

Synthesis, Characterization, and Application of PVP/PAM Copolymer

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ABSTRACT: The aim of this study was to synthesize copolymers from *N*-vinyl-2-pyrrolidinone (NVP) and acrylamide (AM) at different molar ratios and investigate the influence of the different ratios on copolymers' properties. How copolymers affect the washing and stain-repelling effects of carbon black, PET, Nylon, or cotton fabrics was also evaluated. Results show that as the AM content increased, the copolymers decomposed more slowly by heat, indicating better heat stability. In addition, copolymers were characterized as lowering surface tension and having excellent dispersing ability, low foaming properties, and excellent acid and alkaline resistance. The addition of copolymer can

produce stain-repelling effects against carbon black, PET, or Nylon-colored fabrics. It was also determined that fabrics' stain-repelling effects have no significant relationship to the NVP/AM molar ratio in copolymer synthesis. However, carbon black has better stain repellence as the AM monomer content increased. Two types of stain repellence gave better results when a higher concentration of copolymer was added. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2454–2459, 2006

Key words: molar ratio; copolymer; heat decomposition; stain repellence

INTRODUCTION

Fiber products tend to be contaminated by air and water; water pollution usually occurs during normal washing or re-dyeing. Furthermore, protecting fabrics from pollutants is the main factor in maintaining their high quality. Current industrial stain repellents, both hydrophilic and hydrophobic, are surfactants, which are not bio-degradable and cause environmental pollution. It is, therefore, important to explore bio-degradable stain processing chemicals, especially with increasing demand for "green fabrics."¹

Polyacrylamide (PAM), based on acrylamide (AM), displays organic or inorganic responses by reacting with residues, such as oxide (—OH), amine (—NH₂), and thiol (—HS) groups. It can also be used as an initiator, triggering a violent polymerization reaction. Ion properties can change the solubility, stickiness, and solution properties of the PAM amine residues. Since the side chain of the PAM molecule is an active amino residue, and due to the effects of neighboring residues, its reaction cannot proceed completely. Furthermore, it is hydrolyzed faster in alkaline solution, which has better application, but it has poorer heat stability and physical properties in highly ionized alkaline solutions.^{2,3}

Polyvinyl pyrrolidinone (PVP) is found in pharmaceuticals, stain removers, and food. It is a polymer with a high solubilizing ability, since its molecular structure has advanced properties and amide groups able to form hydrogen bonds. It also has functional groups, two of which have the ability to solubilize small molecules. Since small molecules bound to PVP have a lower thermodynamic activity, this increases its stability. Therefore, one can improve the heat stability and alkaline resistance of PAM by polymerizing with AM monomer to form a copolymer; and PVP has excellent physiological inertia and biological compatibility.^{4,5}

In this study, *N*-vinyl-2-pyrrolidinone (NVP) and AM monomers were allowed to polymerize with an initiator, 2,2-azobisisobutyronitrile (AIBN), to form NVP/PAM copolymers. These copolymers were used in stain-repelling experiments, to study their possible use as stain repellents.

EXPERIMENTAL

Materials

Dimethyl sulfoxide, ethanol, urea, sodium hydroxide, and isopropanol (IPA) were purchased from Shimadzu Food Tech (test grade); acrylamide (AM), hydrochloric acid, and AIBN were purchased from Japan Reagent Industry (test grade). Other chemicals used in this research include *N*-vinyl-2-pyrrolidinone (test grade; ACROS), Acidol Brill Yellow M-5GL (Tai-

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wan BASF Group), Everdirect Fast Black VSF600 (Taiwan Everlight Chemical Industrial), and Sumikaron Red S-BDF (Taiwan Fu Mao Chemicals).

Methods

Synthesis of PVP/PAM copolymers

Different molar ratios (1 : 0.5/1 : 1/0.5 : 1) of NVP/AM were measured and mixed. AIBN (5 g/L) was dissolved using 1,2-dichloroethane. The previously described chemicals were then added individually to the reaction trough, followed by addition of 20 mL IPA and 2% urea. The reaction proceeded at 30°C for 3 h in N₂ condition. The product was purified by acetone and dried in a drier.

