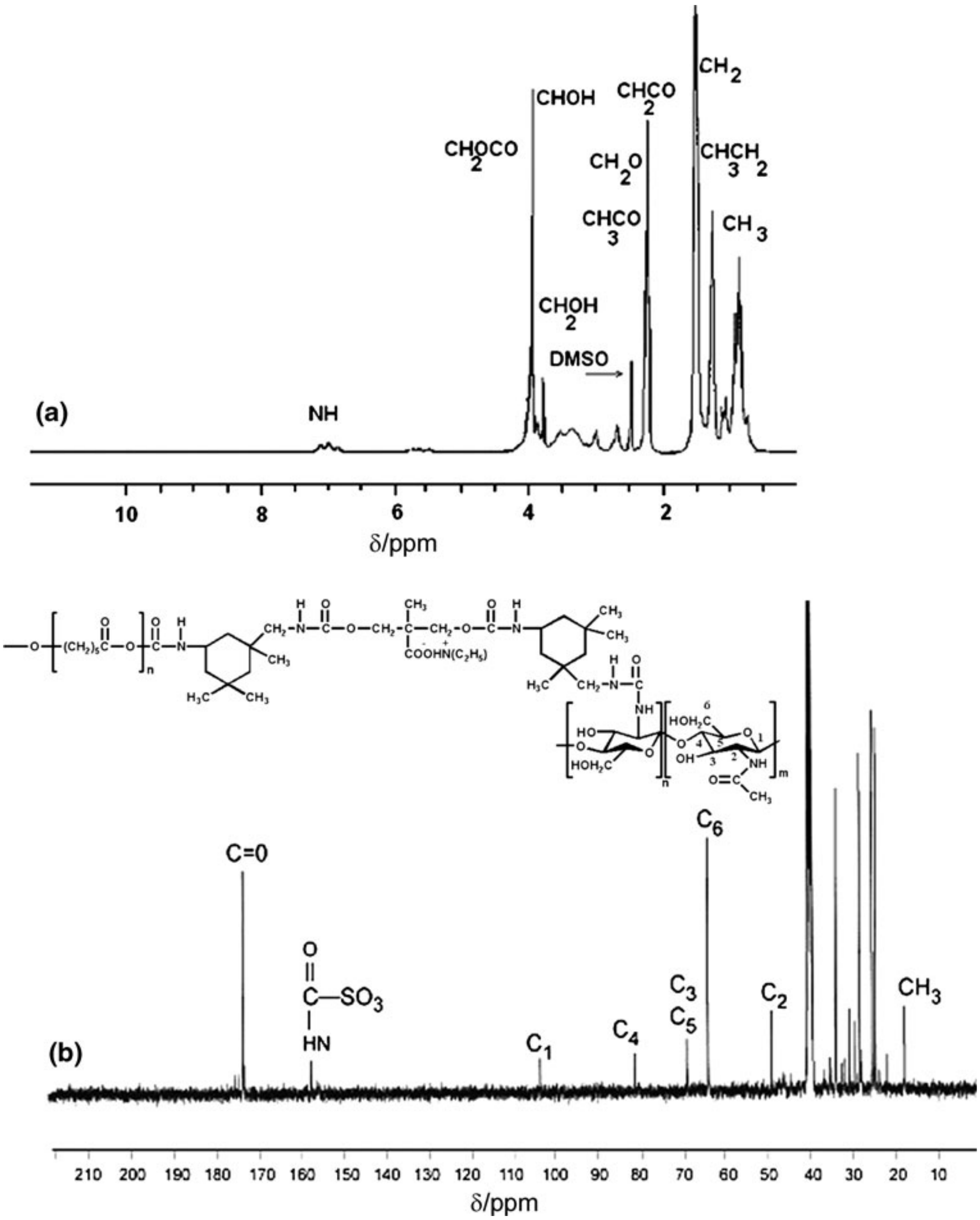


Fig. 3 **a** ^{1}H NMR spectrum and **b** ^{13}C NMR spectrum of the synthesized polymer

CH$_2$CO– appeared at 2.21, 2.23, and 2.25 ppm, respectively. The peak for CH$_2$– of isophorone diisocyanate was observed at 2.47 ppm. Peaks for –CH$_2$OH and –CHOH of chitosan were detected at 3.78 and 3.87 ppm. The peak for –CH$_2$OCO– was observed at 3.94 ppm, and weak peaks appearing at 6.85–7.2 ppm were attributed to chitosan and urethane NH groups.

