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Synthesis of super absorbent polymer using citric acid as a bio-based monomer

Hyun Jae Kim [a, 1], Jun Mo Koo [a, 1], Seong Hun Kim [a], Sung Yeon Hwang [b, c, **], Seung Soon Im [a, *]

[a] Department of Organic and Nano Engineering, College of Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul, 04763, Republic of Korea
[b] Division of Ulsan Research & Business Development Research Center for Industrial Chemical Biotechnology, Korea Research Institute of Chemical Technology, 406-30, Jongga-ro, Jung-gu, Ulsan 44429, Republic of Korea
[c] Advanced Materials and Chemical Engineering, University of Science and Technology (UST), Daejeon 34113, Republic of Korea

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ABSTRACT

Along with the up-rise of environment problems, ecofriendly materials that can replace existing products have become an issue. In the field of superabsorbent polymer (SAP), biobased monomers can be used to reduce petroleum based monomer, i.e. acrylic acid. In this paper, biobased citric acid was chosen to prepare SAP in order to confirm the possibility of ground-up synthesis for biobased SAP, due to its cost-effectiveness, non-toxicity and multifunctionality that can induce random 3D-network structure. With suitable diol counterpart and neutralization of CA, the absorbency was enhanced. To further develop synthesized SAP and compensate the absence of secondary crosslinking, hexamethylene diisocyanate (HDI) was used to stabilize 3D-network structure. The maximum absorbency of CA-based SAP was around 2200%.

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1. Introduction

Simplicity and usability of disposable products have provided convenience along with industrialization. However, due to its rapid use cycle, general waste has been gradually increased that nowadays became an environmental problem. Amongst these products, hygienic goods such as diaper, feminine hygiene products, adult incontinence products, etc. are known for its non-degradable/recyclable characteristic which is mainly caused by superabsorbent polymer (SAP). SAP is a material which can absorb water more than 1000% of its own weight because of its high water affinity and 3D structure [1–3].

Conventional SAP is mainly consisted with polyacrylic acid (PA) which can be synthesized by acrylic acid (AA) [4]. Its cheap and highly reactive nature with numerous hydrophilic group that can provide crosslinking sites, appears to be the most appropriate candidate. But embryo toxicity, non-degradability and petroleum based nature cannot be avoided from causing environmental issues [5–7].

Owing to such issues, biodegradable polymers have received great attention and have been widely studied but its short shelf-life prohibit them from expanding and exploring variety of application field. Thus, instead of inhering such limitation, 'biobased' concepts stand out as a solution [8]. This concept deals with facilitating biobased monomer in the position of petroleum based monomer.

Recent researches on bio-based SAP are based on graft copolymerization of acrylic acid onto bio-based material such as cellulose, starch, chitosan, protein, etc. [9–12] However, suggested natural polymers have high molecular weight, difficult to handle and highly dependent on utilizing acrylic acid. Also there are scarce amount of study regarding the ground-up biobased SAP without using acrylic acid.

To synthesize bio based SAP, the characteristics of monomer must have following points; 1) bio-based mmonomer, 2) presence of hydrophilic groups to attract water, 3) multi-functional group to

* Corresponding author.
** Corresponding author. Division of Ulsan Research & Business Development Research Center for Industrial Chemical Biotechnology, Korea Research Institute of Chemical Technology, 406-30, Jongga-ro, Jung-gu, Ulsan 44429, Republic of Korea.
E-mail address: imss@hanyang.ac.kr (S.S. Im).
[1] 1st author.

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form 3D structure, 4) non-toxicity and 5) low cost. Citric acid (CA) is a monomer that has suitable characteristic in accordance with above conditions. Amongst many candidates, CA is a cost-effective bio-based monomer that has three carboxylic and one hydroxyl group which provides both hydrophilicity and crosslinking sites and it is also known to be non-toxic.

Therefore, in this paper, CA was chosen as a main biobased monomer in the ground-up synthesis of novel ecofriendly SAP. In order to confirm the possibility of CA as an alternative material for acrylic acid, reaction with various diols through simple melt polymerization was performed to optimize the counterpart and incorporation of neutralized CA was conducted in order to increase absorbency. Also after esterification, post-treatment was carried using hexamethylene diisocyanate (HDI) for secondary crosslinking. The final resulting absorbency was more than 2200%.

2. Experimental

2.1. Materials

Citric acid (CA, 99.5%), ethylene glycol (EG, 99.8%), 1,4-butanediol (BD, 99%), neo pentyl glycol (NPG, 99%), 1,4-cyclohexane dimethanol (CHDM, 99%), hexamethylene diisocyanate (HDI, 98.0%), sodium bicarbonate (SB, 99.5%) and sodium chloride were purchased from SIGMA ALDRICH (USA). Isosorbide (ISB, 80% in water) was supplied from SK chemical (Korea). Ethanol (99.5%) and buffer solutions (pH 4, 7 and 10) were purchased DEAJUNG chemical (Korea) and SAMCHUN (Korea), respectively. All of the materials mentioned above were used as received.

