

Degradation of Acrylic Acid/acrylamide Superabsorbent Copolymer

Wichanee Bankeeree

Chulalongkorn University Faculty of Science

Chalermkwan Samathayanon

Chulalongkorn University Faculty of Science

Sehanat Prasongsuk (✉ sehanat.p@chula.ac.th)

Chulalongkorn University Faculty of Science

Pongtharin Lotrakul

Chulalongkorn University Faculty of Science

Suda Kiatkamjornwong

Chulalongkorn University

Research Article

Keywords: Poly(potassium acrylate), poly[acrylamide-co-(potassium acrylate)], soil burial, peroxidase, hydrogen peroxide, phytotoxicity

Posted Date: February 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-212720/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Poly(potassium acrylate), P(KA), and poly[acrylamide-*co*-(potassium acrylate)], P(Am-*co*-KA), were synthesized and an effective degradation technique of the polymers via chemical and biological processes were pursued. Significant reductions in dry mass and water absorbency were observed after P(KA) (53% and 54%, respectively) and P(Am-*co*-KA) (43% and 40%, respectively) were buried in the soil for ten weeks. The living fungal culture failed to degrade the polymers, but the enzymatic treatment using crude peroxidase (20 U/g) for 16 h significantly decreased the dry mass (15%; 15.0 ± 0.3 g) and water absorbency (13%; 16.0 ± 1.0 g/g) of P(KA). Chemical oxidation using H_2O_2 at high temperature with/without peroxidase efficiently degraded P(KA) and P(Am-*co*-KA). The maximum degradation of P(KA) (99.84% weight loss) was obtained when incubated with 12.8% (v/w) H_2O_2 at 65 °C for 7.3 h while 98.43% weight loss was achieved after P(Am-*co*-KA) was incubated with 14.8% (v/w) H_2O_2 at 68 °C for 9.2 h. No significant inhibition was observed in seed germination of mung bean grown on the untreated polymers but sweet corn was slightly inhibited. The effects of degraded products on mung bean germination were not significantly different from the control and untreated polymers. On sweet corn, the degraded products were apparently less toxic than did the untreated polymers. These results suggested that the rapid and efficient degradation of polyacrylate and its copolymer by the thermo-oxidation of H_2O_2 could be applied for a larger scale of SAP waste management.

Highlights

- A simple, rapid, and highly effective thermo-oxidation method for P(KA) and P(Am-*co*-KA) degradations was reported.
- Structural changes of the degraded products were observed by FTIR and 1H -NMR.
- The degraded products are not toxic to plants.

1. Introduction

Superabsorbent polymers (SAPs) are basically the hydrophilic three-dimensional network of water-insoluble polymer chains that can absorb fluids such as water, electrolyte solution, and biological fluids as high as 1,000 g/g of their own dried weight whereas the absorption capacity of common cotton pulp is not more than 1 g/g [1, 2]. Thus, SAPs are employed for a multitude of applications. Commercial production of SAPs began in 1978 for use in feminine napkins and further employing in baby diapers [3], agriculture [4] and commodity products [5]. Currently, the uses of SAP for biomedical purposes such as wound healing and drug carrier are the main goal of their applications [6].

SAPs are prepared on a laboratory scale from a variety of specifically hydrophilic petrochemical-based monomers and natural polymers that contain hydroxyl, carboxylic, amide, sulphonic groups etc., such as, poly(acrylic acid), polyacrylamide, starch, cellulose, etc. On the industrial scale of SAPs, acrylic acid (AA), its sodium or potassium salts, and acrylamide (AM) are the major and common monomers widely

employed for the production of PA or the copolymer of acrylate and amide moieties [3]. The desired features of PAs are fast absorption and swelling, large water absorption capacity, high swelling capacity, good mechanical strength of the swollen gel [6] and adequate release rate of retained water as moisture. Due to their outstanding properties, most of the SAPs available on the market are PA-based products in both homopolymeric and copolymeric forms [7]. The market for the PAs is predicted to continually grow as a result of rise of global population and changes in human lifestyle [8]. As the use of PA disposable items has increased, environmental problems related to the waste disposal have been concerned and needed prompt remedies [5].

Although both PA homopolymer and the copolymer between AA and AM (AA-AM) are reportedly biodegradable in soil, the degradation rates of the PA main chain are very slow and the calculated amount was only 0.12 to 0.24% (w/w) per six months [9, 10]. In addition, Mai et al., [11] reported that the mineralization rate of PA ranged from 4 to 7% (w/w) after one year. Based on those reports, the biological degradation amount and rate of PAs have been considered too slow and too low compared to a much larger amount of PA wastes deposited each year. Consequently, the quick accumulation of PA wastes in landfills raises serious environmental concerns. Therefore, an alternative and “green” technique that can efficiently shorten the degradation period is much desired.

On the degradation of superabsorbent polymers, one has to apply an effective treatment method to break the covalent crosslinked network in order to improve their mineralization either by chemical or biological means or even both means. To the best of the available information currently, there are very few documents reporting on effective non-biological degradations of PA. Thus, the purpose of the current study is to explore a new and effective method for the degradations of homopolymer of AA (potassium salt) and its copolymer of AA/AM. Due to the acidic nature of the PA gels, hydrogen peroxide was selected as the chemical oxidizer. The oxidation of the PA polymers was carried out at various temperatures and the degradation was assessed as the loss of hydrogel property. The contributions of biological factors, both living white rot fungus and its peroxidase enzyme, on the degradation were also evaluated. The structures of the degraded PAs were observed via FTIR and ¹H-NMR analyses. Phytotoxicity of the degraded products was also investigated by seed germination test. Here we reported the rapid, efficient, and environmentally safe protocol for the degradation of P(KA) superabsorbent polymers that can be further optimized and implemented in a larger scale of PA waste treatment.

2. Materials And Methods

2.1. Materials

The AA and AM monomers were purchased from Thai Mitsui Specialty Chemicals (Thailand). Potassium hydroxide (KOH), ammonium persulfate (APS) and hydrogen peroxide (commercial grade) were purchased from Ajax (Australia). N, N'-methylene-bisacrylamide (MBA, Fluka, analytical grade) and N, N, N', N'-tetramethylethylenediamine (TEMED, Sigma-Aldrich, ≥99.5% purity) were used as a crosslinking agent and co-initiator, respectively. Acetone and nitrogen gas (N₂) gas (99.99% purity) were purchased

from Zen point and Praxair (Thailand), respectively. All chemicals were used as received without further purification. Crude peroxidase was produced from *Trametes versicolor* CBR-04 according to Bankeeree et al. [12].

2.2. Synthesis of acrylate superabsorbent polymers

Two types of superabsorbent polymers, poly(potassium acrylate) (P(KA)) and poly[acrylamide-co-(potassium acrylate)] (P(Am-co-KA)), were synthesized via a free radical chain polymerization in aqueous solution of monomers with MBA cross-linker while APS and TEMED were used as an initiator and a co-initiator, respectively. All the reactions were performed under N₂ atmosphere. A KA solution was prepared by neutralization of 27% (v/v) AA in deionized water (110 mL) with 40 mL of 30% (w/v) KOH. The suspension was stirred at room temperature (25±3°C) for 90 min and then the polymerization of KA was conducted by adding APS (2.7 mg), MBA (17.2 mg) and TEMED (0.18 mL). The reaction was heated up to 65°C with vigorous stirring for 90 min to form a viscous gel.

