Catalytic Activities of Amino Acid Modified, Starch-Grafted Acrylamide for the Decomposition of Hydrogen Peroxide

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ABSTRACT: Acrylamide was grafted onto corn starch with ceric(IV) ions as an initiator. Starch-*graft*-polyacrylamide was modified with amino acids through a reaction with the sodium salts of glycine, β-alanine, and phenylalanine. The catalytic activities of the iron(III) complexes of the amino acid modified grafted materials were investigated for the decomposition of hydrogen peroxide (H_2O_2). These new polymeric supports were found to be active in the catalytic decomposition of H_2O_2. The extent of decomposition varied with the composition of the support. The iron(III) complex of the glycine-modified material was the most active of the amino acid supported catalysts. Factors that affected the rate of reaction, such as the concentration of H_2O_2, the amount of the catalyst, the pH, and the temperature, were investigated. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 630–636, 2004

Key words: catalysts; functionalization of polymers; graft copolymers

INTRODUCTION

The production of functionalized polymers and their use in many synthetic organic chemical reactions as catalyst supports, reagents, and carriers in separations and organic synthesis have attracted considerable interest during the last 3 decades.[1–3]

The removal of environmental pollutants through oxidation processes with hydrogen peroxide (H_2O_2) catalyzed by transition metals is increasingly important.[4] H_2O_2 has the advantage of producing oxygen and degrading biologically,[5] and it has recently been extensively used in intrinsically clean processes and in the end-of-pipe treatment of effluents of chemical industries.[6] Furthermore, the adoption of H_2O_2 as an alternative to current industrial oxidation processes offers environmental advantages, including (1) the replacement of stoichiometric metal oxidants, (2) the replacement of halogens, (3) the replacement or reduction of solvent usage, and (4) the avoidance of salt byproducts. The wasteful decomposition of H_2O_2 due to trace transition metals in wash water in the fabric bleach industry has also been recognized.[7] H_2O_2 works either alone or with a catalyst.[8] Iron is the most common homogeneous catalyst for H_2O_2.[9] Heterogeneous catalysts include metal oxides[10,11] and supported metal oxides.[12,13]

Modified naturally available supports, such as cellulose and starch, have been used in catalytic and technological applications. Cellulose modified with phosphonium and ammonium salts has been used as a phase-transfer catalyst in the displacement reaction of phenoxide ions with alkyl halides and the reduction of ketones with borohydride.[14,15] Cobalt phthalocyanine has been supported on cellulose fibers and used as an odor-removing catalyst of thiols.[16] Starch-grafted polyacrylonitrile and polyacrylate modified with hydroxamic groups have been used in heavy-metal removal.[17,18] Starch and cellulose modified via grafting with various vinyl monomers have been used as heavy-metal removers,[19,20] flocculating agents,[21] and oilfield and drilling mud additives.[22] However, postchemical modifications of starch-grafted polymers and applications as catalyst supports in chemical reactions or as carriers in separations and organic synthesis are still lacking.

The objective of this work was to synthesize and characterize amino acid modified starch-*graft*-polyacrylamide (St-*g*-PAM) as a new, environmentally friendly, heterogeneous catalyst support and determine its application as a support for the catalytic decomposition of H_2O_2.

EXPERIMENTAL

Materials and measurements

Acrylamide (Merck, Darmstadt, Germany), ceric(IV) ammonium nitrate (CAN), and divinylbenzene (DVB;

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TABLE I
Characteristics of the Amino Acid Modified Starch-*g*-Acrylamide Polymer

	Functional-group pattern			
	N content (%)		COOH content	mmol of Fe^{III}/g of
Polymer	Calcd	Found	(mequiv/g)	complex polymer
St-*g*-PAM	6.03	3.74	—	—
St-*g*-PAM-glycine	4.84	5.98	3.36	0.278[a]
St-*g*-PAM-β-alanine	4.62	6.39	2.88	0.189[b]
St-*g*-PAM-phenylalanine	3.67	3.38	1.36	0.179[c]

