

Thermal Degradation and Kinetics of Alginate Polyurethane Hybrid Material Prepared from Alginic Acid as a Polyol

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Abstract Alginate polyurethane hybrid materials are prepared by varying mole ratio of 2, 4-TDI as a di-isocyanate and alginic acid as a polyol in presence of dimethyl sulfoxide (DMSO) as a solvent. FT-IR and ^{13}C one-dimensional (1D) solid state NMR (SSNMR) spectroscopy indicates that alginic acid is converted into alginate-polyurethane hybrid material via urethane linkage. Surface morphology of alginate-polyurethane hybrids changes by varying alginic acid: TDI ratio. The peak at near 221 °C in DSC thermogram of alginic acid (Alg) is shifted to higher temperature in alginate-polyurethane hybrid (Algpu1 and Algpu2). TGA study shows that alginate-polyurethane hybrid prepared using alginic acid: TDI = 1:1 (Algpu2) is more stable than alginic acid: TDI = 1:0.5 (Algpu1) at 300 °C. Kinetic analysis was performed to fit with TGA data, where the entire degradation process has been considered as three consecutive 1st order reactions. This study shows that thermal stability of alginate-polyurethane

hybrid material was increased by adjusting mole ratio of 2, 4-TDI and alginic acid.

Keywords Alginic acid · 2, 4-TDI · Alginate-polyurethane hybrid · ^{13}C one-dimensional (1D) solid state NMR (SSNMR) · Scanning electron microscopy · Thermal analysis

Introduction

Polysaccharides, biologically produced (bio-based) materials are renewable, non-toxic and biodegradable have a unique combination of functional properties and eco-friendly features. Alginic acid is a linear polysaccharide copolymer of (1-4)-linked β -D-mannuronic acid (M) and α -L-guluronic acid (G), containing three different functional groups: $-\text{COO}^-$ (carboxylate), $-\text{C}-\text{O}-\text{C}-$ (ether), and $-\text{OH}$ [1–6]. These features make polysaccharide materials a natural fit for sustainable development. Research continues to bring us new materials with improved performance and reasonable prices. Polyurethanes (PUs) are polymers that have urethane linkage within their backbone structure and are prepared by the polyaddition polymerization between polyisocyanates and a molecule containing two or more hydroxyl groups ($-\text{OH}$) [7]. Natural polymers (alginic acid) containing more than two hydroxyl groups ($-\text{OH}$) in their main chain are expected to be used as polyols for the preparation of alginate polyurethane (Algpu) hybrid material because alginic acid has many $-\text{OH}$ groups in its chain [8–11]. Polyurethane, a unique polymeric material with a wide range of physical and chemical properties, has been extensively used to meet the highly diversified demands of modern industrial technologies such as coatings, adhesives, fiber, foams, and thermoplastic elastomers [12]. They are

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also used as structural, cushioning, insulating, electrical, floating and packaging materials [13–17]. Packaging waste has increased environmental concerns because of non-degradable nature of polyurethane. The development of biodegradable packaging materials has received growing attention [18–21].

Due to rare aptness to disintegration and biodegradation, the use of polyurethane increases environmental problem [22]; a solution to this problem would be to include a material in the formulation of polyurethanes that provides biodegradability. Many researchers have developed bio-polymer based material to increase a bio-degradability [23–26]. Cellulose, starch, proteins, lignin and polysaccharides are naturally occurring polymers obtained from renewable sources. They are readily biodegradable and tend to degrade in biologically active environments such as soil, sewage and marine locations where bacteria are active [27]. Here, one of polysaccharides, alginic acid, has been chosen in polyurethane formulations to promote disintegration property.

The main objective of our study is to prepare alginate polyurethane hybrid materials from alginic acid as a polyol, toluene diisocyanate (TDI) as a diisocyanate, and dimethyl sulfoxide (DMSO) as a solvent. Effects of mole ratios of alginic acid and toluene di-isocyanate, surface morphology and thermal degradation behaviour were also studied.