For the copolymer synthesis of P(Am-co-KA), the monomer solution was prepared by dissolving AM (3 g) in KA solution at the ratio of 5:95 and stirring at room temperature (28±3°C) for 90 min. APS (14.3 mg), MBA (16.1 mg) and TEMED (0.18 mL) were then added and stirred at 65°C for 10 min to form a viscous gel. Each viscous gel was soaked in acetone to remove the absorbed water and unreacted monomers. The gels were oven dried at 65°C until a constant weight was reached, and then ground to reduce the particle sizes and collected the size portions by sieving through a set of ASTM E11-certified steel test sieve of 63, 108 and 212 mm (Retsch, Germany).

2.3. Polymer structure and property determination

The functional groups of P(KA) and P(Am-co-KA) were examined by Fourier transform infrared spectroscopy (FTIR; Perkin Elmer, Spectrum One, USA) with KBr disc for a direct compression over a wavenumber ranging from 400 to 4,000 cm⁻¹, with 32 scans. For water absorbency analysis, the dry P(KA) and P(Am-co-KA) weighing 0.1 g were each immersed in deionized water (500 mL) at room temperature for 24 h to reach an equilibrium swelling. The residual water was removed by filtration through an 80-mesh stainless steel screen. The retained polymer was left on the screen for at least 1 h to completely drain off the unabsorbed water. The water absorption was determined using Eq. (1) as follows:

$$\text{Water absorbency (g/g)} = \frac{(W_s - W_d)}{W_d} \quad (1)$$

where W_d is the weight of the dried SAP and W_s is the weight of the swollen sample.

2.4. Biological degradation

The biodegradations of P(KA) and P(Am-co-KA) were carried out using a soil burial method (Sharma et al., 2014). Five samples (150 g each) of each swollen gel were separately put in a 14 ´ 14 cm linen bag and buried in the natural garden soil at a depth of ten cm with a three-cm spacing between bags. The soil moisture was maintained by adding 200 mL of tap water every 24 h. To determine the extent of biodegradability, the samples were taken out from the soil after ten weeks, rinsed thoroughly with distilled water to remove the contaminated soil particles and dried in hot air oven at 60°C till a constant weight was obtained. The percentage of weight loss was evaluated based on the following Eq. (2):

$$\text{Weight loss (\%)} = [(W_i - W_f) / W_i] \times 100 \\ (2),$$

where W_i and W_f are dry weights of the polymer before and after the treatment, respectively. The structural changes were determined by comparing the FTIR spectra of each sample before and after the biological degradation. Further the changes in the morphological appearance were evaluated by scanning electron microscopy (SEM) and the presence of element was identified by energy dispersive X-ray spectrometry (EDXS) (JSM-6610; JEOL, Tokyo, Japan).

2.5. Effects of peroxidase, hydrogen peroxide and temperature on SAP degradation

The equilibrium swellings of each P(KA) and P(Am-co-KA) were performed by soaking 0.1 g of each SAP in deionized water (100 mL) for 24 h, filtrated through an 80-mesh screen and the products were used as initial polymers for the following studies. These swollen SAPs were incubated in a culture of *T. polyzona* (100 mL of minimal medium) under a static condition at room temperature ($28\pm3^\circ\text{C}$) for 20 days. Then, the treated SAPs were filtrated and dried. The degradation efficiency was investigated by the weight loss and water absorbency as described above. To evaluate the enzymatic degradation, the crude peroxidase at different concentrations (0, 5, 10, 15 and 20 U/g) in the same working volume of 50 mL was incubated with each SAP at room temperature for 16 h. The effect of hydrogen peroxide pretreatment was investigated by adding 50 mL of hydrogen peroxide with the different concentrations at 0%, 4%, 8% and 12% (v/w of the dry polymer) to each SAP and incubated at room temperature for 2 h. Weight loss and water absorbency were analyzed from each treatment and the best effective concentration of hydrogen peroxide was used as a basis in the next optimization step. The impact of temperatures was investigated by incubation of the SAP with hydrogen peroxide at the selected concentration for 2 h at different temperatures from 40 to 60°C. The degradation was evaluated according to weight loss and water absorbency reduction as mentioned above. All experiments were performed in triplicate and the results shown are means \pm one standard deviation.

2.6. Optimization of SAP degradation

The optimal conditions for SAP degradation were separately determined for the swollen P(KA) and P(Am-co-KA) by the Response Surface Methodology (RSM). The Box-Behnken experimental design with three levels of the three variable factors including three replicates at the center point is shown in Table 1 (Box and Behnken, 1960). The percentages of SAP degradation were taken as the response in each reaction. Statistical analysis of the data was performed by Design-Expert (version 8.0.7.1, Stat-Ease, Inc., Minneapolis, USA) to evaluate the analysis of variance (ANOVA) and to determine the significance of each term in the equations. The fitted polynomial equation was then expressed in the form of three-dimensional plots to illustrate the main and interactive effects of the independent variables on the dependent variables. To verify the accuracy of the predicted model, the experiment was repeated in triplicate using the predicted optimal condition. The structures of the treated SAPs at the optimal condition were identified by $^1\text{H-NMR}$ using a Bruker spectrometry (400 MHz).

2.7. Toxicity assessment of the products from SAP degradation

The phytotoxicities of the untreated and treated SAPs were evaluated via the seed germination test using mung bean (*Vigna radiata L.*), and sweet corn (*Zea mays L.*). The certified seeds were purchased from Chia Tai Co., Ltd. (Thailand) and imbibed in distilled water overnight before use. The experiments were carried out at room temperature by placing 25 seeds in each petri dish (15 ' 100 mm.) containing 10 mL of either distilled water, the untreated or treated SAPs (5 g/L) and incubated for three days in the dark. All experiments were performed in five replicates and the results obtained are means \pm one standard deviation. The percentages of germination were calculated using the following Eq. (3):

$$\text{Germination (\%)} = \left(\frac{\text{seed germinated}}{\text{total seed}} \right) \times 100 \quad (3)$$

All the experiments were performed in triplicate and the results so obtained are means \pm one standard deviation.