[a] Fe^{III} complex of glycine-modified St-*g*-PAM.
[b] Fe^{III} complex of β-alanine-modified St-*g*-PAM.
[c] Fe^{III} complex of phenylalanine-modified St-*g*-PAM.

technical; 55% mixture of 3- and 4-ethylvinylbenzene isomers; Aldrich, Steinheim, Germany) were used as received. The amino acids glycine, β-alanine, and phenylalanine (BDH, Poole, England) were used as received. The Cairo Co. for Starch & Glucose (Egypt) supplied the cornstarch. Iron(III) chloride (Merck) was used as received.

Elemental microanalysis, IR spectroscopy, and X-ray diffraction (XRD) were performed at the Central Laboratory of Microanalysis at Tanta University. IR spectra were recorded on a PerkinElmer 1430 ratio-recording IR spectrophotometer from KBr pellets. The wide-angle XRD studies were performed with a Phillips PW 1840 diffractometer. The pure starch and graft copolymer were scanned at $2\theta = 5$–$70°$. The thermogravimetric analysis was carried out at the Central Laboratory of Microanalysis at Cairo University on a Shimadzu TGA-50H from 25 to 500°C.
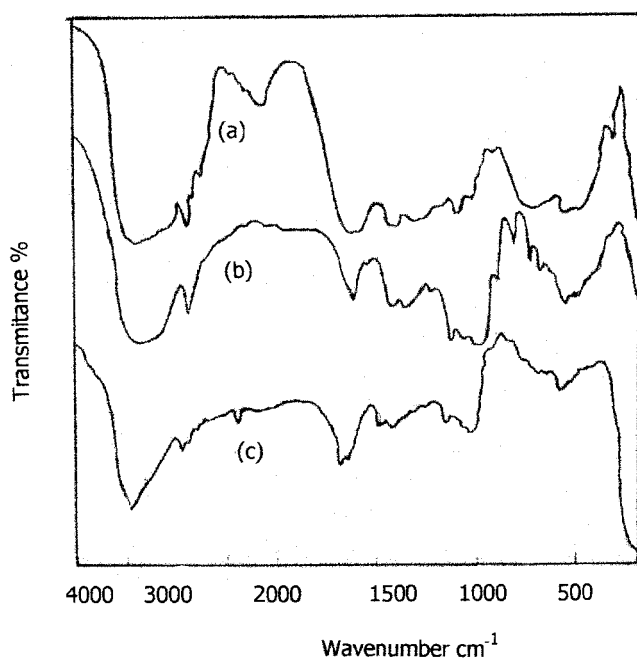
Preparation of the St-*g*-PAM copolymer

Grafting acrylamide onto starch was performed according to the following procedure.[20] Starch (8.0 g) was added to distilled water (200 mL) in a 1-L flask, and the mixture was stirred magnetically under a nitrogen atmosphere. A solution of CAN (0.50 g) in distilled water (10 mL) was added. This treatment was followed by the addition of an acrylamide solution (20.0 g) in 40 mL of distilled water and a solution of
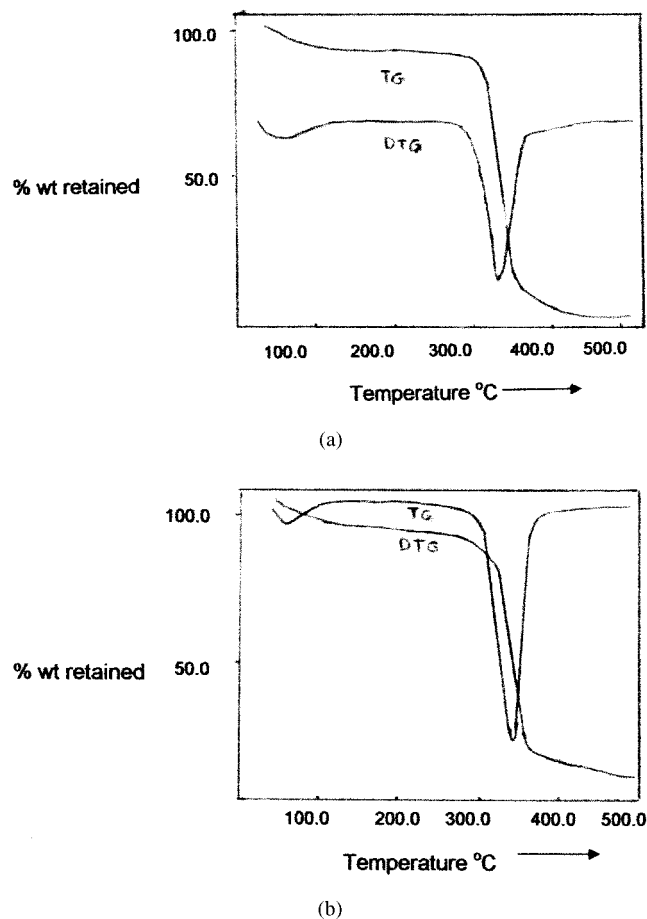