Experimental

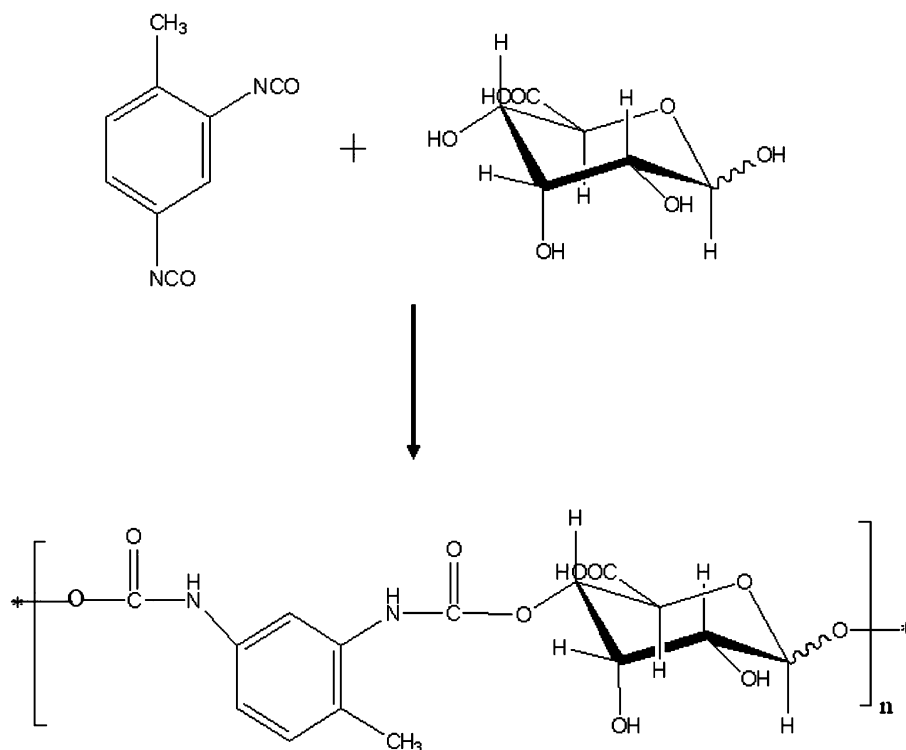
Materials Used

Alginic acid (Alg) and 2, 4-toluene di-isocyanate (2, 4-TDI) were purchased from Sigma, Aldrich each. Dimethyl sulphoxide (DMSO) was also supplied from Aldrich chemicals.

Preparation of Alginate-Polyurethane Hybrid

Alginic acid is dissolved in anhydrous DMSO in a 250 ml three necked round bottom flask fitted with mechanical stirrer, thermometer, condenser, nitrogen inlet and pipette outlet and kept at 80 °C for 24 h under stirring. After that, 2, 4-TDI is slowly added to alginic acid solution through Dean-Stark trap and kept at 80 °C for 12 h under stirring. The unreacted precipitate is removed by filtration and methanol is added to the reaction mixture. The final product is recovered by filtration and dried in oven. The mole ratio of alginic acid and 2, 4-toluene di-isocyanate is 1: 0.5 for Algpu1 and 1:1 for Algpu2, respectively. The Reaction scheme for the preparation of alginate-polyurethane hybrid is given in Fig. 1.

Fig. 1 Reaction scheme for the preparation of alginate modified polyurethane (Algpu2)



Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of alginic acid and alginate-polyurethane hybrid (Algpu1 and Algpu2) were recorded on a Perkin Elmer Spectrometer (Perkin Elmer Ltd., Beaconsfield, BUCKS-HP9 2FX, UK). The spectra were collected from 4,000 to 650 cm^{-1} range in the transmission mode with 4 cm^{-1} resolution over 40 scans.

Solid State Nuclear Magnetic Resonance Spectroscopy (SSNMR)

The ^{13}C one-dimensional (1D) SSNMR spectra of alginate-polyurethane hybrid (Algpu1 and Algpu2), alginic acid and 2, 4-TDI were recorded on Unity INOVA 400 MHz wide-bore(WB) Solid-state NMR Spectrometer (Varian Inc., CA, USA).

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed in a DSC-60, using sample mass of 6 mg in a covered aluminum sample holder with a central pin hole at heating rates of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen atmospheres, and at the flow rate of 40 mL min^{-1} and atmospheric pressure circumstances.

Scanning Electron Microscopy (SEM)

The surface properties of alginic acid and alginate-polyurethane hybrid were studied using SEM. Specimen preparation was performed as follows: the dried samples were mounted on stubble and then sputter-coated with gold. Micrographs were taken on a SEM instrument (Hitachi, S-4100).

Thermogravimetric Analysis (TGA)

Thermal analyses of samples were recorded on a thermal analyzer (Universal V4.1D) system. TGA scans were done from 30 to 1,000 $^{\circ}\text{C}$ at heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen atmospheres.