3. Results And Discussions

3.1. Structure and property of the synthesized SAP polymers

The P(KA) synthesized by thermal initiation of ammonium persulfate via the free radical chain polymerization in the presence of a di-functional crosslinker of N-MBA took place via thermal dissociation of the initiator to generate free radicals. The free radicals open the vinyl carbon-carbon double bonds of

the acrylic acid or its salt to give monomer radicals. Under the presence of the crosslinker and growing monomer radicals, the covalently cross-linked networks of the resulting SAP are produced continuously until the polymerization reaction is terminated. For P(AM-*co*-KA), a copolymerization between Am and KA competes for the free radical centers to add more reactive monomer. The extent of KA and AM amounts covalently crosslinked network depends mainly on the reactivity of both monomers which also depends significantly on the reaction condition. In our case, AA was partially neutralized by KOH in an attempt to enhance the rate of polymerization and to reduce the residual monomers remained in the system [13, 14]. The chain polymerization is caused by the radicals, generated by the thermal initiator (APS) under the heating condition, added to the double bonds of the vinyl monomers through the radical routes (KA with/without AM). Simultaneously, the double bonds in the MBA created the cross-linked structures [15]. The chemical structures of the obtained polymers were analyzed by FTIR-spectrophotometry and the IR spectra of P(KA) and P(Am-*co*-KA) are shown in Fig. 1 (dashed lines).

Both IR spectra were very similar between the two polymers and it might be due to the low amount of AM available in P(Am-*co*-KA) with the molar ratio of AM:KA at 5:95. Polymeric formation was indicated by the presence of C-C fraction from the peak at 1168 cm^{-1} and the absence of peak assigned to the vibration of H in C = C-H at 980 cm^{-1} which was reportedly apparent in KA and AM monomers [15]. Asymmetrical and symmetrical stretchings of the carboxylate groups (COO^-) of acrylate (AA neutralized with KOH) and C-N from acrylamide were observed with the peaks at 1555 and 1405 cm^{-1} , respectively. An absorption peak at 1724 cm^{-1} indicated the stretching vibrations of carbonyl (C = O) connected to the carboxyl group. In addition, the peak of the vibration of H in $\text{CH}_2 = \text{CH}-\text{COOR}$ at 3329 cm^{-1} was present in KA while the adsorption peak of C–H in the methylene group at 2925 cm^{-1} was visible in the copolymer [16]. The presence of absorbed water was seen by the band at 3350 – 3366 cm^{-1} in all spectra.

Water absorbency of the obtained polymers was determined according to Dispat et al. [17]. After 24-h of equilibrium swelling, P(KA) exhibited a slightly higher water absorbency ($387 \pm 12\text{ g/g}$) than that of P(Am-*co*-KA) ($338 \pm 16\text{ g/g}$) which might be contributed by the greater degree of ionization of the carboxylic groups originated from KA solely in distilled water. Basically, the extent of water absorbency related directly to the cross-link density which controls the expansion of polymer network to enable penetration of water molecules [18]. Electrostatic interactions between the amino cations originated from AM and the carboxylate anions formed a rather rigid network structure that prohibited the expansion of polymer networks [19]. In addition, the water absorbency of both SAPs is in the same range of commercial SAPs that has been used in agricultural applications [20].

3.2. Biological degradation

Compared to another widely used poly(sodium acrylate), PKA is far more suitable for applications in agriculture, horticulture and soil care since it does not increase soil salinity [21]. Although there have been a number of reports on biodegradability of P(KA), the fate of P(KA) in the soil still cannot be clearly drawn, both chemically and biologically, and there have been environmental concerns about its accumulation in agricultural lands [9–11, 22]. Therefore, biodegradations of P(KA) and P(Am-*co*-KA) were

evaluated after being buried in soil compared with the unburied one but incubated at room temperature for the same period. After ten weeks, the reductions of dry mass were $53 \pm 3\%$ for P(KA) and $43 \pm 2\%$ for P(Am-co-KA) compared to the unburied negative control (Table 1).

The difference in the degradation rate between P(KA) and P(Am-co-KA) is probably related to the crystallinity of the two polymers [23] and the lower degradation rate of P(Am-co-KA) was suggestively attributed by the chain stiffness of its cross-linked structure. Changes in water absorbency of the buried SAPs were also in accordance with the weight loss. An approximately 54% (183 ± 7 g/g) and 40% (135 ± 11 g/g) of water absorbency were lost from P(KA) and P(Am-co-KA), respectively. Decrement in water absorbency of both SAPs could be described by the partial destruction of network linkages that led to the loss of polymer density and the generation of lower molecular weight fragments and disintegration of its chain flexibility that could not have the same degree of water absorption capability [2].

To determine the changes in chemical structure of the buried polymers, FTIR spectra were compared between the treated SAP and the control, the unburied one (Fig. 1). The peak intensity of the molecular bonds of C–H (2925 cm^{-1}), C = O (1724 cm^{-1}), and C–O (1168 cm^{-1}) clearly decreased in both buried polymers. The change of absorbance intensity for P(Am-co-KA) was less significant than that of P(KA) which reflected in the reduction of their dry weight and water absorbency. In addition, the absorbance intensity in the range of $3340\text{--}3360\text{ cm}^{-1}$ attributed to the N–H hydrogen bonds and O–H vibration was increased and broadened due to the increasing of OH groups that overlap with the NH groups [24]. The appearance of a new peak at 1030 cm^{-1} attributed to the Si–O group from the soil was detected in the buried polymers. This result indicated the adhesion of soil inorganic and organic compounds to the treated polymers by surface contact, suggestively resulting in the degradation from outside layer to inside layer of SAP [23]. This observation was further evidenced via SEM-EDXS. The unburied SAPs had a relatively smooth and homogeneous surfaces (Figs. 2A, 2B) while the surfaces of the buried SAPs became completely heterogeneous with a number of holes, cracks, fissures, cavities, surface irregularities and microbial colonization (Figs. 2C, 2D). According to the EDXS spectra, the major elements including Si (8.06%), Al (2.73%), Ca (2.69%), Au (1.14%), Fe (1.02%), K (0.36%), Mg (0.26%), Ti (0.17%), Ni (0.13%) and Na (0.13%) were observed in the buried P(Am-co-KA) while the higher amounts of Si, Al, Fe, K, Au, Ti and Mg at 23.71%, 7.23%, 2.47%, 2.08%, 1.95%, 0.40% and 0.36%, respectively, were found in the buried P(KA) (Figs. 2E, 2F).

3.3. Effects of crude peroxidases, hydrogen peroxide and temperature on the SAP degradation

It has been reported that certain white rot fungi such as *Phanerochaete chrysosporium* and *Pleurotus ostreatus* can degrade some acrylic copolymers including P(guaiacol-Am-AA) and P(3,4-dihydroxybenzoic acid-AM-AA) within 15 – 18 days [11, 25]. Therefore, the swollen P(KA) and P(Am-co-KA) were separately incubated in a liquid culture of the white rot fungus *T. polyzona*. After incubation for 20 days, *T. polyzona* did not cause a significant decrease in the dry weight and water absorbency compared to the controls incubated in the same medium without white rot fungus (Supplementary data I). The growth of

the fungus was strongly inhibited by both SAPs and the activity of extracellular peroxidase that has been reported to oxidize a broad range of chemicals including lignin, PAM, and PAA into the unstable free radicals [2, 22] was not detectable in the fungal cultures containing P(KA) and P(Am-co-KA). Therefore, the crude peroxidase was produced from *T. polyzona* and used to treat P(KA) and P(Am-co-KA) at different concentrations ranging from 5 to 20 U/g. A slight but significant reduction of the dry weight (6.5 and 15%) and water absorbency (8 and 13%) were observed in the P(KA) treated with the crude peroxidase at 15 and 20 U/g, respectively, while no significant difference was detected in the treated P(Am-co-KA) (Table 2). The slight changes after 16-h peroxidase treatment suggested that a pretreatment step might be required prior to enzymatic digestion.