Figure 1 IR spectra of (a) polyacrylamide, (b) starch, and (c) ST-*g*-PAM.

Figure 2 Primary TGs and DTGs for (a) starch and (b) St-*g*-PAM.

TABLE II
Thermal Decomposition of Starch and St-g-PAM

Substance	Initial decomposition temperature (°C)			Maximum decomposition temperature (°C)			Weight loss (%)			Char yield at 495°C
	1	2	3	1	2	3	1	2	3	
Starch	36.6	283	416.5	56.5	332.8	479	8.5	75.6	11.6	4.30
St-g-PAM	46.2	276	412	55.3	340	493	7.9	69.5	14.1	14.5

0.70 mL of DVB in 1.0 mL of methanol. The polymerization proceeded under a nitrogen atmosphere for 24 h at 35°C. The grafted material was then filtered and washed thoroughly with distilled water. The solid product was thoroughly extracted with acetone. The final product was then dried *in vacuo* for 48 h. The dry product (St-g-PAM) weighed 16.7 g. Elemental microanalysis yielded 3.6% N, which corresponded to 39.3% grafting.

Modification of the grafted copolymer with amino acids

In a typical run,[23] St-g-PAM (1.0 g) was swollen in distilled water at 60°C for 1.5 h. It was then treated with the sodium salt of the amino acid in a molar ratio of 1:10 and refluxed at 80°C for 12 h. The product was filtered and washed thoroughly with distilled water, ethanol, and acetone to remove unreacted amino acid and NaOH. Elemental microanalysis yielded 5.97% N for the glycine-modified graft (the calculated value was 4.48), 6.39% N for the β-alanine-modified graft (the calculated value was 4.64), and 3.38% N for the phenylalanine-modified grafted material (the calculated value was 3.67).

The carboxyl contents of the functionalized grafted materials were determined through the equilibration of 250 mg of the modified grafted material with HCl (0.2N and 10 mL) for 24 h with magnetic stirring. The modified starch derivatives were filtered and washed well with water to remove unreacted HCl, and the filtrate was titrated against NaOH (0.2N).

Decomposition of H_2O_2 by the graft copolymer/Fe(III) complex

Iron(III) complexes of the amino acid functionalized graft copolymers were first prepared through the equilibration of the grafted material (0.50 g) with a solution of Fe(III) (25 mL, 0.0157 mol). The grafted copolymer complex was filtered and washed with distilled water. The amount of Fe(III) bound to the grafted material was determined from the difference in the metal-ion concentration before and after the treatment with the grafted materials with a standard ethylenediaminetetraacetic acid (EDTA) solution (Table I).

