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Formation and characterization of P(AN-AM-AA)/PVA intermacromolecular complex through hydrogen bonding

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In this paper, the poly(acrylonitrile–acrylamide–acrylic acid) [P(AN–AM–AA)]/poly(vinyl alcohol) (PVA) intermacromolecular complex formed through hydrogen bonding is described. The experimental results show that P(AN–AM–AA), which was prepared by hydrolysis of polyacrylonitrile followed by acidifying, complexes with PVA through hydrogen bonding, as verified by pH value testing and *FT*i.r. thermal analysis demonstrates that the complex formed is superior in thermal stability, compared with its component polymers. Favourable conditions for complexation of P(AN–AM–AA) with PVA are: AA content in P(AN–AM–AA): 41–46%; a ratio of P(AN–AM–AA) to PVA in the range 1:20–1:10; and a solution pH value of 5.0–5.5. © 1997 Elsevier Science Ltd.

(Keywords: P(AN–AM–AA)/PVA; intermacromolecular complex; formation)

INTRODUCTION

In recent years, intermacromoloecular complexation of the chemically and structurally complementary synthetic polymers has attracted more and more attention[1-6] for the following reasons. First, since the phenomena occurring *in vivo* are closely related to the intermacromolecular complexation of biopolymers, study of the intermacromolecular complexation of the synthetic polymers of simpler structure is helpful for understanding the mechanism of similar processes in living cells. Second, and perhaps more importantly for material scientists, intermacromolecular complexation offers new and effective ways to develop polymer materials with high performances. It is common knowledge that the final properties of polymer materials not only depend on their first or second order structure, but also on their higher order structure. Intermacromolecular complexation occurring among macromolecules with complementary structures, mainly through secondary binding forces such as Coulombic forces, hydrogen bonding, Van der Waals forces, charge transfer interactions, etc., will confine the mobility of polymer chains, resulting in unique supermolecular structure, which will endow the materials with better properties than those of their constituents[2,7-11]. In principle or by definition, tailoring the supermolecular structure and properties mainly through intermolecular interactions, rather than through chemical bonding among atoms, is in the field of modern supermolecular chemistry, which developed rapidly recently.

Poly(vinyl alcohol) (PVA) is a widely used water-soluble polymer, from which vinylon fibres are made. It has excellent gas barrier properties and fairly good water absorption, but its elasticity (modulus), strength and dyeability are not good enough for high quality applications. Many methods[12-14] have been employed to modify PVA or PVA based fibres (vinylon), such as increasing molecular weight, organic solvent spinning, gel spinning, crosslinking, chemical modification, etc., however, it is still a challenge to obtain PVA based materials with high modulus, strength and good dyeability via a relatively simple and economic process.

In our laboratory, a new strategy, i.e. intermacromolecular complexation through hydrogen bonding, was employed to enhance the modulus, strength and dyeability of PVA. As mentioned above, intermacromolecular complexation is a physical way to control the supermolecular structure of polymers at the molecular level and may be treated as a molecular design at higher structure level, it is hoped to modify PVA via complexing it with some materials with adjustable complementary groups, and also with desired properties. Poly(acrylonitrile–acrylamide–acrylic acid) [P(AN–AM–AA)] is one of such materials in which the AM and AA groups are the complementary structures to the hydroxyl group of PVA. In our preceding paper[15], we reported the preparation and structural characterization of P(AN–AM–AA). Alkaline hydrolysis of polyacrylonitrile (PAN) fibres followed by acidifying gave P(AN–AM–AA) with an adjustable AA content. The structure of the copolymer and the optimum conditions for obtaining P(AN–AM–AA) with suitable complementary groups to PVA were determined. In this paper we describe a study of the intermacromolecular complexation of P(AN–AM–AA) with PVA, focusing on the formation and characterization of P(AN–AM–AA)/PVA intermacromolecular complex through hydrogen bonding.

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EXPERIMENTAL

Materials

PAN fibres: product of Zibo Synthetic Fiber Factory, China. Composition: acrylonitrile (AN) 90%, methyl acrylate (MA) 9%, acrylic acid (AA) 1%. PVA 1799: product of Sichuan Vinylon Factory, China. PVA was purified by the following procedure: it was dissolved in water at 100°C, precipitated with ethanol, washed by water, then dried at 60°C to constant weight. KOH (CP): Chongqing Chemical Agent Factory, China. HCl (AR): Chemical Agent Factory of Deyang Mineral Testing Center, China.

Sample preparation

P(AN–AM–AA) was prepared by alkaline hydrolysis of PAN fibres followed by acidifying[15,16]. The AA content of P(AN–AM–AA) could be controlled by varying the reaction time, temperature and amount of alkali. When the PAN fibres were hydrolysed at temperatures of 90–95°C in 10% alkaline solution for a certain time the AA content in the P(AN–AM–AA) obtained reached 36.8–56.8%, determined through potentiometric titration.