^{13}C NMR spectra (Fig. 3b) obtained for the chitosan-based PU samples (WPU3) exhibited peaks at 155.6–157.1 and 172.9–175 ppm, which were attributed to the (NHSO$_3$C=O) and carbonyl (C=O) groups of the prepared polyurethanes, respectively. Moreover, peaks located at about 48.9, 63.9, 72, 71.1, 82, and 103 ppm were attributed to C2, C6, C3, C5, C4, and C1 positions of chitosan. Appearance of new peaks in ^{1}H NMR spectra at 2.21 ppm (assigned to the proton of the acetyl group), and in ^{13}C NMR spectra at 25.3 ppm (attributed to the methyl group of chitosan) provides evidence of involvement of chitosan in the final polyurethane structure. Although there is a possibility of reaction between NCO groups of the prepolymer and OH groups of chitosan, it was expected that most of the reactions take place between NCO terminal groups of the polyurethane and NH$_2$ groups of the chitosan owing to the higher reactivity of NH$_2$ relative to the OH groups of the chitosan repeating units.

TGA studies

Thermal stability of the prepared water-based polyurethanes with different amounts of chitosan as chain extender was evaluated by the TGA technique. The rate of heating was 10 °C min^{-1} and samples were heated from room temperature to 600 °C. The thermal decomposition of all the PU samples was evaluated at different percent of weight loss (i.e., 50% and maximum) and results are presented in Table 1 and Fig. 4. It is quite clear that the samples extended with 100% chitosan (WPU5) are more thermally stable than the samples extended with 100% DMPA (WPU1) owing to the higher thermal stability of the chitosan polymeric structure compared with the DMPA molecular structure. The molecular chain of chitosan composed of D-glucosamine monomers (Fig. 1) and the linked glucosamine rings on chitosan had better miscibility with the linked alicyclic ring in the hard segment of PU. This can allow the formation of hydrogen bonds between soft segments and NH groups in the hard segments. Therefore intensity of crystallinity and shift of thermogravimetric values for 100% chitosan-PU (WPU5) is more obvious than that of 100% DMPA-PU (WPU1). This behavior may also imply that chitosan, a crystalline polymer of D-glucosamine, does not melt but degrades at elevated temperature [21] and can play a role in enhancement of thermal properties. Of course the possibility of more hydrogen bonding formation between urethane and chitosan chains and its effect on improving thermal stability of chitosan-based polyurethane elastomers are also important and cannot be ignored. The investigation of the data in Table 1 showed that for the samples of WPU1 to WPU5 the thermal stability increased with increasing chitosan content in the final polymer.

Table 1 Thermal degradation behavior of the PU films with different amounts of CS replacing DMPA

Sample no.	CS (%)	Td (50%) (°C)	Td max (°C)
WPU1	0	385.35	592.47
WPU2	25	395.41	593.13
WPU3	50	408.30	594.09
WPU4	75	431.76	597.13
WPU5	100	454.96	598.07

Td decomposition temperature

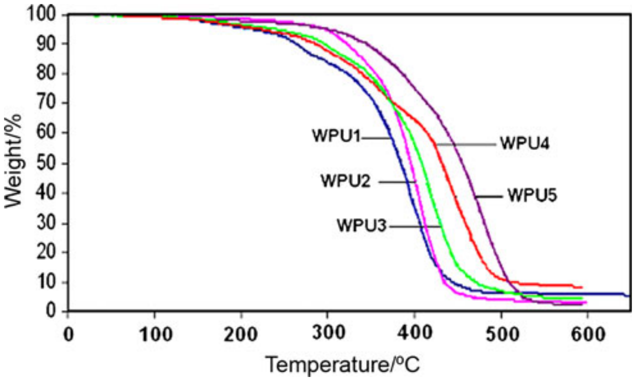


Fig. 4 TG thermograms of the PU films with different chitosan content

Contact angle

Hydrophilicity of the samples was evaluated by measuring the contact angle formed between water drops and the surface of the samples. For this purpose, the drops of water were placed on five different areas of the surface by using a microsyringe. Results are presented as the mean value of five measurements on different parts on the films. The results show that the contact angle of PU films without chitosan is 54.3° and with increasing chitosan content the contact angle is increased and hydrophilicity is decreased. The results are shown in Table 2 and Fig. 5.