Most of the reported processes including mechanical, thermal, and chemical treatments to break the main chain (C-C) of PA and PAM have been involved with the activation of polymer by free radicals. The polymer radicals (P^{\cdot}) are generated from the attack of free radicals at the secondary and tertiary carbons, as well as the carbon of primary amine. These polymer radicals reacted well with the dissolved oxygen gas to form the polymer peroxy radicals (PO_2^{\cdot}) that could react to each other to generate the polymer fragments [26, 27]. Hydrogen peroxide is recognized as the reactive oxygen species that can derive free radicals in water, especially under acidic condition, and considered as a sustainable or green liquid oxidant [27]. Under the conditions applied in this experiment, increasing the hydrogen peroxide concentration enhanced the degradation of P(KA) and P(Am-co-KA) as observed from the significant reductions of weight loss and water absorbency (Table 3). The highest degree of degradation was found in the reaction with 12% (v/w) of hydrogen peroxide; therefore, this concentration was used for the further experiments.

The impact of temperatures was investigated by incubation of P(KA) and P(Am-co-KA) with hydrogen peroxide (12% (v/w)). The corresponding increments in weight loss of both SAPs were related to the rising temperature (Table 4). Although the weight loss of P(Am-co-KA) was not significantly different at 30°C, 40°C and 50°C, the significant differences in water absorbency were observed in each temperature indicating that the structural changes did occur. These results corresponded well with the previous studies that reported a much higher rate of polyacrylamide chain scission reactions by free radicals under higher temperature conditions ranging from 50°C to 80°C [28, 29]. After the incubation at 50°C with 12% (v/w) of hydrogen peroxide for 2 h, the pretreated P(KA) and P(Am-co-KA) were subsequently incubated with the crude peroxidase at 20 U/g for 16 h at room temperature ($28\pm3^{\circ}C$). However, the degradations of the pretreated SAPs with and without the enzyme were not significantly different (Supplementary data II); therefore, the crude peroxidase was omitted in the further optimization experiments.

3.4. Optimization of the SAP degradation

The optimum concentration of hydrogen peroxide, incubation times and temperatures for the degradation of P(KA) and P(Am-co-KA) were analyzed by RSM according to the Box-Behnken experimental design. The observed and predicted responses on weight loss of P(KA) and P(Am-co-KA) are shown in Tables 5 and 6, respectively. The maximum percentages of weight loss were found at $99.2 \pm 6.2\%$ (trial number 12

in Table 5) from the treated P(KA) and $99.7 \pm 6.4\%$ (trial number 10 in Table 6) from the treated P(Am-*co*-KA). The second-order regression equations that provided the percentage of weight loss as the function of variables are presented in terms of coded factors in the following equations:

$$Y_1 = 86 + 24A + 12B + 9C + 16AB + 1AC - 13BC - 39A^2 - 3B^2 - 4C^2 \quad (4)$$

$$Y_2 = 92 + 21A + 13B + 10C + 12AB + 8AC - 4BC - 53A^2 - 3B^2 - 14C^2 \quad (5)$$

where Y_1 and Y_2 are the response values of weight loss (%) of P(KA) and P(Am-*co*-KA), respectively. A , B and C are hydrogen peroxide concentration (% v/w), time (h) and temperature ($^{\circ}\text{C}$), respectively. Comparison of the predicted and experimental values revealed a good correspondence between them. In this case, the model showed insignificant lack of fit ($P_1 = 0.15$ and $P_2 = 0.83$). It indicated that the second-order model equation was adequate for the prediction of weight loss across the specified range of variables employed. According to the statistical analysis, the models in this study were significant. In addition, the coefficient of determination (R^2) was calculated to be in the range of 0.96 to 0.97, indicated that these models could explain more than 95% of the variability.

Three-dimensional response plots and their corresponding contour plots were drawn to investigate the interaction among the variables and to determine the optimum condition of each factor for the maximum degradation (Figs. 3 and 4). The canonical analysis revealed a complete degradation with >99% of the weight loss of P(KA) under the optimal condition of 12.8% (v/w) hydrogen peroxide at $65\text{ }^{\circ}\text{C}$ for 7.3 h while the predicted condition to optimally degrade P(Am-*co*-KA) was at 14.8% (v/w) hydrogen peroxide at $68\text{ }^{\circ}\text{C}$ for 9.2 h. The validity of predicted results by the regression model was confirmed by repeating the experiment under the optimal concentrations. The results obtained from three replications showed that the degradations of P(KA) ($99.84 \pm 4.40\%$) and P(Am-*co*-KA) ($98.43 \pm 5.95\%$) were close to each other and were not significantly different from the predicted value of $100.00 \pm 1.9\%$ and $98.98 \pm 2.2\%$, respectively. It implied that the empirical models derived from RSM can be used to adequately describe the relationship between the factors and response in the degradations of P(KA) and P(Am-*co*-KA). After being treated under these optimized conditions, both polymers completely lost their hydrogel appearance and were turned into clear liquids suggesting that the chains were shorten and dissolved. When the optimized hydrogen peroxide treatment was applied to two different SAPs, significant reductions in dry weight and water absorbency were observed although they were not completely dissolved. This finding suggested that the process can be applied to other polyacrylate hydrogels but to achieve the maximal efficiency, further optimization specific to each polymer is needed.

The structures of the treated SAPs under the optimal conditions were identified by $^1\text{H-NMR}$ and the spectra are shown in Fig. 5. The degraded products exhibited the peaks representing the carboxylate group (n-a, b; Fig. 5) at 1.6–1.8 ppm in both of P(KA) and P(Am-*co*-KA), and the amide group (m-a,b; Fig. 6B) at 2.2–2.4 ppm only in P(Am-*co*-KA). Since the degraded products from both SAPs were completely liquidized, it is suggestively indicated that these peaks represented the shortened chains of the SAPs. These treated products were used for the further assessment of their toxicity.

3.5. Toxicity assessment of the products from SAP degradation

The phytotoxicity of the untreated and treated SAPs evaluated via seed germination is shown in Table 7. There were no significant differences in seed germination of mung bean among all the treatments. However, the untreated P(KA) and P(Am-co-KA) moderately (36 %) to slightly (14 %) inhibited sweet corn germination suggesting the higher sensitivity of this plant to the polymers. Significantly less inhibition of seed germination was found in sweet corn treated with the degraded P(KA) and P(Am-co-KA) suggesting that the degraded products were less toxic to the plant than the untreated polymers. Overall, the results clearly indicated the less toxic nature of P(KA) and P(Am-co-KA) after thermo-oxidized by hydrogen peroxide, compared to the untreated controls, to germinating seeds of both dicotyledonous and monocotyledonous plant representatives. Our current research conforms to part of the Goal 15, the Department of Economic and Social Affairs, United Nations under the Sustainable Development on the point of “halt and reverse land degradation and halt biodiversity loss” [30].