The decomposition of H_2O_2 was carried out as follows: the grafted-metal catalyst (0.10 g) was stirred with 50 mL of H_2O_2 (0.20N) in a reaction flask at 30°C

and pH 9.0. The concentration of the peroxide was determined through the titration of 5.0 mL of a solution of H_2O_2 taken from the reaction vessel at time intervals against a standard potassium permanganate solution. The values of the specific rate k were calculated from the plots of the natural logarithm of the concentration ($a/a - x$) against time t, where $a =$ the initial substrate concentration and $x =$ the product concentration after time t.

RESULTS AND DISCUSSION

Synthesis of the St-g-PAM copolymer

The grafting reaction of acrylamide with starch was carried out with CAN as an initiator. CAN was used because of the ease with which free radicals are formed at ambient temperatures in aqueous solutions, the formation of radicals on the backbone polymer itself, and the production of the pure graft copolymer. It is well known that St-g-PAM swells rapidly in water and then dissolves because of the high mobility of linear polyacrylamide chains attached to the hydrophilic starch.[20] The grafting reaction included a minute amount of DVB as a crosslinking agent to
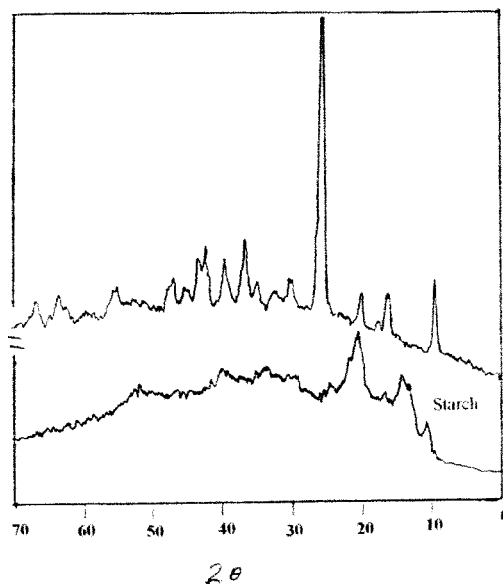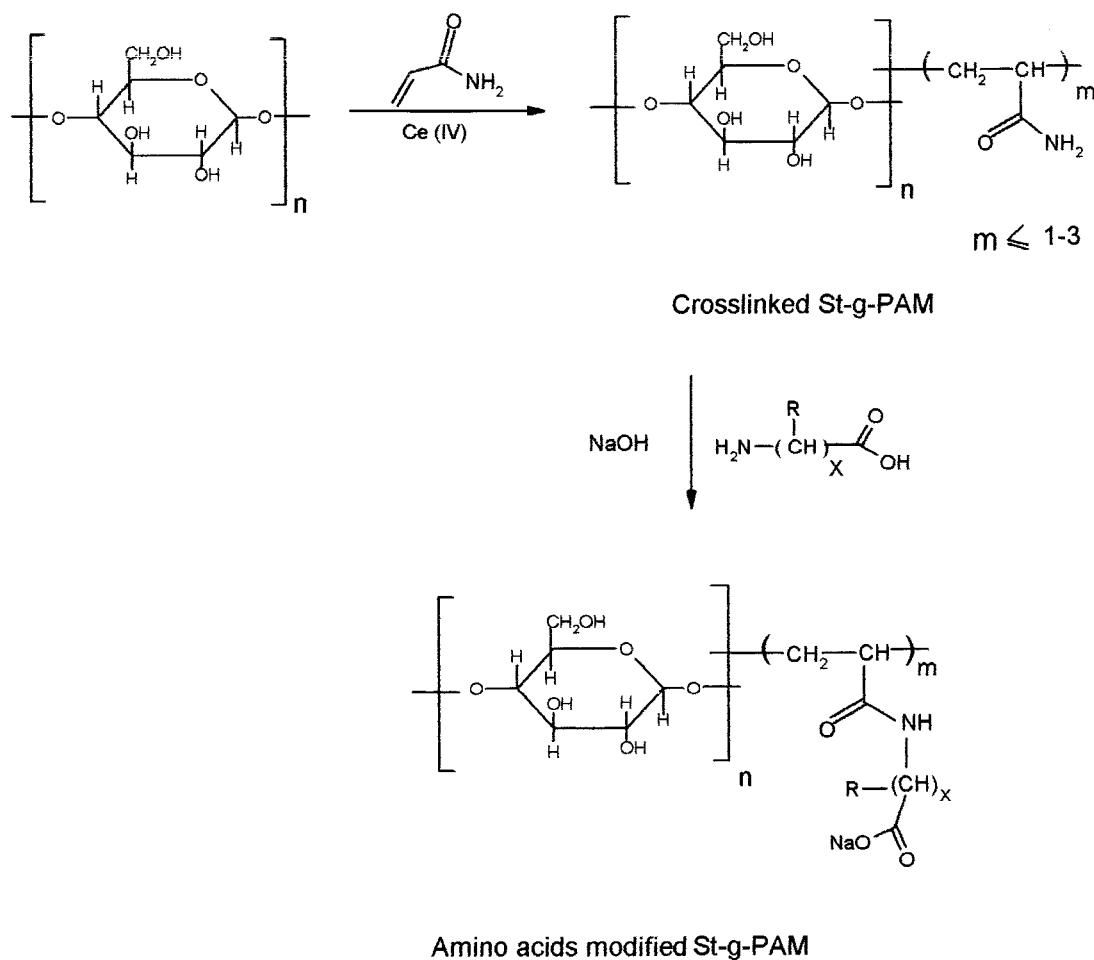