Analysis of PVP/PAM copolymers

Functional groups of copolymers were analyzed using a Bio-Rad Digilab FTS-200 Fourier optical spectrum analyzer; heat weight loss was measured by a DuPont 2200 weight loss analyzer. Molecular weight was determined by GPC of Bio-Rad FTS-3000Mx analyzer, using polystyrene as a standard and tetrahydrofuran as solvent.

Measurement of basic properties

Determination of acidic and alkaline resistance. A 1 g/L sample solution and 10, 20, 30, and 40% HCl and NaOH solutions were prepared. Then, 10 mL of the solution was continuously dropped into the HCl and NaOH solution to reach a final volume of 20 mL. After constant stirring, it was left to stand to observe any changes. If the solution divided into two layers, it indicated phase division.

Sodium morrhuate dispersing ability. A 5-mL sodium morrhuate solution (0.5%) and a 10-mL calcium chloride solution (1 g/L) were placed in a titrating cylinder, into which the sample solution was dropped. After vigorous shaking, the sample solution became turbid and opaque. The depleted amount (ml) of sample solution was recorded.

Sodium carbonate dispersing ability. Calcium carbonate (1 g) and 0.1 g of copolymer were accurately measured and placed in a burette, which was then vigorously shaken and allowed to rest. The time particles required to sediment to the half height were recorded.

Foaming properties. This was tested based on the CNS 3384-K1357 method.

Surface tension and angles of contact. Surface tension and angles of contact were determined by a surface tension measuring instrument (DCAT-11 Dataphysics).

Stain-repelling tests

1. Three kinds of fabrics, PET, Nylon, and cotton, which had each been stained with disperse, acidic, and direct dyes were divided into two tubs. Both tubs contained dyed and white fabrics, and one had the addition of different concentrations of copolymer solution. These fabrics were allowed to stain at 70°C for 30 min. Fabrics were then dried before determination by a color-difference tester.
2. Carbon black powder (1 g/L) was added to a steel cup containing white and sample fabrics and an appropriate amount of copolymer. Carbon black staining then proceeded at 40°C for 30 min and the fabric was dried before testing for color difference.

RESULTS AND DISCUSSION

FTIR

FTIR spectra of PVP/PAM are shown in Figure 1. The line in Figure 1(a) indicates an obvious absorption peak at 1646 cm⁻¹ in the analysis of PVP FTIR. This peak is the amide(I) peak, whose vibrating wave results from the combination of two functional groups, >C=O and C—N.⁶ Since it is a combination, it has a lower absorbing peak than pure C=O (1750–1700 cm⁻¹). Figure 1(e) shows the FTIR spectrum of PAM, where there is an obvious absorption peak of >C=O at 1647 cm⁻¹, and a peak of —NH₂ at 3331 cm⁻¹. In Figures 1(b)–1(d), IR spectra of PVP/PAM copolymerized from NVP/AM monomers with different molar ratios (1 : 0.5, 1 : 1, 0.5 : 1) are displayed; all three have an obvious absorption peak, which is the peaks of the >C=O and —NH₂ functional groups. This implies that NVP and AM polymerization proceeds under suitable conditions, but these peaks become more obvious when molar ratios are increased.

TGA

TGA spectra and datas of PVP/PAM copolymers are shown in Figure 2 and Table I. Figure 2(a) is a pure PVP curve, where the decomposing temperature of PVP is 449.2°C and the decomposing speed is -1.652% per °C—a very rapid decomposition. When the decomposing temperature reaches 501.2°C, only 2.57% of the copolymer remains. Figures 2(b)–2(d) show TGA spectra of PVP/PAM copolymers produced from different molar ratios of NVP/AM (1 : 0.5, 1 : 1, 0.5 : 1). The temperature of decomposition initiation is 438.3, 422.6, and 401.7°C, and its speed is -1.318, -0.934, and -0.781% per °C, respectively. When the temperature increases to 500°C, the copolymer residue is only 7.25, 11.08, and 12.95%, respec-