4. Conclusion

In conclusion, the simple, rapid and effective thermo-oxidation for the degradation of P(KA) and P(Am-co-KA) was firstly reported. Both SAPs were completely liquidized within ten hours with little chemical and energy input. The degraded products obtained from the process were evidently safe for plants. Since this thermo-oxidation by hydrogen peroxide can also degrade other PA polymers in a preliminary attempt, it has a high potential to be further optimized for a larger scale for polyacrylate waste treatment.

Declarations

Acknowledgement

This research was supported by the Distinguished Professor Grant from Thailand Research Fund (DPG6080001 for Suda Kiatkamjornwong), and Sci-Super VI fund from the Faculty of Science, Chulalongkorn University (63-005).

Conflict of interest

The authors declare that they have no conflicts of interest in relevant to the content of this article.

Author Contributions

W.B. designed and performed the experiments with assistance of C.S. whereas S.P. and P.L. were involved in planning and supervised the work. S.K. conceived the original idea, supervised, reviewed and edited the

manuscript, and research fund provider. This manuscript was written and approved through contributions of all authors and they all contributed equally.

References

1. Kiatkamjornwong S (2007) Superabsorbent polymers and superabsorbent polymer composites. *ScienceAsia* 33(1):39–43. doi:10.2306/scienceasia1513-1874.2007.33(s1).039
2. Oksińska MP, Magnucka EG, Lejcuś K, Pietr SJ (2016) Biodegradation of the cross-linked copolymer of acrylamide and potassium acrylate by soil bacteria. *Environ Sci Pollut Res* 23(6):5969–5977. doi:10.1007/s11356-016-6130-6
3. Zohourian mehr MJAD, Kabiri KJIPJ (2008) Superabsorbent polymer materials: A review. *Iran Polym J* 17(6):451–477
4. Behera S, Mahanwar PA (2020) Superabsorbent polymers in agriculture and other applications: a review. *Polymer-Plastics Technology Materials* 59(4):341–356. doi:10.1080/25740881.2019.1647239
5. Zhang M, Zhang S, Chen Z, Wang M, Cao J, Wang R (2019) Preparation and Characterization of Superabsorbent Polymers Based on Sawdust. *Polymers* 11(11):1891
6. Sinha S (2018) 14 - Biodegradable superabsorbents: Methods of preparation and application—A review. In S. Thomas, P. Balakrishnan, & M. S. Sreekala (Eds.), *Fundamental Biomaterials: Polymers* (pp. 307–322): Woodhead Publishing
7. Relleve LS, Aranilla CT, Barba BJD, Gallardo AKR, Cruz VRC, Ledesma CRM, Nagasawa N, Abad LV (2020) Radiation-synthesized polysaccharides/polyacrylate super water absorbents and their biodegradabilities. *Radiat Phys Chem* 170:108618. doi:10.1016/j.radphyschem.2019.108618
8. Espinosa-Valdemar RM, Turpin-Marion S, Delfín-Alcalá I, Vázquez-Morillas A (2011) Disposable diapers biodegradation by the fungus *Pleurotus ostreatus*. *Waste Manag* 31(8):1683–1688. doi:10.1016/j.wasman.2011.03.007
9. Wilske B, Bai M, Lindenstruth B, Bach M, Rezaie Z, Frede H-G, Breuer L (2014) Biodegradability of a polyacrylate superabsorbent in agricultural soil. *Environ Sci Pollut Res* 21(16):9453–9460. doi:10.1007/s11356-013-2103-1
10. Zhou Z, Du C, Li T, Shen Y, Zeng Y, Du J, Zhou J (2015) Biodegradation of a biochar-modified waterborne polyacrylate membrane coating for controlled-release fertilizer and its effects on soil bacterial community profiles. *Environ Sci Pollut Res* 22(11):8672–8682. doi:10.1007/s11356-014-4040-z
11. Mai C, Schormann W, Majcherczyk A, Hüttermann A (2004) Degradation of acrylic copolymers by white-rot fungi. *Appl Microbiol Biotechnol* 65(4):479–487. doi:10.1007/s00253-004-1668-5
12. Bankeeree W, Prasongsuk S, Imai T, Lotrakul P, Punnapayak H (2016) A Novel Xylan-Polyvinyl Alcohol Hydrogel Bead with Laccase Entrapment for Decolorization of Reactive Black 5. *BioResources*, 11(3), 6984–7000. doi:10.15376/biores.11.3.6984-7000

13. Khanlari S, Dubé MA (2015) Effect of pH on poly(acrylic acid) solution polymerization. *Journal of Macromolecular Science Part A* 52(8):587–592. doi:10.1080/10601325.2015.1050628
14. Barleany DR, Lestari D, Yulvianti RS, M., & Susanto TR (2017) Acrylic acid neutralization for enhancing the production of grafted chitosan superabsorbent hydrogel. *International Journal on Advanced Science Engineering Information Technology* 7(2):702–708. doi:10.18517/ijaseit.7.2.2340
15. Feng L, Yang H, Dong X, Lei H, Chen D (2018) pH-sensitive polymeric particles as smart carriers for rebar inhibitors delivery in alkaline condition. *J Appl Polym Sci* 135(8):45886. doi:10.1002/app.45886
16. Santos FB, Miranda NT, Schiavon MIRB, Fregolente LV, Maciel W, M. R (2020) Thermal degradation kinetic of poly(acrylamide-co-sodium acrylate) hydrogel applying isoconversional methods. *J Therm Anal Calorim.* doi:10.1007/s10973-020-09899-y
17. Dispat N, Poompradub S, Kiatkamjornwong S (2020) Synthesis of ZnO/SiO₂-modified starch-graft-polyacrylate superabsorbent polymer for agricultural application. *Carbohyd Polym* 249:116862. doi:10.1016/j.carbpol.2020.116862
18. Leitão RCF, Moura CP d., Silva LRD d., Ricardo NMPS, Feitosa JPA, Muniz EC, Fajardo AR, Rodrigues FHA (2015) Novel superabsorbent hydrogel composite based on poly(acrylamide-co-acrylate)/nontronite: characterization and swelling performance. *Química Nova*, 38, 370–377
19. Erceg T, Dapčević-Hadnađev T, Hadnađev M, Ristić I (2021) Swelling kinetics and rheological behaviour of microwave synthesized poly(acrylamide-co-acrylic acid) hydrogels. *Colloid Polym Sci* 299(1):11–23. doi:10.1007/s00396-020-04763-9
20. Mahon R, Balogun Y, Oluyemi G, Njuguna J (2019) Swelling performance of sodium polyacrylate and poly(acrylamide-co-acrylic acid) potassium salt. *SN Applied Sciences* 2(1):117. doi:10.1007/s42452-019-1874-5
21. Başak H (2020) The effects of super absorbent polymer application on the physiological and biochemical properties of tomato (*Solanum lycopersicum* L.) plants grown by soilless agriculture technique. *Appl Ecol Environ Res* 18(4):5907–5921
22. Oksińska MP, Magnucka EG, Lejcuś K, Jakubiak-Marcinkowska A, Ronka S, Trochimczuk AW, Pietr SJ (2019) Colonization and biodegradation of the cross-linked potassium polyacrylate component of water absorbing geocomposite by soil microorganisms. *Appl Soil Ecol* 133:114–123. doi:10.1016/j.apsoil.2018.09.014
23. Liang D, Du C, Ma F, Shen Y, Wu K, Zhou J (2018) Degradation of polyacrylate in the outdoor agricultural soil measured by FTIR-PAS and LIBS. *Polymers* 10(12):1296. doi:10.3390/polym10121296
24. Oprea S, Oprea V (2016) Biodegradation of crosslinked polyurethane acrylates/guar gum composites under natural soil burial conditions. *e-Polymers* 16(4):277–286. doi:10.1515/epoly-2016-0038
25. Sutherland GRJ, Haselbach J, Aust SD (1997) Biodegradation of crosslinked acrylic polymers by a white-rot fungus. *Environ Sci Pollut Res* 4(1):16–20. doi:10.1007/BF02986258