Figure 3 Wide-angle XRD patterns of starch (bottom) and St-g-PAM (top).

Scheme 1 Synthesis of St-*g*-PAM and its modification.

prevent the product from dissolution during catalytic applications. We did not expect the formation of a homopolymer of acrylamide because the solubility of acrylamide is higher in water (2.155 g/mL) than in methanol (1.55 g/mL),[24] and the presence of 1.0 mL of methanol enhanced the mixing of the minute amount of the 55% active DVB with other components. Evidence for grafting was found in the nitrogen microanalysis of 3.74% (Table I), which corresponded to a grafting percentage of 39.3%. The IR spectrum of the grafted material (Fig. 1) shows a broad band at 3400–3600 cm^{-1} due to OH stretching and amide NH. Another band appears at 1670 cm^{-1} due to an amide C=O stretching vibration.

Thermogravimetric analysis

The grafted material was subjected to thermogravimetric analysis so that we could study its thermal stability in comparison with that of pure starch. Figure 2(a,b) shows the primary thermograms (TGs) and derivatograms (DTGs) for both pure starch and the graft copolymer. Figure 2(a) shows a characteristic three-step TG of pure

starch; a slight weight loss can be observed in the first stage that is probably due to moisture evaporation. Rapid decomposition occurs in the second stage, with a major weight loss of 75.6% (Table II). The maximum decomposition temperature occurs at 332°C, as indicated by the DTG curve. The final stage of decomposition occurs at 493°C and is probably due to the evaporation of some volatile compounds; it results in an 11.6% weight loss. The grafted starch copolymer shows a thermal behavior slightly similar to that of pure starch [Fig. 2(b)]. The second stage, however, shows a slight increase in the maximum temperature decomposition at 340°C and a 70% weight loss. Although the TG/DTG curve of the grafted material slightly differ from that of pure starch, the char yield of the graft copolymer is slightly increased because of the contribution of supporting polyacrylamide chains.