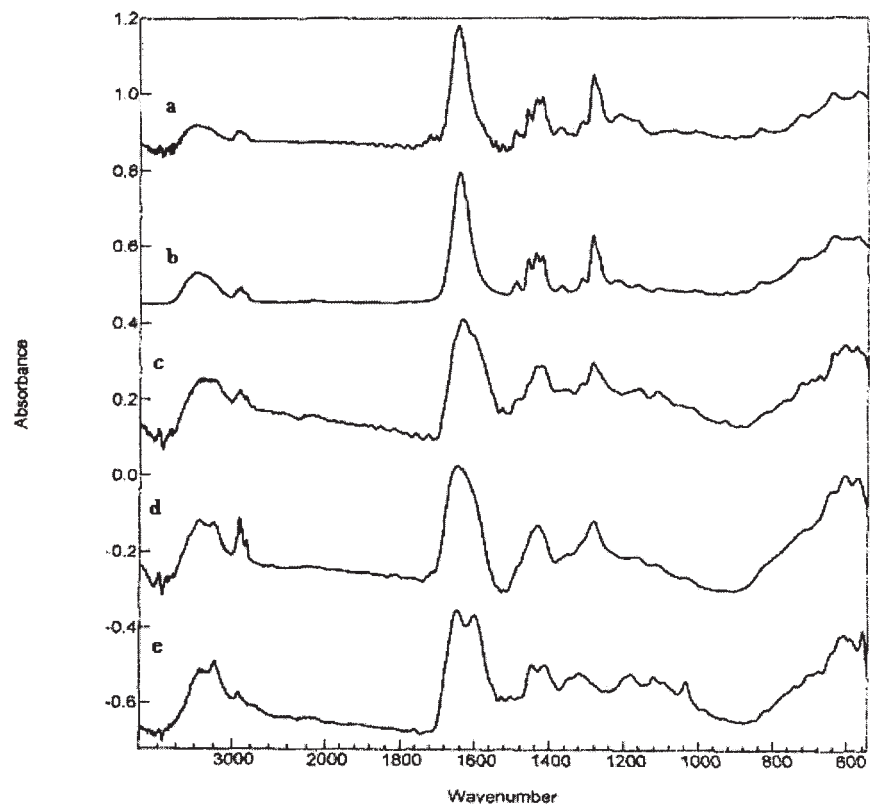


Figure 1 FT-IR spectra of PVP/PAM copolymers. (a) PVP, (NVP/AM); (b) 1/0.5; (c) 1/1; (d) 0.5/1; and (e) PAM.