Results and Discussion

Fourier Transform Infrared Spectroscopy (FTIR)

To confirm the reacted species between isocyanate groups of 2,4-TDI and $-\text{OH}$ group of polyol, FTIR analysis was performed. FTIR spectra of alginic acid (Alg) and alginate-polyurethane hybrid (Algpu1 and Algpu2) are given in Fig. 2. The stretching of $-\text{C}=\text{O}$ of protonated carboxylic

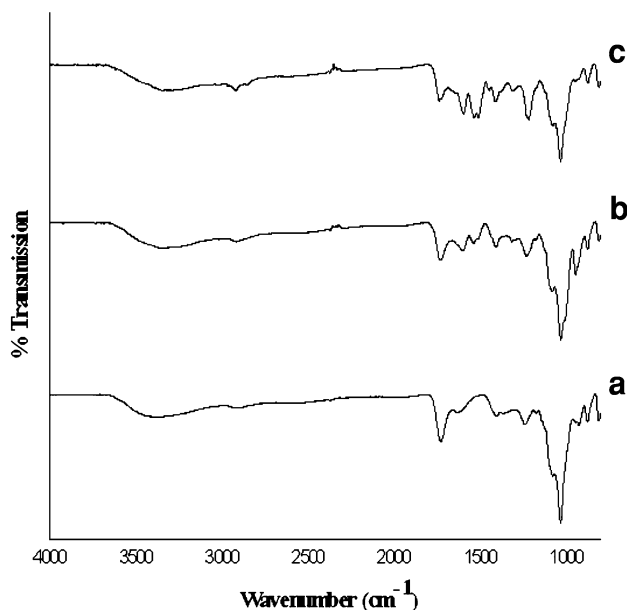


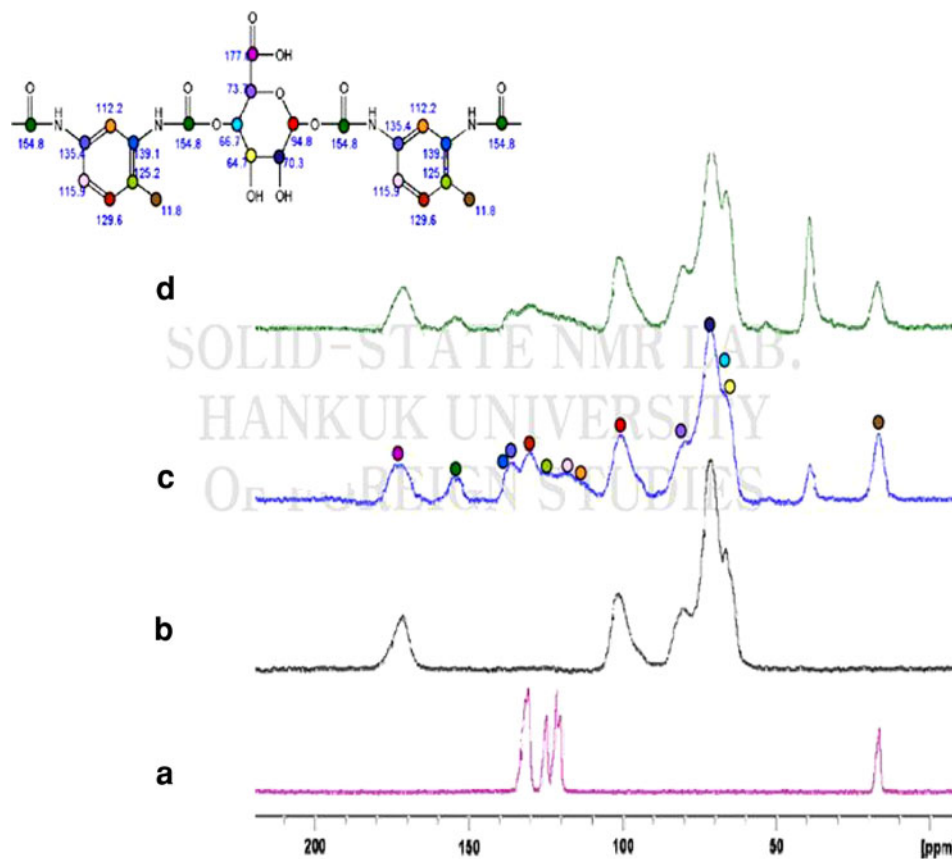
Fig. 2 FTIR spectra of **a** alginic acid (Alg), **b** Algpu1 and **c** Algpu2