26. Gröllmann U, Schnabel W (1982) Free radical-induced oxidative degradation of polyacrylamide in aqueous solution. *Polym Degrad Stab* 4(3):203–212. doi:10.1016/0141-3910(82)90027-1
27. Gilbert WJR, Johnson SJ, Tsau J-S, Liang J-T, Scurto AM (2017) Enzymatic degradation of polyacrylamide in aqueous solution with peroxidase and H₂O₂. *J Appl Polym Sci* 134(10):44560. doi:10.1002/app.44560
28. Neira A, Tarraga M, Catalan R (2007) Degradation of polyacrylic acid by fenton's reagent. *Journal of the Chilean Chemical Society* 52:1314–1317
29. Gao J, Lin T, Wang W, Yu J, Yuan S, Wang S (1999) Accelerated chemical degradation of polyacrylamide. *Macromolecular Symposia*, 144(1), 179–185. doi:10.1002/masy.19991440116
30. Xiong B, Miller Z, Roman-White S, Tasker T, Farina B, Piechowicz B, Burgos WD, Joshi P, Zhu L, Gorski CA, Zydny AL, Kumar M (2018) Chemical Degradation of Polyacrylamide during Hydraulic Fracturing. *Environmental Science Technology* 52(1):327–336. doi:10.1021/acs.est.7b00792
31. Department of Economic and Social Affairs, Goal 15, Sustainable Development (2020), United Nations, <https://sdgs.un.org/goals>

Tables

Due to technical limitations, tables are only available as a download in the Supplemental Files section.

Figures

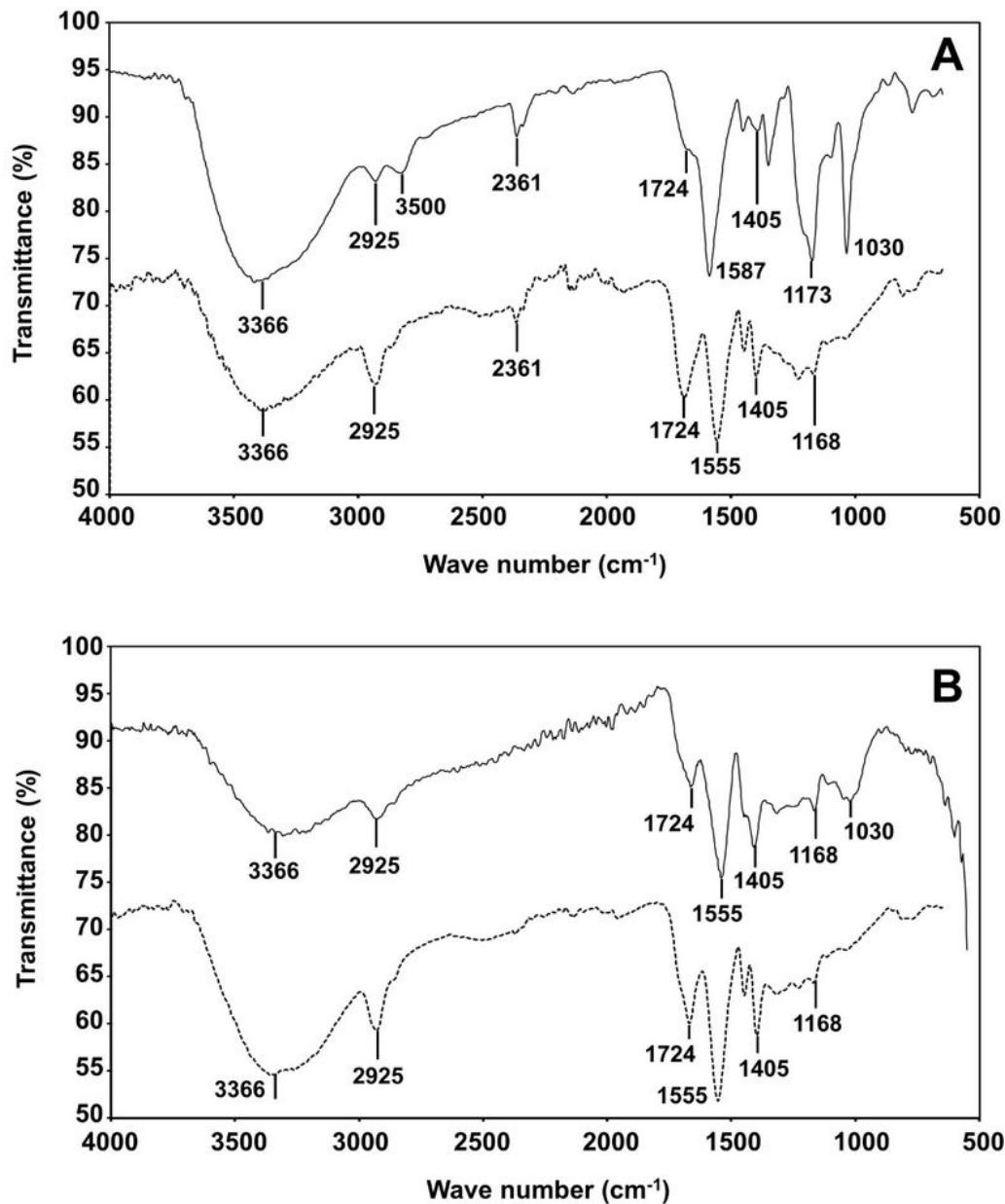
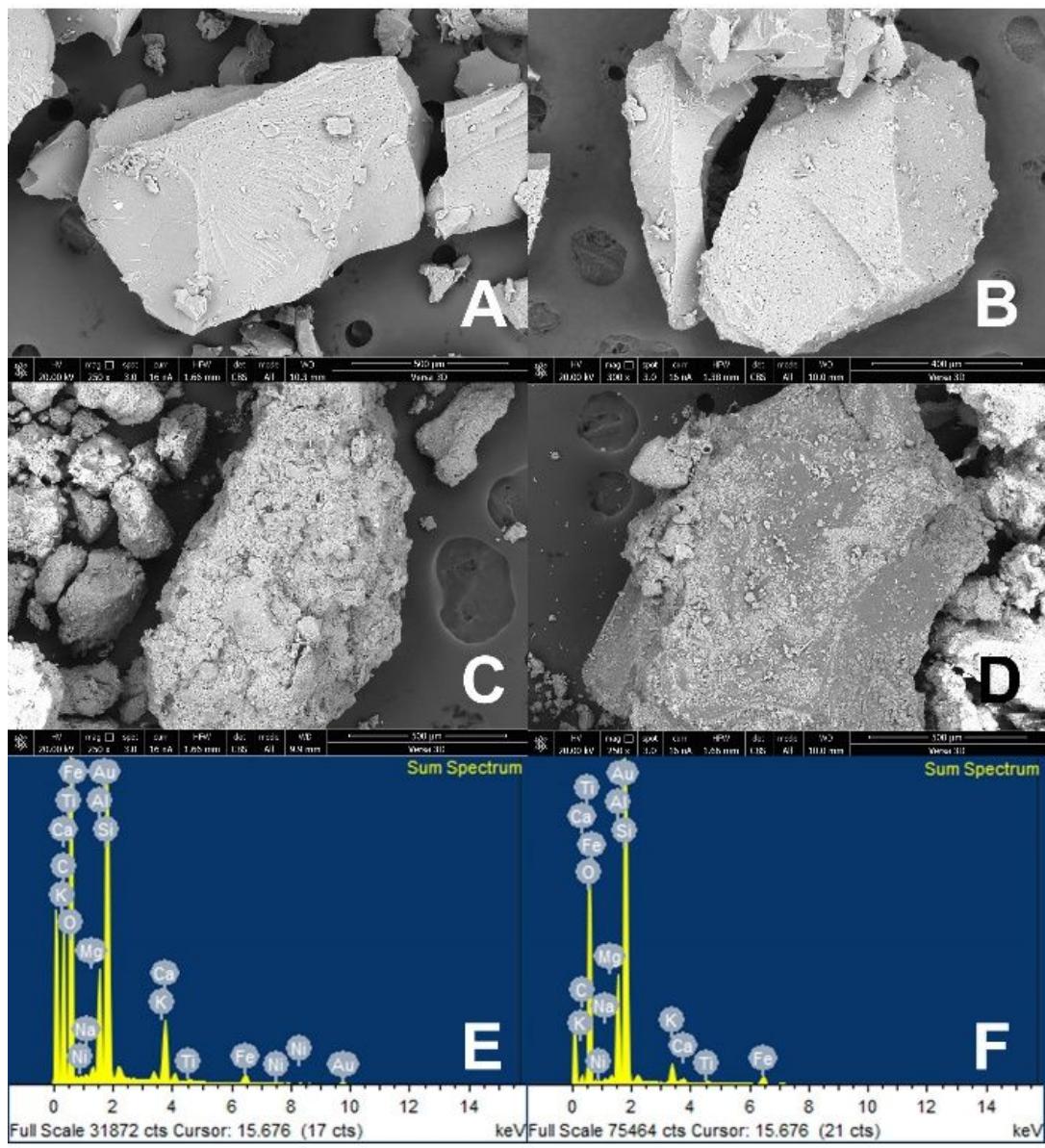