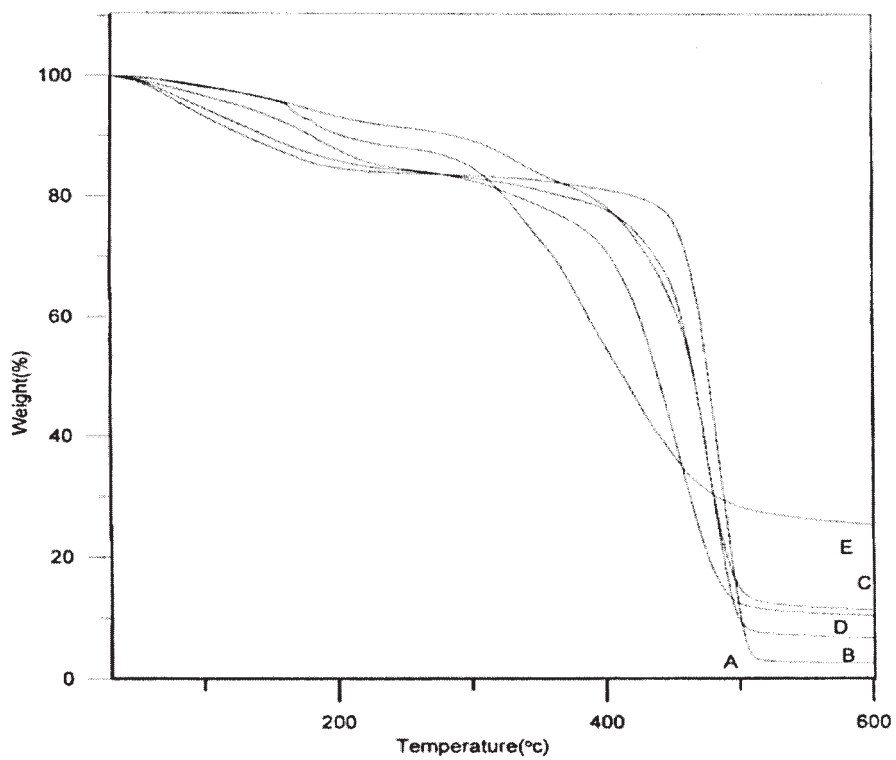


Figure 2 TGA of PVP/PAM copolymers. (a) PVP, (NVP/AM); (b) 1/0.5; (c) 1/1; (d) 0.5/1, and (e) PAM.

TABLE I
Thermoresistance of Various Copolymers

Materials ^a	Properties	
	Initial decomposition temperature (°C)	Decomposition rate (%/°C)
Pure PVP	449.2	-1.652
1 : 0.5 ^b	438.3	-1.318
1 : 1	422.6	-1.070
0.5 : 1	401.7	-0.781
Pure PAM	296.4	-0.360

^a Copolymers synthesized from NVP/AM with different molar ratios.

tively. Thus, these copolymers are superior, in terms of decomposing rate and residual amount, to pure PVP. This implies that fabrics containing copolymers will have better heat stability. Figure 2(e) shows a pure PAM curve, where the decomposing temperature and speed of PAM are 296.4°C and -0.360% per °C, respectively. When the temperature is increased to 500°C, the residual amount is 27.96%, which shows the superior heat stability of PAM.

Molecular weight

The molecular weight of each copolymer is shown in Table II, indicating that the copolymer's molecular weight increases as the NVP molecule increases. This is because the effect of conjugate double bonds, formed in the NVP molecule, is stronger than in AM.⁷ Therefore, there is less free radical activity formed from NVP than from AM because there is more polymerization activity with NVP than AM monomers.

Dispersing and foaming properties

Calcium carbonate in water during dyeing causes spots and affects fabric quality and brilliance. Therefore, calcium carbonate must be dispersed in water to reduce its attachment and to protect the fabric quality and brilliance. If a surfactant has various advantages, one can avoid using other chemicals and, thereby, lower costs.

TABLE II
Molecular Weight of PVP/PAM Copolymers

Materials ^a	Properties		
	M_w	M_n	M_w/M_n
1 : 0.5	57,400	31,160	1.842
1 : 1	49,300	27,340	1.803
0.5 : 1	32,540	18,120	1.796

^a Copolymers synthesized from different molar ratios of NVP/AM.

TABLE III
Copolymers' Dispersing Property for Sodium Morrhuate and Calcium Carbonate

Materials ^a	Properties		
	Dispersing metallic soap (mL)	CaCO ₃ sediment time (h)	Foaming height (cm)
1 : 0.5	2	Above 20	0
1 : 1	2	Above 20	0
0.5 : 1	1	Above 20	0
Pure water	50	Above 10	0

^a Copolymers synthesized from different molar ratios of NVP/AM.

The dispersing value of synthetic surfactants to calcium carbonate and sodium morrhuate is shown in Table III. Three kinds of synthetic copolymers can excellently disperse sodium morrhuate, because when the surfactant reaches the cell micro-concentration, surfactant molecules form micro-vesicles, which increase the solubility of sodium morrhuate. Thus, sodium morrhuate can dissolve in micro-vesicles, forming lacteous liquid drops and dispersing in solution. Furthermore, since the surface of micro-vesicles has the same electrical charge, there is no repulsion between micro-vesicles, and, thus, they can appear in stable dispersion in a water solution.