Conclusions

Chitosan-based water dispersion polyurethane elastomers based on PCL and IPDI extended with different mass ratios of chitosan and DMPA were synthesized. The conventional spectroscopic characterization of the samples with FTIR, ^{1}H NMR, and ^{13}C NMR was in accordance with the proposed polyurethane structure. TGA data showed that thermal stability increased with increasing chitosan content. Contact angle is also increased by increasing the amount of chitosan. The increased contact angle is ascribed

Table 2 Variation of contact angles with ratio of chitosan

Sample no.	CS (%)	Contact angle (°)
WPU1	0	54.3
WPU2	25	56.2
WPU3	50	59
WPU4	75	62.7
WPU5	100	65.7

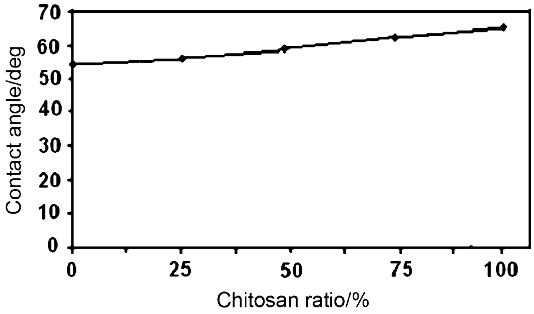


Fig. 5 Contact angles versus ratio of chitosan

to the decrease of the hydrophilicity of the polyurethanes, which is reduced by increasing the amount of chitosan with respect to the DMPA chain extender.

Experimental

Materials

Poly(ε-caprolactone)diol (CAPA 225) with a molecular weight of 2,000 was obtained from Solvay Chemicals, UK. *N*-Methylpyrrolidone (NMP), isophorone diisocyanate, triethylamine (TEA), sodium hydrogen sulfite, dimethyl sulfoxide, and hydrogen peroxide (30%) were obtained from Merck, Germany. Dimethylol propionic acid and low molecular weight chitosan (degree of deacetylation (DD) 80%) were purchased from Aldrich, and chitosan was treated with H_2O_2 before use.

CAPA and DMPA were dried at 60 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapor that may otherwise interfere with the isocyanate reactions. IPDI and all other materials were used as received. All the reagents used in this work were of analytical grade.

Treatment of chitosan

Chitosan as a high molecular weight natural polymer is not meltable or soluble in organic solvent, so using it as a chain extender in polyurethane synthesis is not possible easily. One of the reported procedures for solving this problem is to reduce the MW by depolymerization with oxidants such as O_3, $NaNO_2$, and H_2O_2. Oxidative destruction of β-D-glucoside bonds between units in macromolecules of polysaccharides is a basic reaction and reported in literature [19, 20, 22, 23].

For the preparation of treated chitosan, an appropriate amount was added to a mixture of distilled water and H_2O_2 (3:1 v/v). This mixture was stirred at room temperature for 48 h. During this process, cleavage of 1,4-β-D-glucoside bonds in the macromolecule proceeds and oligosaccharides are formed [19, 20]. Then the resulting mixture of oligosaccharides was precipitated by addition of acetone. The precipitated solid was collected and dried under vacuum overnight. This product is soluble in some organic solvents such as DMSO and can be dissolved 24 h before preparation of polyurethane.

Preparation of polymer

A 250-cm^3 round-bottomed, four-necked flask equipped with a mechanical stirrer, heating oil bath, thermometer, condenser, dropping funnel, and nitrogen inlet and outlet was used as reaction vessel. CAPA (20 g, 0.01 mol) was placed in the reactor and the temperature of the oil bath was increased to 60 °C. Then 8.95 g IPDI (0.04 mol) was added dropwise and the temperature was increased to 90 °C. The mixture was heated at 90 °C for 3 h to obtain NCO-terminated prepolymer. A solution of DMPA in NMP was then added and stirring continued for another 1 h. Then TEA and chitosan solution were added into the reactor and the system was cooled to 65 °C, $NaHSO_3$ was added, and stirring was continued for 30 min [24, 25]. This reaction was very exothermic and the rate of stirring was increased to prevent gel formation. As the final step the required amount of deionized water was added dropwise