XRD

The X-ray powder diffraction patterns of pure starch and St-*g*-PAM were recorded at $2\theta = 5$–70°. Pure starch is semicrystalline because of amylopectine frac-
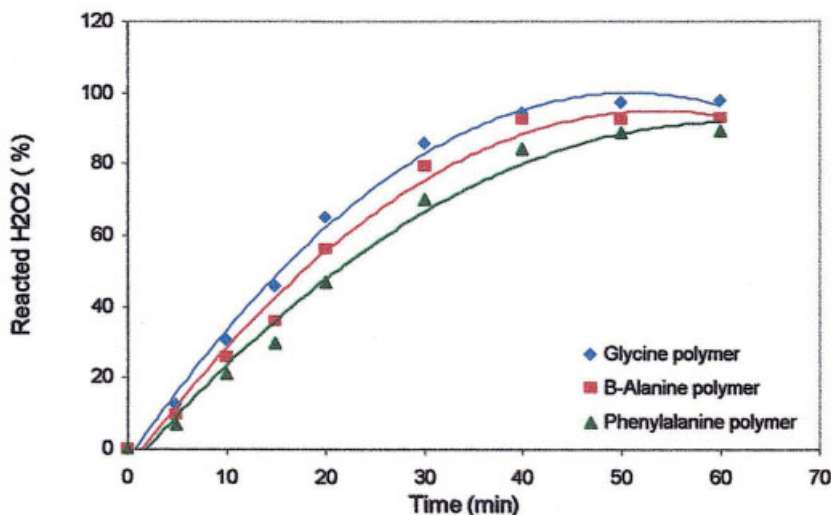
Figure 4 Catalytic activities of amino acid modified St-g-PAM for the decomposition of H_2O_2 at 40°C. The total volume was 50 mL, the pH was 9.0 (with a borate buffer), the amount of the catalyst was 100.0 mg, and the H_2O_2 concentration was 0.40N.

tions, and the crystalline area is about 20–25% of the total volume of starch.[25] Figure 3 shows approximately four peaks between $2\theta = 10°$ and $2\theta = 30°$, which on grafting appear to have been altered and sharpened in addition to the appearance of new peaks in the amorphous region. It can be inferred that both the amorphous and crystalline regions are involved in grafting.

Modification with amino acids

The amino acid functions glycine, β-alanine, and phenylalanine were added to St-g-PAM by a transamidation reaction[23] with excess sodium salt of the amino acid of interest. The reactions were carried out for a shorter time period (12 h) and at a lower temperature (80°C) than the original procedure[23] to prevent the hydrolysis of the amide group (Scheme 1). The higher

amino acid results of the elemental analysis may be due to adsorption on the graft surface because the possibility of a transesterification reaction is difficult under these reaction conditions. The carboxyl content of the modified grafted copolymer was determined through the equilibration of a definite amount of the graft copolymer with an excess amount of HCl and back-titration of the excess acid against a standard NaOH solution. The maximum carboxyl content was observed for the glycine-functionalized graft copolymer; this was followed first by β-alanine and then by phenylalanine.

Decomposition of H_2O_2

Iron(III) complexes of the grafted copolymers were obtained by the stirring of the iron(III) solution with the graft copolymer for 24 h. The polymer was sepa-

TABLE III
Kinetic Parameters for the Decomposition of H_2O_2 Catalyzed by Fe^{III} Complexes of Amino Acid Modified Starch-g-Acrylamide Polymer

Polymer	Temperature (°C)	k (s^{-1})	E_a (kJ/mol)	$\Delta H^{\pm}$ (kJ/mol)	$\Delta S^{\pm}$ (kJ/mol)	$\Delta G^{\pm}$ (kJ/mol)
Glycine-modified polymer	30	1.25×10^{-3}				
	40	1.57×10^{-3}	12.5	9.93	150.30	−37.0
	60	1.90×10^{-3}				
β-Alanine-modified polymer	30	6.0×10^{-4}				
	40	7.51×10^{-4}	16.3	13.72	128.72	−26.6
	60	1.01×10^{-3}				
Phenylalanine-modified polymer	30	5.60×10^{-4}				
	40	8.60×10^{-4}	19.3	16.72	106.67	−16.7
	60	1.08×10^{-3}				