Pure water does not foam, but when a solution containing surfactants is stirred, air goes into the solution, forming bubbles. The enhancer will be absorbed at the interface between liquid and gas phases, forming an elastic gel membrane. Thus, if gas is present in a solution, foam will be produced. During the process of dyeing, the machine operation brings gas into the dyeing solution, causing bubbles. Excess bubbles obstruct contact between the staining solution and fibers, giving rise to uneven staining. Therefore, throughout the staining process, the surfactants used must have low-foaming properties.

As shown in Table III, three synthetic PVP/PAM copolymers produced almost no foam because synthetic copolymers have hydrophilic and hydrophobic functional groups in their structures. These two kinds of molecular arrangements destroy bubble formation, giving them lower foaming properties and higher foaming stability.

Surface tension

The outcome is the attracting force pulling toward the liquid; thereby, when the condensing force between molecules increases, the surface tension will also in-

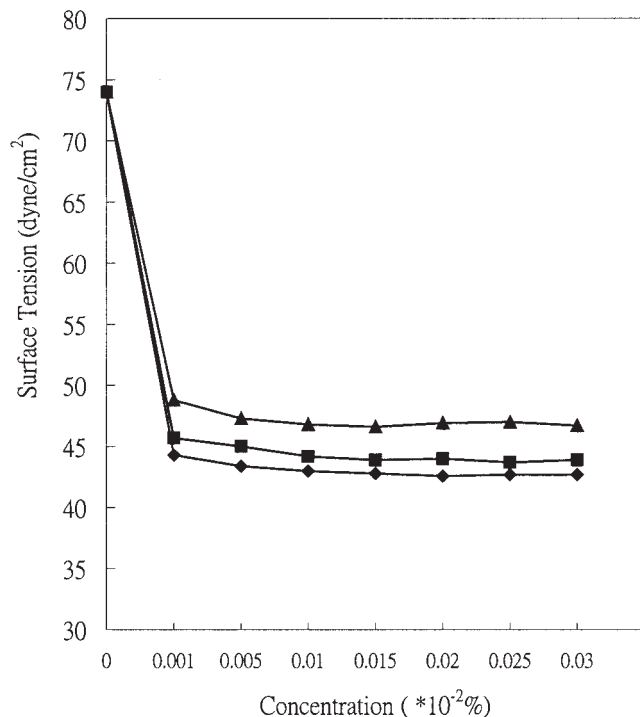


Figure 3 Relationship between concentration and surface tension of copolymers. Mole ratio of NVP/AM: \blacklozenge —1 : 0.5, \blacksquare —1 : 1; \blacktriangle —0.5 : 1.

crease (Fig. 3). As seen in Table IV, when PVP and PAM have more hydrophilic residues, the surfactant can more easily align on the surface, and so its ability to lower surface tension is improved. This can also be seen from the contact angle determination data, where the addition of PVP/PAM surfactant increases the moisture of materials. An NVP/AM ratio of 1:0.5 gives the best surfactant to prevent staining.

TABLE IV
Surface Tension^a and Contact Angle^b of PVP/PAM Copolymer

Concentrations of copolymers (%)	Molar ratios of NVP/AM		
	1 : 0.5	1 : 1	0.5 : 1
Surface tension (dyne/cm ²)			
0.001	44.3	45.7	48.8
0.005	43.4	45.0	47.3
0.010	43.0	44.2	46.8
0.015	42.8	43.9	46.6
0.020	42.6	44.0	46.9
0.025	42.7	43.7	47.0
0.030	42.7	43.9	46.7
Contact angle (°)			
Acrylic plate	48.8	50.1	52.6
Original white fabric	60.2	61.3	63.4

^a Surface tension of pure water is 74 dyne/cm². Surface tension measuring machine: DCAT-11, Dataphysics Co.Ltd.

^b Without adding surfactant, the contact angle of an acrylic plate is 76.8° and the original white fabric is 115°.

TABLE V
Acidic and Alkaline Resistance of PVP/PAM at Different Temperatures

Copolymers ^a	NaOH conc. (%)				HCl conc. (%)			
	10	20	30	40	10	20	30	40
25 (°C)								
1 : 0.25	• ^b	•	•	•	•	•	•	•
1 : 1	•	•	•	•	•	•	•	•
0.25 : 1	•	•	•	•	•	•	•	•
90 (°C)								
1 : 0.25	•	•	•	•	•	•	•	•
1 : 1	•	•	•	•	•	•	•	•
0.25 : 1	•	•	•	•	•	•	•	•

^a Copolymers synthesized from different molar ratios of NVP/AM.