group of alginic acid occurs at 1,730, and 1,609 cm^{-1} , respectively as it is shown in Fig. 2 [27]. The characteristic peaks at 1,404 and 1,238 cm^{-1} represents the $\text{C}-\text{O}-\text{H}$ stretching of carboxylic acid group, whereas peak around 1,030 cm^{-1} is attributed to the stretching of $-\text{C}-\text{O}-\text{C}$ group of alginic acid. The FTIR spectra of Algpu1 shows a typical bands of $\text{N}-\text{H}$ (3,323 and 1,538 cm^{-1}), $\text{C}=\text{O}$ (1,730 and 1,597 cm^{-1}), $\text{C}-\text{O}-\text{H}$ (1,405 and 1,229 cm^{-1}) and $\text{C}-\text{O}-\text{C}$ (1,030 cm^{-1}) group. Meanwhile, Algpu2 shows a typical bands of $\text{N}-\text{H}$ (3,323 and 1,538 cm^{-1}), $\text{C}=\text{O}$ (1,730 and 1,597 cm^{-1}), $\text{C}-\text{O}-\text{H}$ (1,405 and 1,220 cm^{-1}) and $\text{C}-\text{O}-\text{C}$ (1,030 cm^{-1}) group, respectively. With a disappearance of characteristic peak of $-\text{N}=\text{C}=\text{O}$ group of TDI at 2,270 cm^{-1} in Algpu1 and Algpu2, we can confirm that the urethane linkage in alginate-polyurethane hybrid (Algpu1 and Algpu2) were formed newly.

Solid State Nuclear Magnetic Resonance Spectroscopy (SSNMR)

The ^{13}C one-dimensional (1D) SSNMR spectra of alginate-polyurethane hybrid each (Algpu1 and Algpu2), alginic acid and 2, 4-TDI are shown in Fig. 3. The Fig. 3 (c and d) indicates the formation of urethane linkage in Algpu2 and Algpu1. The δ values of all the carbon in the alginate-polyurethane hybrid (Algpu2) are assigned in the chemical structure of alginate-polyurethane hybrid (Algpu2) in Fig. 3c. The peak appears at 177 ppm are due to acidic carbon ($-\text{COOH}$) of alginic acid. The peak around 154.8 ppm are due to urethane carbon ($-\text{NHCOO}$), whereas peak around this range ($\delta = 112.2-139.1$ ppm) are due to aromatic carbon. The peak appeared at 38 ppm

Fig. 3 ^{13}C 1D SSNMR spectra of **a** 2,4-TDI, **b** Alg, **c** Algu2 and **d** Algu1



in Algu2 and Algu1, would be due to polyurethane cross-linking. The methyl carbon attached to aromatic ring shows peak at 11.8 ppm.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) has been used to characterize the thermal behavior of natural polymer which is correlated to their genuine structure, hydrophilic properties and association rate [28]. It is based on the heat capacity of the sample as a function of temperature.

The DSC curves of Alg, Algu1 and Algu2 at heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere are presented in Fig. 4. In Fig. 4a, an endothermic peak was appeared around $142\text{ }^{\circ}\text{C}$, followed by a strong exothermic peak around $226\text{ }^{\circ}\text{C}$. The decomposition of Alg could be expected with following appearance of this exothermic peak. Figure 4b is representing the DSC curve of alginate modified polyurethane (Algu1), which was presented with an endothermic peak around $137\text{ }^{\circ}\text{C}$, followed by a strong exothermic peak around $236\text{ }^{\circ}\text{C}$. Similarly, the DSC curve of alginate modified polyurethane (Algu2) was shown in Fig. 4c, in which one endothermic peak was seen around $96\text{ }^{\circ}\text{C}$. Another strong exothermic peak was also appeared around $256\text{ }^{\circ}\text{C}$, like that of other components.

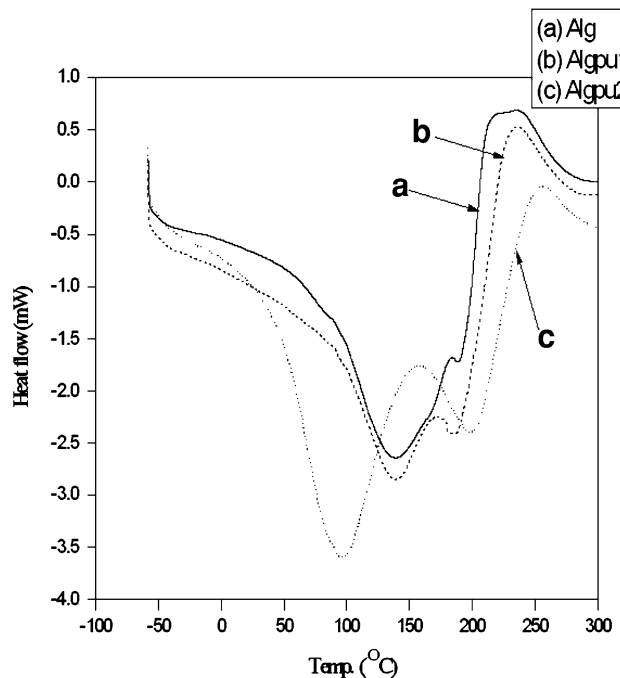


Fig. 4 DSC of **a** Alg, **b** Algu1 and **c** Algu2

The endothermic peak is decreased from pure alginic acid ($142\text{ }^{\circ}\text{C}$) to Algu1 ($137\text{ }^{\circ}\text{C}$), much further to Algu2 ($96\text{ }^{\circ}\text{C}$). Actually, this peak is correlated with loss of water