2.2. Preparation of monosodium citrate

Distilled water (250 g) was weighted into a 1 L beaker and CA (250 g, 1.30 g) was added into the beaker with magnetic stirring. After CA was dissolved, SB (109.34 g, 1.30mol, equal molar ratio of CA) was added into the beaker. Solution was stirred until transparent and then was added into excess ethanol for precipitation of monosodium citrate (CN). Precipitated CN was filtered and dried at 80 °C for 24 h in vacuum oven.

2.3. Synthesis of CA-based SAP

The esterification of CA-based SAP carried out by melt condensation reaction using a reactor. CA (120 g, 0.62 mol), CN (57.31 g, 30% of total acid) and BD (124.99 g, 0.94mol, 1.5 molar ratio of total acid) were added into a 600 ml 4-neck reactor that would be fitted with mechanical stirrer, thermometer, condenser and nitrogen inlet. Before reaction, nitrogen purging in reactor conducted for 1 h and the reaction mixture was stirred by the mechanical stirrer with 300 rpm. Esterification was carried out at 155 °C with a rate of 10 °C/min for 60 h. The product was dried at 40 °C for 24 h in vacuum. The content of CN in each reaction was changed from 10% to 30% against total acid. After esterification, HDI treatment was conducted as post-treatment. 1 g of SAP sample was pulverized and put into the beaker and excessive 25 ml (0.16mol) of HDI poured into a 100 ml beaker and was stirred by a magnetic bar. The reaction between SAP and HDI conducted for 1.5, 3 and 5 h at each temperature (R.T and 60 °C) without catalyst. And then sample was filtered and added into beaker containing methanol for washing. Methanol washing was carried out with magnetic stirring for 20 min and filtered again. Finally, filtered sample was dried at 40 °C for 12 h in vacuum.

Denotation of synthesized $PC_aN_bD_c$ are as follows C: CA, N: CN and D: diol where a, b and c are molar ratio in each monomer.

2.4. Characterization of SAP

Fourier Transform Infrared (FT-IR) was performed using a Nicolet iS10 spectrometer (ThermoFisher scientific) with a rage of 650–4000 cm^{-1} and a resolution of 4 cm^{-1} to confirm functional groups of monomer. The method of Attenuated Total Reflection (ATR) was used. The morphology of samples was characterized by a Scanning Electron Microscope (SEM, NOVA NANOSEM 450, FEI company) equipped with an Energy Dispersive X-ray Spectroscopy (EDS, TEAM EDAX, In-TEC company). The EDS was used to examine dispersion of sodium atom in sample surface. The samples were coated with Pt prior to SEM and EDS analysis. ^{1}H NMR spectra were obtained on a Varian VNMRS 600 MHz (UTK Chemistry) operating at 600 MHz D_2O was used as a solvent. Tetramethylsilane (TMS) was used as an internal standard and as a reference for chemical shifts. Sixteen scans with 16 K data points each were acquired for each ^{1}H NMR spectrum. The relaxation delay was 5s. Absorbency was measured by AMB 50 (ADAM EQUIPMENT) through removing of water in swelled sampled at 130 °C. Absorbency was calculated from weight of swelled sample and dried sample.

2.5. Measurement of absorbency

The CA-based SAP was cooled by liquid nitrogen and pulverized. The powder sample (1 g) was dried for 24 h in vacuum. It was immersed in various solution medium for 10–60 min. Distilled water, saline solution (0.9, 3 and 5%) or buffer solution (pH 4, 7 and 10) were used as medium. Absorbency of CA-based SAP was measured by commonly known sieve method which is equally called filtering and rubbing method [13]. The sample is poured into excess amount of water. And the swollen sample is filtered at desired time through sieve until the gel no longer slips from the sieve when it is held vertical. The absorbency was measured by moisture determination balance and calculated following equation.

$$\text{Asorbency}(\%) = \frac{\textit{swelled SAP} - \textit{dried SAP}}{\textit{dried SAP}} \times 100$$

3. Results and discussion

3.1. Synthesis and monomer selection of CA-based SAP

CA is a multifunctional monomer that has two α-carboxylic acids, β-carboxylic acid and a hydroxyl group. By utilizing most of its functionality, it has a potential for forming random 3D-network structure by incorporating suitable counterpart through melt polymerization without any external catalyst. Scheme 1 shows initial synthesis of SAP where selected diols with different structure and affinity are in the groups of ring/bulky, branched/linear and simple linear structure which corresponds to [CHDM, ISB], [NPG] and [EG, BD], respectively. The non-toxic and bulky monomers, CHDM and ISB, were thought to form larger free space allowing better water permeation. However, as shown Table 1, $PCC_{1.5}$ and $PCI_{1.5}$ was not able to absorb water at all. In case of $PCC_{1.5}$, the flexibility of cyclohexane is believed to be overwhelmed by its hydrophobicity and non-polarity, resulting no absorption. The other ring structured diol, ISB, has two furan ring having oxygen that contributes polarity. But since one of secondary hydroxyl

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