^b • indicates one phase.

Common surfactants can reduce liquid surface tension and lower free energy on the surface. With its moisturizing property, it can be applied to color-stain engineering, which can both increase the moisture that staining solution gives to fibers and also enhance the dispersal of dye in a staining solution.

Acidic and alkaline resistance

In the dyeing process, dye bathing is usually either acidic or alkaline, and in the pretreatment of fabrics, bleach, and refinement, more alkaline chemicals are added. Thus, the acidic and alkaline resistance of surfactants is very important. As shown in Table V, three kinds of synthetic copolymers were added in 10, 20, 30, and 40% HCl or NaOH and then left at room temperature or heated in a constant temperature shaking heater to 90°C. The results show that these three copolymers were still maintained in one phase because the PVP in the copolymer is resistant to acid and alkali. Therefore, synthetic copolymers have excellent resistance to acids and alkalis.

Stain repelling tests

Carbon black was used as a contaminant in stain repelling tests on PET fabrics. In Table VI, blank fabric has the lowest result, and other fabrics were added with different copolymers made from NVP/AM at different molar ratios and concentrations. It is clear from the data that, without copolymer treatment, fabrics are seriously stained with carbon black. This is because both fabrics and carbon black are nonpolar, giving strong attraction. In the presence of copolymers, these copolymers give excellent stain-repelling effects, which increase as the NVP ratio of NVP/AM and copolymer concentration increases. The PVP of copolymers has excellent membrane-forming properties, which can form a thin membrane on fabrics,

TABLE VI
Influence of PVP/PAM Copolymers on Fabric's Discoloration^a and Carbon Black Staining

Copolymers ^b	Concentrations (%)	Dyes and carbon black			
		Sumikaron red S-BDF	Acidol brill yellow M-5GL	Everdirect fast black VSF 600	Carbon black
Blank	0.0	59.57	68.94	66.67	31.10
1 : 0.5	0.5	64.16	75.38	73.28	60.33
	0.2	61.43	75.19	72.66	50.93
1 : 1	0.5	64.45	75.22	72.56	65.18
	0.2	61.72	74.89	72.24	58.69
0.5 : 1	0.5	64.05	74.28	71.82	67.94
	0.2	62.21	71.28	70.57	63.57

^a The average whiteness of original fabrics is 75.72.

^b Shown in molar ratio of NVP/AM monomers.

indirectly stopping contamination from carbon black. PAM itself also gives the same effect.

As shown in Table VI, copolymer-treated fabrics have significantly better whiteness than nontreated fabrics. This indicates that copolymers can reduce the contamination of white fabrics during water-washing. The stain-repelling effect depends on copolymer concentration, with a superior effect at higher concentrations. When copolymers, stained, and white fabrics are combined in bathing and washing, PAM and PVP in the copolymers have a better affinity to fabric dyes and thus increase the fastness of fabrics.⁸ In addition, PVP has better abilities for stain removing, stain binding, and membrane formation. Therefore, the stain-repelling effect increases with the increase in NVP molar ratio of NVP/AM, but the difference is small, and so the concentration of copolymers is more important to stain repulsion.

CONCLUSIONS

Copolymers synthesized from NVP and AM, with different molar ratios, were tested and analyzed for their basic properties, with the following conclusions:

1. The decomposing rate of copolymers slows as AM content increases, but heat stability is improved.

2. Molecular weight of copolymers increases as NVP ratio goes up.
3. Copolymers have properties, such as lowering surface tension, excellent dispersing ability, good heat stability, and improved acid and alkaline resistance.
4. Synthetic copolymers give excellent stain-repelling effects, as shown in the test for carbon black staining, and the stain-repelling effect is improved as the AM content increases. Thus, higher concentrations of copolymers give a better stain repelling effect for both carbon black and fabric stains.

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