associated to hydrophilic groups of polymer. In comparison amongst the Alg, Algpu1 and Algpu2, the exothermic peak of pure alginic acid (226 °C) is lower compared to Algpu1 (236 °C) and Algpu2 (256 °C). The exothermic peak might speak for the decomposition of pure alginic acid and alginate modified polyurethane, as we can speculate. Therefore, the decomposition of Algpu2 occurs at higher temperature compared to Algpu1 and Alg; which could be concluded as the higher stability of Algpu2, in comparison to Algpu1 and Alg.

Scanning Electron Microscopy (SEM)

Surface morphological analysis of alginic acid (Alg) and alginate-polyurethane hybrid (Algpu1 and Algpu2) were confirmed using scanning electron microscopy (SEM) and is presented in Fig. 5a–c. Surface morphology of alginate-polyurethane hybrid (Algpu1 and Algpu2) is different compared to alginic acid (Alg) as it is shown in Fig. 5. Alginic acid shows rough surface, whereas alginate-polyurethane hybrids (Algpu1 and Algpu2) show smooth surface.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a method, which provides a fast preliminary evaluation of thermal decompositions and kinetics of degradation process for polymers, biopolymers and hybrid materials with a very small amount of sample. Thermal degradation and mode of decomposition at the surrounding of heat is highly recommended in the processing optimization. The threshold decomposition temperature gives an indication of the highest processing temperature that could be used, whereas the study of the kinetics of the different decomposition processes helps us identify the degradation mechanism.

The TGA curves of Alg, Algpu1 and Algpu2 are shown in Fig. 6. The weight loss percentage values at different temperatures were also calculated from TGA curves for all the samples to evaluate the exact variation in degradation trend of alginic acid and alginate polyurethane hybrid materials with change in the compositions. The weight loss percentage values are presented in Table 1. It is seen from the results that, all the materials started initial degradation at 100 °C; although rapid degradation had taken place around 200 °C.