Catalytic activities of amino acid modified St-g-PAM for the decomposition of H_2O_2 at different temperatures. The reaction conditions were as follows: total volume = 50 mL, pH = 9.0 with borate buffer, amount of catalyst = 100.0 mg, H_2O_2 concentration = 0.40 N.
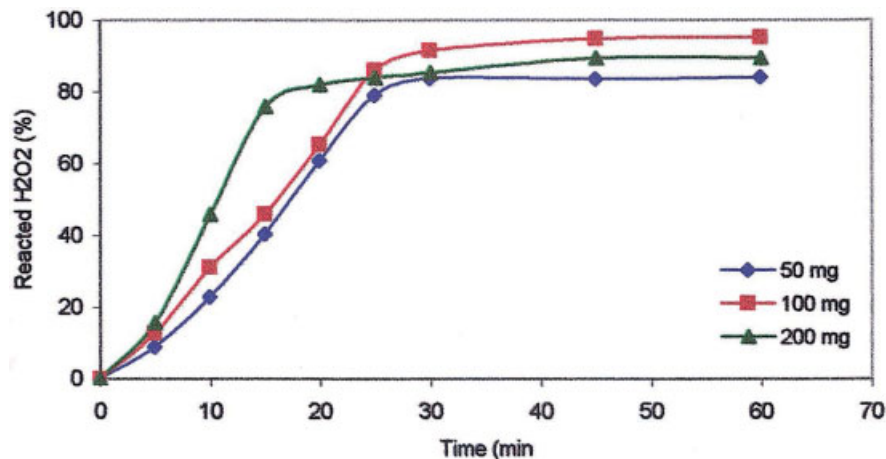
Figure 5 Decomposition of H_2O_2 with different amounts of the glycine-based catalyst system. The total volume was 50 mL, the pH was 9.0 (with a borate buffer), the reaction temperature was 40.0°C, and the H_2O_2 concentration was 0.40N.

rated by filtration, and the amount of the loaded metal was determined from the difference in the metal-ion concentration before and after the treatment with the grafted materials with a standard EDTA solution (Table I). The catalytic decomposition of H_2O_2 was chosen as a model reaction to study the catalytic activities of these new polymeric supports. The polymeric supports were found to be active in the catalytic decomposition of H_2O_2 (Fig. 4). The decomposition of H_2O_2 with these supported catalysts was found to follow first-order kinetics with respect to the H_2O_2 concentration. The glycine catalyst was the most efficient for H_2O_2 decomposition; it was followed first by the β-alanine catalyst and then by the phenylalanine catalyst.

The increased reactivity of the glycine catalyst, compared with that of the other two, is probably due to (1) the increased loading of Fe^{III} ions by the glycine-modified graft in comparison with the other two systems, (2) the increased accessibility of H_2O_2 to the reactive Fe^{III}-glycine sites distributed throughout the polymer particles, and (3) the increased stability constant of the complex (a greater stability constant leading to a higher reaction rate).[26] This substrate accessibility is reduced, probably because of steric hindrance in the case of the large ligands β-alanine and phenylalanine.

Temperature effect

The catalytic decomposition of H_2O_2 was studied at three different temperatures (30, 40, and 60°C) for the three catalyst systems. The rate of decomposition increased with increasing temperature for all three systems. The activation energies (E_a's) were calculated from the Arrhenius plots; the lowest value was for the glycine catalyst system, as observed previously. The changes in the entropy of activation ($\Delta S^{\pm}$), enthalpy of

activation ($\Delta H^{\pm}$), and free energy of activation ($\Delta G^{\pm}$) were calculated. The values are presented in Table III.

Effect of the catalyst amount

The glycine catalyst system was chosen to study the factors that affected the rate of reaction, such as the amount of the catalyst, the concentration of H_2O_2, and pH. The decomposition of H_2O_2 increased with an increase in the amount of the catalyst (50 < 100 < 200 mg; Fig. 5). This increase in the reactivity with an increasing amount of the catalyst was most likely due to the increased number of active sites available for substrate interaction.