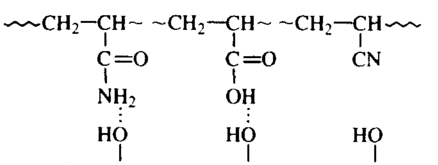
P(AN–AM–AA) and PVA were separately dissolved in water, then mixed together in a certain ratio with stirring. The solution was left for 24 h and then decanted. The remaining solvent was volatilized and the precipitate was dried *in vacuo* at 60°C.

Characterization

The formation of P(AN–AM–AA)/PVA intermacromolecular complex through hydrogen bonding was identified by means of pH value testing (pHS-3D pH tester) and *FT* i.r. (Nicolet 208 XB i.r. spectrometer). The crystallizing behaviour and thermal stability of P(AN–AM–AA), PVA and P(AN–AM–AA)/PVA complexes were studied by d.s.c. and t.g. (TA 2000 system, Dupont) at a rate of increasing temperature of 10°C min^{-1} in a N_2 atmosphere.

RESULTS AND DISCUSSION

Hydrogen bonding could be formed among the hydrogens of the acrylamide group and carboxylic acid group in P(AN–AM–AA) with oxygen of the hydroxyl group in PVA. When the contents of the acrylamide and carboxylic acid groups are high enough, a P(AN–AM–AA)/PVA intermacromolecular complex could be formed through hydrogen bonding, as described as follows[2,17,18].



$$\begin{array}{ccc} \sim\!\sim CH_2-CH\sim & \sim CH_2-CH\sim & \sim CH_2-CH\sim\!\sim \\ | & | & | \\ C=O & C=O & CN \\ | & | & \\ NH_2 & OH & \\ \vdots & \vdots & \\ HO & HO & HO \\ | & | & | \\ \sim\!\sim CH_2-CH\sim & \sim CH_2-CH\sim & \sim CH_2-CH\sim\!\sim \end{array}$$

The formation of a P(AN–AM–AA)/PVA complex upon mixing of P(AN–AM–AA) solution with PVA solution resulted in a change in the pH of the solution. *Figure 1* compares the pH changes induced by mixing PVA solution with P(AN–AM–AA) solution (1/1, v/v) or by mixing distilled water with P(AN–AM–AA) solution (1/1, v/v) at various initial pH values. The initial pH of the solution was adjusted by adding drops of aqueous 0.1 N HCl. It can be seen that at various initial pH values, the pH rise induced by adding PVA solution (line 1) is higher than that induced by adding water (line 2). This fact demonstrates that the more remarkable pH rise upon mixing of PVA solution with P(AN–AM–AA) solution is surely owing to the intermacromolecular complexation of P(AN–AM–AA) with PVA, which makes it more difficult for the hydrogen of the carboxylic acid group on the P(AN–AM–AA) molecular chain to be dissociated, and results in increase of the pH of the solution. Therefore, the pH rise as well as the extent of rise may be used to judge the formation of the P(AN–AM–AA)/PVA intermacromolecular complex, and measurement of the pH change is a convenient and effective

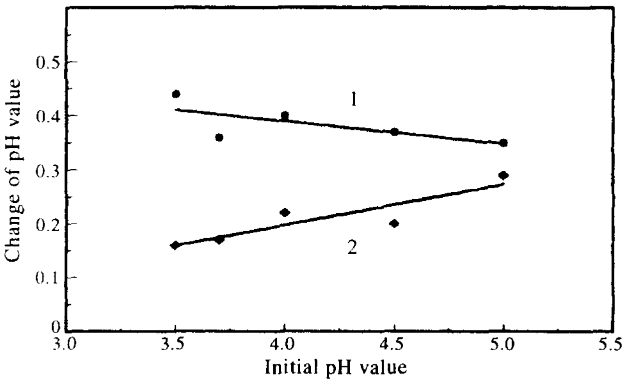


Figure 1 pH rise induced by the complexation of P(AN–AM–AA) with PVA: (1) adding PVA solution; (2) adding distilled water

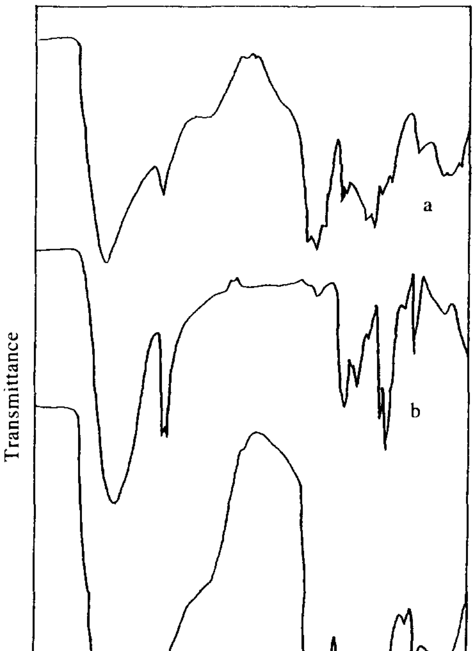


Figure 2 I.r. spectra of (a) P(AN–AM–AA), (b) PVA, and (c) P(AN–AM–AA)/PVA complex

way to investigate the complexation of P(AN–AM–AA) with PVA.