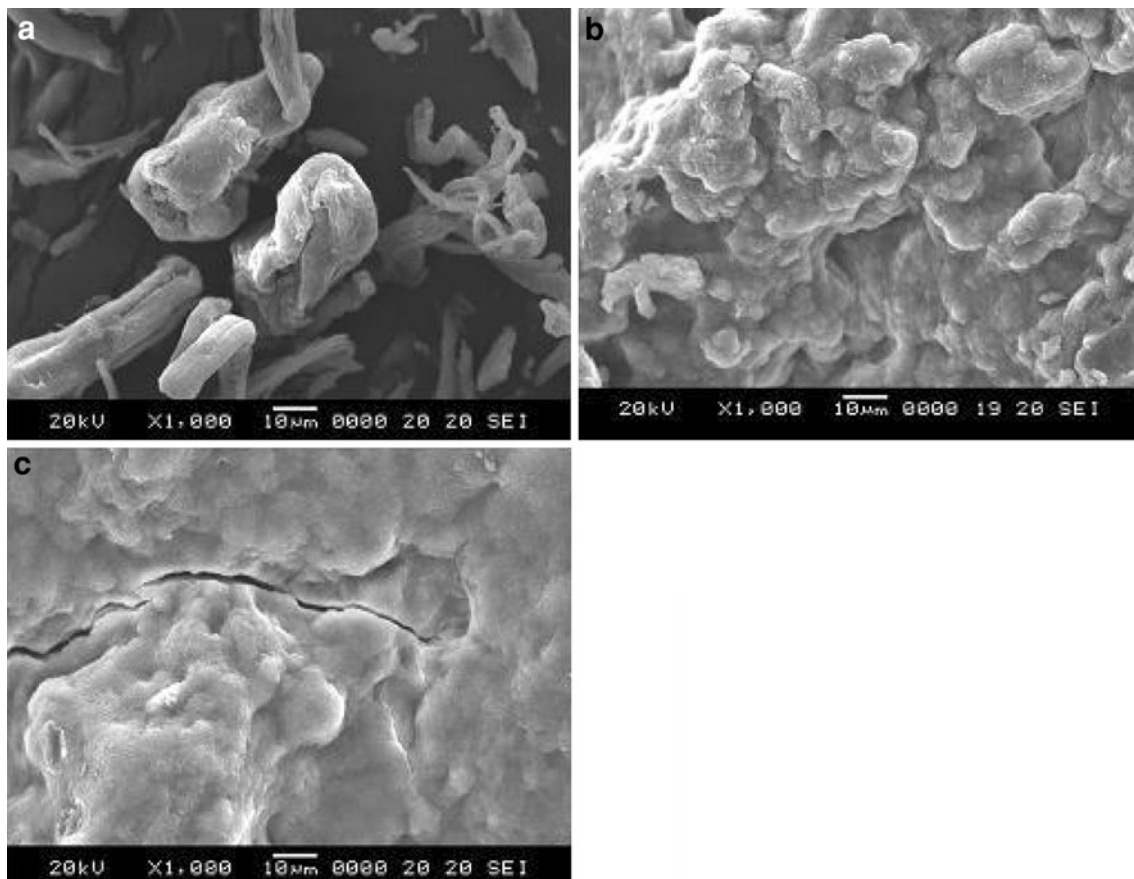


Fig. 5 SEM of a Alg, b Algpu1 and c Algpu2

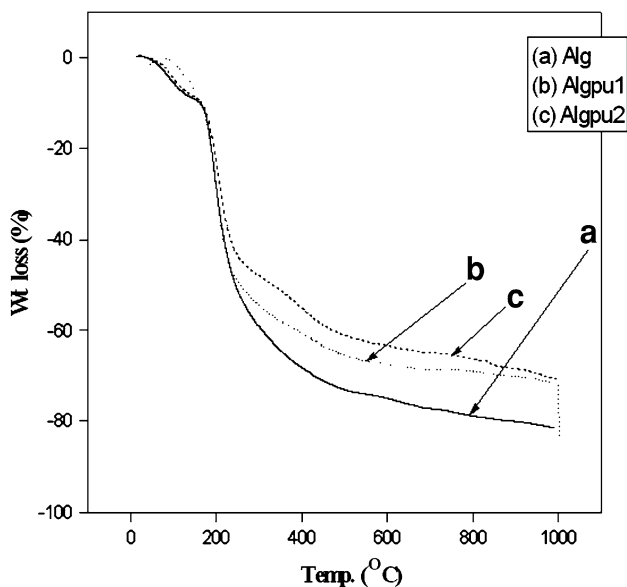


Fig. 6 TGA of a Alg, b Algpu1 and c Algpu2

The initial weight loss may be attributed to the physical loss of water from the alginate samples. All the TGA curves are showing various steps with similar trend in their degradation. First step of rapid degradation was situated around 200–300 °C, resulting in the biopolymer degradation during this step; whereas the next step is situated around 300–500 °C. TGA analysis had further performed up to 1,000 °C for all the samples. It is seen from this thermogram that, alginate sample has degraded mostly at over 500 °C. TGA analysis and percentage weight loss values clearly indicates that alginate modified polyurethane samples are thermally more stable than the pure alginic acid. Similarly, the sample with more amount of polyurethane has degraded much less at every thermal sweep. Thus, it can be concluded that, the addition of polyurethane to alginic acid has increased the thermal stability of the materials.

Kinetic Analysis

Various kinetic parameters such as activation energy and pre-exponential factor value of thermal degradation reaction for natural polymers and synthetic ones have been studied for several decades [29]. Alginic acid (Alg) and alginate-polyurethane hybrid materials (Algpu1 and Algpu2) were also calculated using the integral method in this study.

The thermal processes were divided into three suitable steps, and each step was assumed as 1st order reaction. Therefore, the kinetic equation can now be written simply by the following expression for each step:

$$dx/dt = A \exp(-E/RT)(1 - x) \tag{1}$$

In this expression A is pre-exponential factor, E is activation energy, T is temperature, t is time, and x represents the mass fraction of the sample. Here, x is expressed as the following equation: $x = (W_0 - W_t)/(W_0 - W_f)$, where W_0 , W_t , and W_f are representing the initial weight, weight at temperature T, and final weight of the test sample, respectively. Eq. (1) can be presented in rearranged form, at a constant heating rate H (= dT/dt) during thermal degradation and after integration it can be written as:

$$\ln[-\ln(1 - X)/T^2] = \ln \left[\frac{AR}{HE} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \tag{2}$$

In Eq. (2), the expression $\ln \left[\frac{AR}{HE} \left(1 - \frac{2RT}{E} \right) \right]$ is constant for the most E values and written in Eq. (2) is constant for most values of E and for the temperature range used during the thermal degradation process. Therefore, for a first order reaction a straight line could be obtained, with plotting the left side of Eq. (2) against 1/T. The value of slope and intercept was obtained from the graph for all samples (Alg, Algpu1 and algpu2) for every degradation temperature range. The value of slope (-E/R) was used to calculate the activation energy. Similarly, pre-exponential factor can also be calculated from the intercept value [30–32].