Figure 1

FTIR spectra of P(KA) (A) and (P(Am-co-KA) (B), before (—) and after (—) being buried in soil for ten weeks



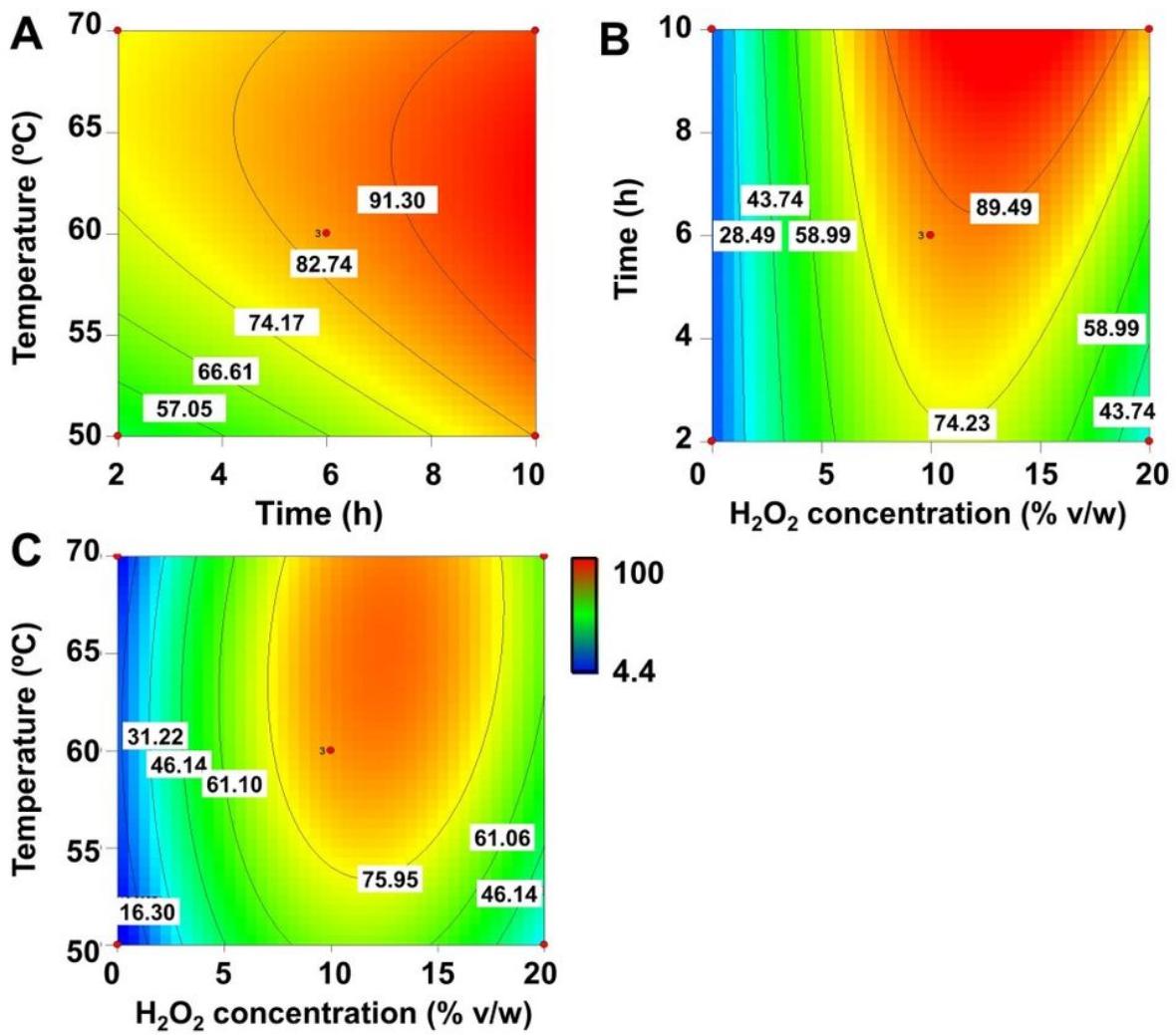


Figure 3

The contour plots showing the interactions between the different concentrations of hydrogen peroxide, temperature and reaction time on the weight loss of P(KA). The experiment was performed according to the Box-Behnken experimental design.