The formation of intermacromolecular complexes of P(AN–AM–AA)/PVA through hydrogen bonding could also be characterized by *FT*i.r. *Figure 2* shows the *FT*i.r. spectra of PVA, P(AN–AM–AA) and P(AN–AM–AA)/PVA complex, and *Table 1* compares some characteristic i.r. bands of PVA, P(AN–AM–AA) and P(AN–AM–AA)/PVA complex. The band broadening and wavenumbers decrease of ν_{OH} and ν_{NH} in the P(AN–AM–AA)/PVA complex demonstrates the existence of a large amount of intermolecular hydrogen bonding[19], and the weakening of the 2700–2500 cm^{-1} band shows that the self-association ν_{OH} is reduced due to the formation of intermolecular hydrogen bonding between P(AN–AM–AA) and PVA. Compared with PVA and P(AN–AM–AA), the wavenumbers of ν bands in the P(AN–AM–AA)/PVA complex decrease, and those of δ bands increase, further confirming the formation of intermolecular hydrogen bonding[19].

Thermal analysis further confirms the formation of the P(AN–AM–AA)/PVA complex. *Figures 3* and *4* show t.g. curves and d.s.c. traces for PVA, P(AN–AM–AA) and the P(AN–AM–AA)/PVA complex, respectively. It is obvious that the t.g. curve and d.s.c. trace for the P(AN–AM–AA)/PVA complex are quite different from those of its constituents, not being their simple superposition. From this experimental result the conclusion can be drawn that a new material can be created mainly through intermolecular forces. *Table 2* lists the T_1 (temperature at the beginning of weight loss), T_{50} (temperature at 50% weight loss) and T_{max} (temperature at the maximum weight loss rate) of PVA, P(AN–AM–AA) and P(AN–AM–AA)/PVA complex. It can be seen that the T_1, T_{50} and T_{max} of the P(AN–AM–AA)/PVA complex are 275, 415 and 450°C, respectively, much higher than those of its constituents, i.e. the P(AN–AM–AA)/PVA complex is superior to both PVA and P(AN–AM–AA) in thermal stability. The thermal behaviour of the above three materials could be further studied by comparing their t.g. curves (*Figure 3*) with d.s.c. traces (*Figure 4*). For PVA, a sharp peak appears at 230.38°C in the d.s.c. trace (*Figure 4a*). According to the literature[20], the melting point of PVA is around 232°C, so this sharp peak should be due to the crystal melting of PVA. However, at this temperature, PVA already commences thermal decomposition, its T_1 is 225°C, as revealed by t.g.a. (*Figure 3a* and *Table 1*). For P(AN–AM–AA), a broad peak concentrated at 220.84°C in the d.s.c. trace (*Figure 4b*) is due to its thermal decomposition, for its T_1 starts at 110°C as demonstrated in its t.g.

Table 1 Characteristic i.r. bands of PVA, P(AN–AM–AA) and P(AN–AM–AA)/PVA complex

Assignment	Polymer	I.r. bands (cm^{-1})
ν_{OH} or ν_{NH}	PVA	3340
	P(AN–AM–AA)	3428
	P(AN–AM–AA)/PVA	3447–3171 (b)
ν_{OH}	P(AN–AM–AA)	2500–2700 (sb)
	P(AN–AM–AA)/PVA	2470–2660 (w)
$\nu_{C=O}$	P(AN–AM–AA)	1714
	P(AN–AM–AA)/PVA	1706
$\nu_{C=O}$	P(AN–AM–AA)	1453
	P(AN–AM–AA)/PVA	1449
ν_{C-O-H}	PVA	1094
	P(AN–AM–AA)/PVA	1090
δ_{C-N}	P(AN–AM–AA)	1409
	P(AN–AM–AA)/PVA	1413
δ_{C-O-H}	PVA	1236
	P(AN–AM–AA)/PVA	1239