Table 1 Percent weight loss of Alg, Algpu1 and Algpu2 at heating rate of 10 °C/min in N₂ atmosphere from TGA analysis

Alg		Algpu1		Algpu2	
Temp.(°C)	% wt loss	Temp. (°C)	% wt loss	Temp. (°C)	% wt loss
100	5.5096	100	1.1623	100	4.5035
200	28.7013	200	28.7222	200	23.3705
300	59.2211	300	54.3938	300	47.8638
400	68.3223	400	60.6663	400	55.041
500	73.0572	500	65.5309	500	61.1124
600	74.9551	600	67.4535	600	63.3837
700	77.1933	700	68.6518	700	64.9432
800	78.8571	800	69.0493	800	66.4488
900	80.0544	900	70.1659	900	68.4864
1000	81.4668	1000	71.6043	1000	70.813

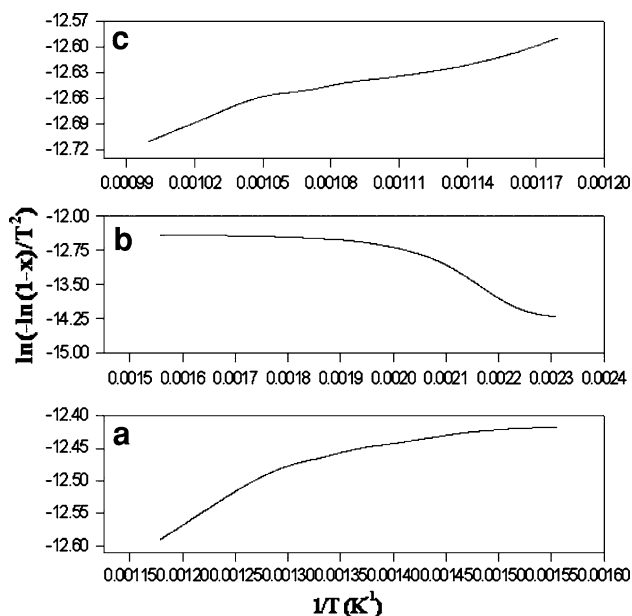


Fig. 7 Plot of $\ln[-\ln(1-X)/T^2]$ versus $1/T$ at heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in the temperature range **a** 433 to 641 K, **b** 641 to 847 K and **c** 847 to 1,000 K from TGA data for Alg

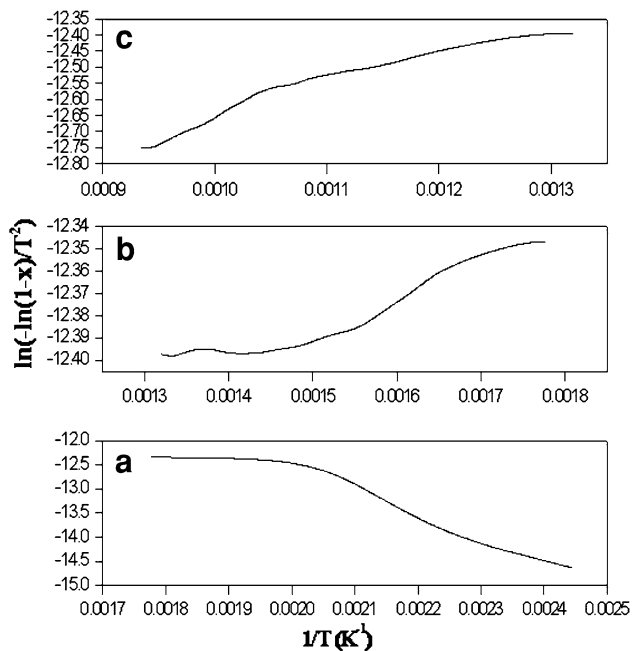


Fig. 8 Plot of $\ln[-\ln(1-X)/T^2]$ versus $1/T$ at heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in the temperature range **a** 409 to 562 K, **b** 562 to 757 K and **c** 757 to 1,070 K from TGA data for Algu1

Now, Figs. 7, 8 and 9 are showing the typical plots of $\ln[-\ln(1-x)/T^2]$ versus $1/T$ for Alg, Algu1 and algu2, respectively. In the whole process, the heating rate was maintained as $10\text{ }^\circ\text{C}/\text{min}$. For all the samples, the entire thermal process was divided into three consecutive 1st order reactions. Eq. (1) has been applied separately to each