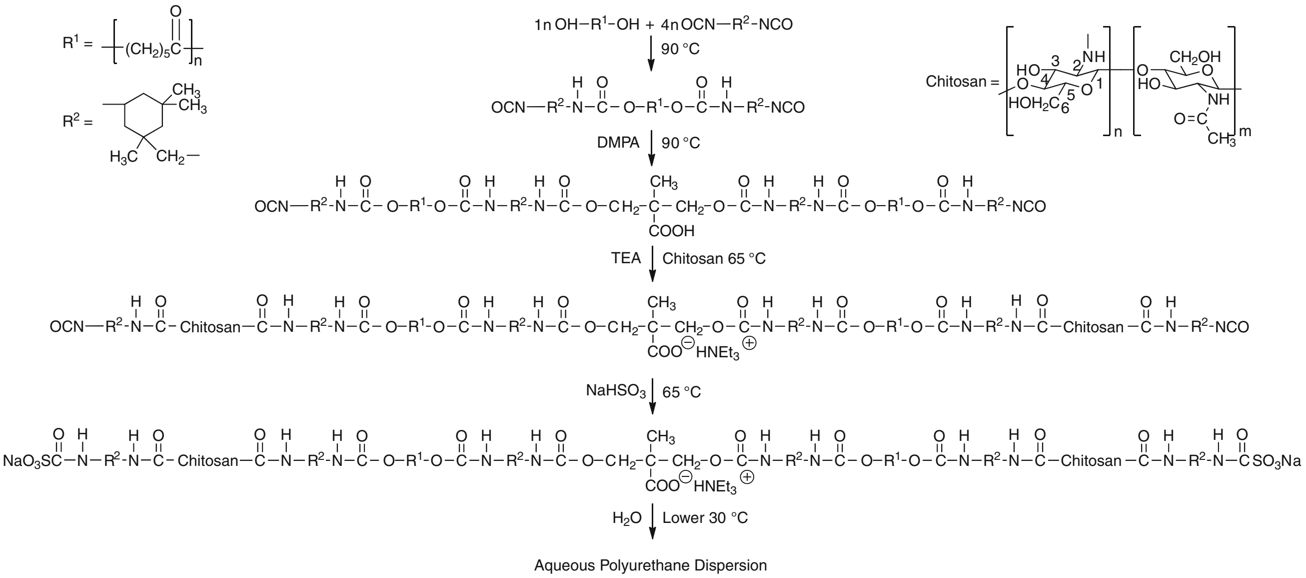


Fig. 6 Synthesis of the polyurethane dispersions

Table 3 Feed composition of polyurethanes with variable CS content

Sample no.	CS[a] (g; mmol)	TEA (g; mmol)	DMPA (g; mmol)	CS (%)
WPU1	0.00; 0.0000	2.02; 20	2.68; 20	0
WPU2	0.56; 0.0194	1.51; 15	2.01; 15	25
WPU3	1.12; 0.0388	1.01; 10	1.34; 10	50
WPU4	1.69; 0.0582	0.05; 5	0.67; 5	75
WPU5	2.25; 0.0776	0.00; 0	0.00; 0	100

All samples were prepared using 20 g CAPA (10 mmol), 8.95 g IPDI (40 mmol), 2.08 g $NaHSO_3$ (10 mmol)

[a] Such an amount of CS replaced DMPA which corresponded to the same number of functional groups present in the replaced amount of DMPA. MW of CS = 29,000; degree of deactylation = 80%, thus, monomer unit mass of CS = 0.8 × 161 + 0.2 × 203 = 169.4; number of monomer units per CS molecule = 29,000/169.4 = 171.2; number of functional groups per monomer unit = 3, thus, number of functional groups per CS molecule = 3 × 171.2 = 513.5; 0.0776 mmol CS contains 40 mmol functional groups which is the same number as in 20 mmol DMPA which possesses 2 OH groups

while stirring was continued. The reaction mixture was cast onto a Teflon plate to form a uniform sheet at room temperature followed by drying at 100 °C in a hot air circulating oven for 24 h. The cured sample sheets were then stored for 1 week at ambient temperature (25 °C) and 40% relative humidity before testing [26]. An overall PCL/IPDI/CS-DMPA/$NaHSO_3$ block ratio of 1:4:2:1 was used for the synthesis. The polymer synthesis is summarized in Fig. 6, and the compositions of the prepared polyurethanes are also given in Table 3.

Instrumental analysis

Infrared measurements were performed on a Bruker-Equinox 55 FTIR spectrometer (Ettlingen, Germany) by H.ATR accessories equipped with a ZnSe crystal. It is possible to use a polymer film as a strip with ATR (attenuated total reflectance) technique without further preparation. The ^1H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6 solution by using a Bruker Avance 400 MHz spectrometer (Germany). Chemical shifts (δ) are given in ppm with tetramethylsilane (TMS) as a standard.

Contact angle was measured at room temperature by a G10 (Kruss, Hamburg, Germany) instrument via the sessile drop method. Thermogravimetric analysis (TGA) was recorded on a Polymer Lab TGA-1500 (London, UK) under nitrogen atmosphere from room temperature up to 600 °C with heating rate of 10 °C min^{-1}. During the heating cycle, the weight loss and the temperature difference were recorded as a function of temperature.

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