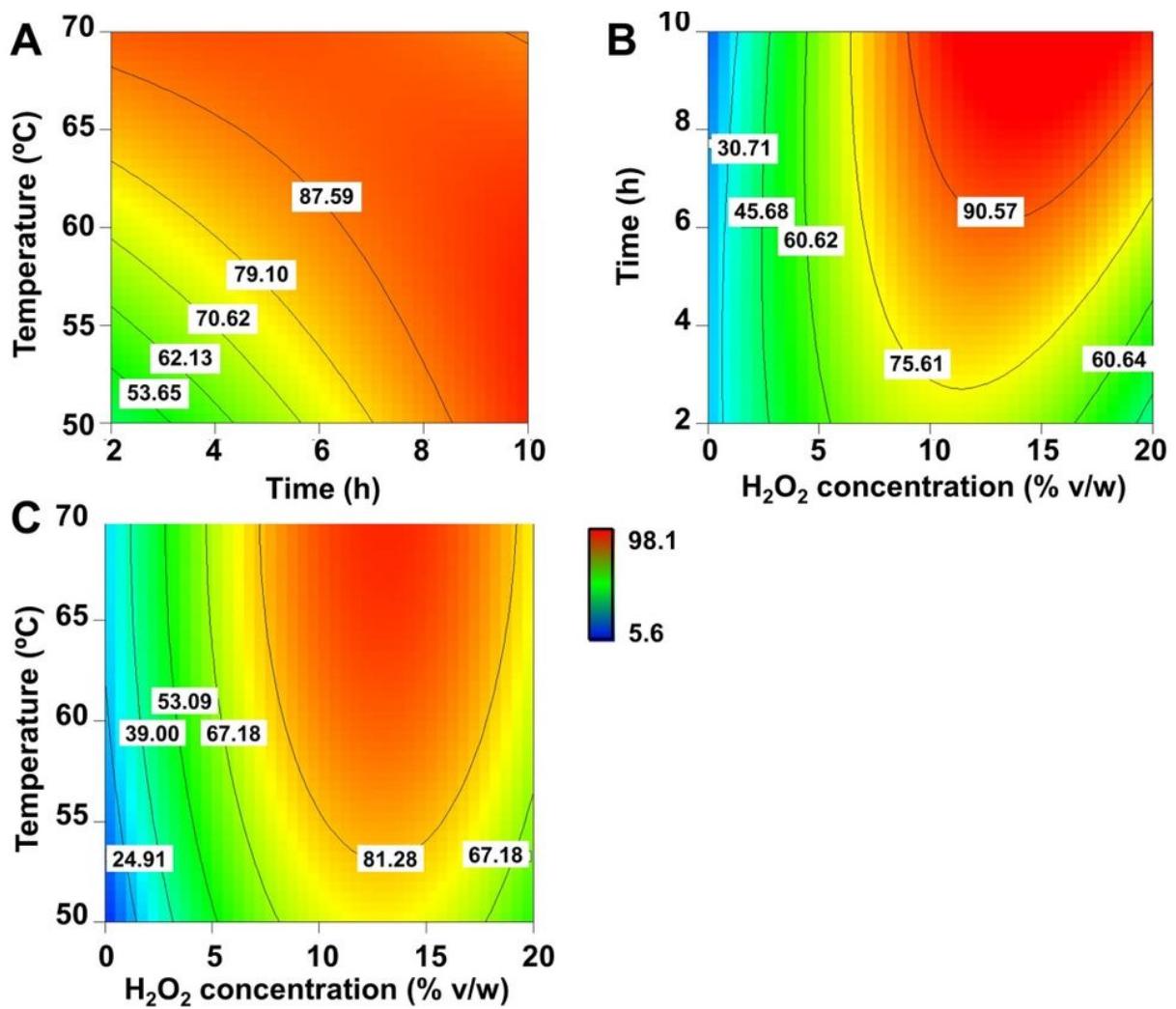


Figure 4

The contour plots showing the interactions between the different concentrations of hydrogen peroxide, temperature and reaction time on the weight loss of P(Am-co-KA). The experiment was performed according to the Box-Behnken experimental design.

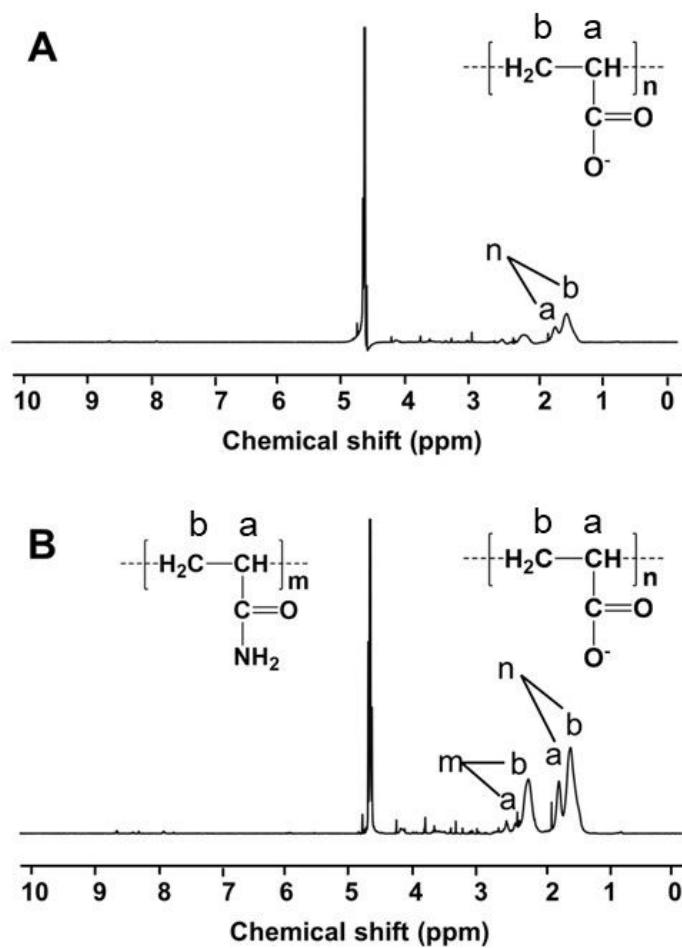


Figure 5

^1H NMR spectrum (CDCl_3 , 400 MHz) of products from P(KA) (A) and P(Am-co-KA) (B) degradation by hydrogen peroxide.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementalData.docx](#)
- [GraphicaAbstract.jpeg](#)
- [Tables.docx](#)