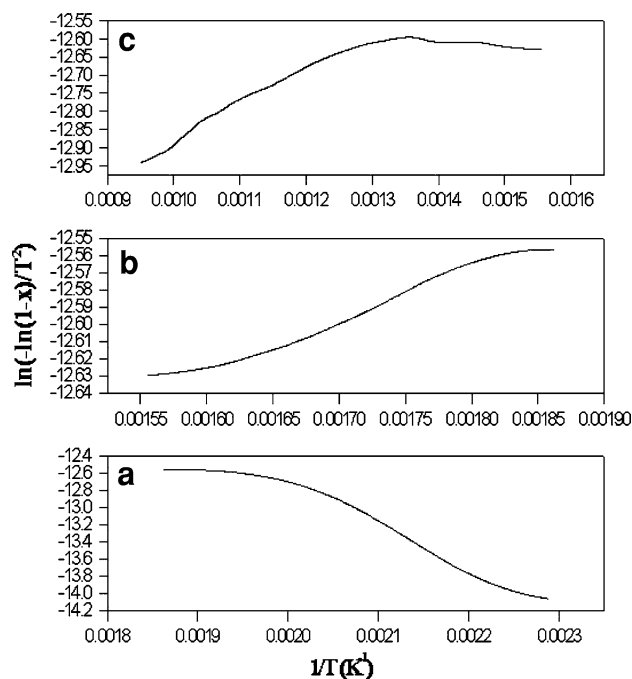


Fig. 9 Plot of $\ln[-\ln(1-X)/T^2]$ versus $1/T$ at heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in the temperature range **a** 437 to 537 K, **b** 537 to 643 K and **c** 643 to 1,054 K from TGA data for Algu2

of the stages by calculating the value of x separately for each reaction, and thus essentially straight line has come in each independent step. Table 2 represents the kinetic parameters calculated for all samples (Alg, Algu1 and algu2) for various stages at heating rate of $10\text{ }^\circ\text{C}\text{ min}^{-1}$ using the same method. The kinetic parameters are obtained from 5.08–9.79 % to 45.16–77.49 %, which is the main degradation region for all the alginate samples.

Some groups have studied the relation between activation energy and fire retardant efficiency and it was informed that the reaction with high activation energy requires a high temperature or a long residence time [33]. Usually, in thermal degradation process, high activation energy means the reaction needs more energy from the surroundings during the reaction. Here, the first step of degradation possesses the positive valued activation energy for all the samples. Algu1 sample have showed highest activation energy value of 69.25 kJ/mol in this case. On the other hand, the second and final steps have the negative activation energy. Generally, the process with negative activation energy is the one in which, reaction rate decreases with increasing temperatures. Reactions exhibiting these negative E values are typically barrierless reactions.

Conclusions

Alginate-polyurethane hybrid materials (Algu1 and Algu2) were prepared by varying mole ratio of isocyanate

Table 2 Kinetics parameters of Alg, Algpu1 and Algpu2 obtained from TGA analysis

Sample	Heating rate (°C/min)	Temp. (K)	Conversion range (%)	E (kJ/mol)	A (min ⁻¹)
Alg	10	433–641	9.70–66.03	66.5	11.3211
	10	641–847	66.03–74.42	-5.19	0.0077
	10	847–1,000	74.42–77.49	-8.314	0.0146
Algpu1	10	409–562	5.08–53.44	69.25	4.2736
	10	562–757	53.44–64.89	-2.76	0.0032
	10	757–1,070	64.89–69.00	-7.33	0.0097
Algpu2	10	437–537	9.79–45.16	54.87	0.8672
	10	537–643	45.16–52.53	-3.26	0.0034
	10	643–1054	52.53–65.88	-16.628	0.0348

(2, 4-TDI) and polyol (alginic acid). The hybrid materials were characterized using FTIR spectroscopy, ¹³C 1D solid state NMR (SSNMR), DSC analysis, Scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA). Kinetic parameters, including activation energy and pre-exponential factor of thermal degradation reaction, for alginic acid (Alg) and alginate-polyurethane hybrid materials (Algpu1 and Algpu2) were determined by using Coats and Redfern method. The formation of alginate-polyurethane hybrid material via urethane linkage was confirmed using FTIR and ¹³C 1D SSNMR spectroscopy. Surface morphology of Algpu2 showed more smooth surface compared to Algpu1 and Alg. The peak at around 221 °C in DSC thermogram of alginic acid (Alg) is shifted to higher temperature in alginate-polyurethane hybrid (Algpu1 and Algpu2). TGA study showed that alginate-polyurethane hybrid prepared using alginic acid: TDI = 1:1 (Algpu2) was more stable than alginic acid: TDI = 1:0.5 (Algpu1) at 300 °C. Kinetic analysis was performed to fit with TGA data, where the entire degradation process had been considered as three consecutive 1st order reactions. Highest activation energy value (69.25 kJ/mol) was observed in Algpu1 sample and we can control the thermal stability with adjusting the mole fraction finely, as a result of such process we will get the proper alginate-polyurethane hybrid materials.

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