Effect of the H_2O_2 concentration

The rate of decomposition increased as the H_2O_2 concentration increased (Fig. 6). The observed rate increase could be attributed to an increased number of substrate molecules within the catalyst particles,
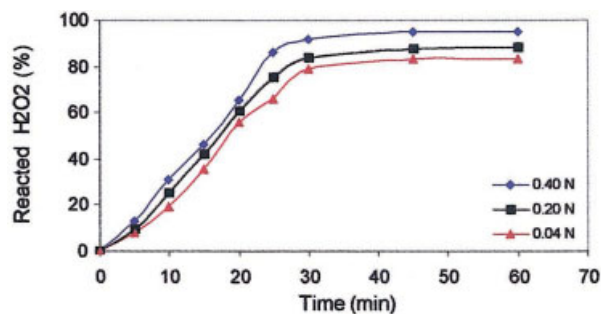

Figure 6 Dependence of the rate of decomposition on the H_2O_2 concentration with the glycine-based catalyst system. The total volume was 50 mL, the pH was 9.0 (with a borate buffer), the reaction temperature was 40.0°C, and the amount of the catalyst was 100.0 mg.
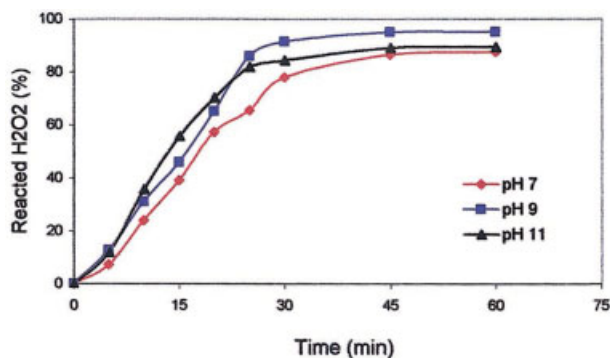
Figure 7 Dependence of the rate of H_2O_2 decomposition on the pH of the reaction medium with the glycine-based catalyst system. The total volume was 50 mL, the reaction temperature was 40.0°C, the H_2O_2 concentration was 0.40N, and the amount of the catalyst was 100.0 mg.

which allowed for close contact and, therefore, good interactions between the catalytic sites and the peroxide substrates.

Effect of the pH

Figure 7 indicates that the rate of H_2O_2 decomposition increased as the pH increased. This result agrees with Schumb et al.:[27] H_2O_2 is more stable at a low pH.
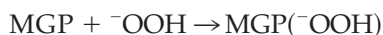
The decomposition of H_2O_2 can be schematically represented as involving the interaction of H_2O_2 or ^-OOH ions on the metal graft copolymer (MGP)[23,28] as follows:
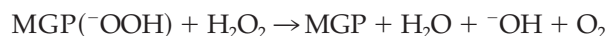
$$MGP + H_2O_2 \rightarrow MGP\text{—}H_2O_2$$
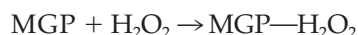
In the second step, H_2O_2 is deprotonated:

$$MGP\text{—}H_2O_2 \rightarrow MGP(^-OOH) + H^+$$

The formation of ^-OOH ions may be due to the decomposition of H_2O_2:[28]

$$H_2O_2 \rightarrow H^+ + {}^-OOH$$

$$MGP + {}^-OOH \rightarrow MGP(^-OOH)$$

The reaction may then proceed with the following common step, which involves another molecule of H_2O_2:

$$MGP(^-OOH) + H_2O_2 \rightarrow MGP + H_2O + {}^-OH + O_2$$

CONCLUSIONS

St-g-PAM was modified with amino acids to produce a new, environmentally friendly, heterogeneous catalyst support. The new polymeric supports were found to be active in the catalytic decomposition of H_2O_2 at different pHs. The results indicate that Fe^{III} complexes of amino acid modified St-g-PAM can serve as good catalysts in the treatment of organic pollutants in industrial effluents and wastewater. In addition, this new support may be useful in solid-phase and combinatorial syntheses.

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