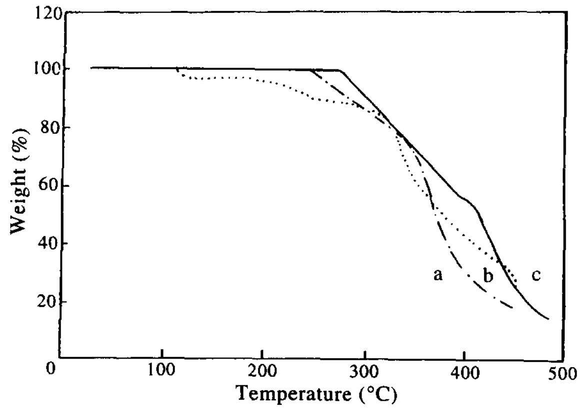


Figure 3 T.g. curves for (a) PVA, (b) P(AN–AM–AA) and (c) P(AN–AM–AA)/PVA complex

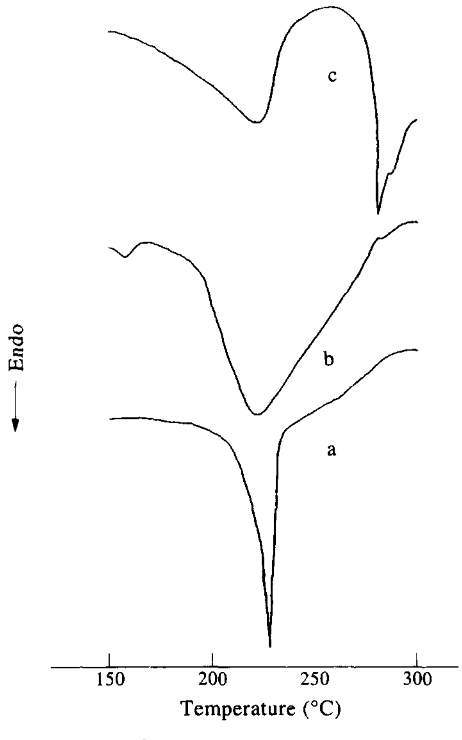


Figure 4 D.s.c. curves for (a) PVA, (b) P(AN–AM–AA) and (c) P(AN–AM–AA)/PVA complex

Table 2 Thermal stability of PVA, P(AN–AM–AA) and P(AN–AM–AA)/PVA complex

Sample	T_1[a] (°C)	T_{50}[b] (°C)	T_{max}[c] (°C)
PVA	225	370	370
P(AN–AM–AA)	110	380	345
P(AN–AM–AA)/PVA complex	275	415	450

[a] Temperature at the beginning of weight loss
[b] Temperature at 50% weight loss
[c] Temperature at the maximum weight loss rate

curve (*Figure 3b*). For the P(AN–AM–AA)/PVA complex, a peak appearing at 221.05°C in the d.s.c. trace (*Figure 4c*) should be the crystal melting peak of PVA, for at this temperature no thermal decomposition of material takes place; its T_l starts at 275°C, as shown in its t.g. curve (*Figure 3c*). It is interesting to notice that the crystal melting peak of PVA in the P(AN–AM–AA)/PVA complex is much broader than that of pure PVA, and the peak position of the complex drifts down almost 9°C, demonstrating that the intermacromolecular complexation has great influence on the crystalline behaviour of PVA, making its crystallinity less perfect, and broadening its crystal melting process. The peak concentrated at 281.25°C in the d.s.c. trace for the P(AN–AM–AA)/PVA complex is a thermal decomposition peak as confirmed by its t.g. curve (*Figure 3c*), 60°C higher than that of P(AN–AM–AA), demonstrating that the intermacromolecular complexation of P(AN–AM–AA) with PVA greatly improves the thermal stability of materials.

As mentioned above, measuring the pH change resulting from intermacromolecular complexation is a convenient way to characterize the formation of complex. The affecting factors on the complexation of PVA with P(AN–AM–AA) was mainly investigated by this method.

The carboxylic acid group and acrylamide groups in the P(AN–AM–AA) molecular chain are complementary and are also effective groups interacting with the hydroxyl group of PVA to form intermolecular hydrogen bonds. In particular, the hydrogen of the carboxylic acid group has a strong tendency to form hydrogen bonds[2]; therefore, its content has a more pronounced effect on complexation. *Figure 5* shows the influence of acid content of P(AN–AM–AA) on its complexation with PVA at different initial pH values of the solution. The higher the induced pH rise, the better the complexation of P(AN–AM–AA) with PVA. It can be seen that in our experimental range, the better complexation could be obtained when the acid content of P(AN–AM–AA) is 41.2–45.8%. *Figure 6* shows the influence of the ratio of P(AN–AM–AA) to PVA on their complexation at different initial pH values of the solution. The suitable ratio of P(AN–AM–AA) to PVA should be 1/20–1/10.

For intermacromolecular complexation through hydrogen bonding, the pH value of the solution plays a very important role. There exists a critical pH value[2], above which the hydrogen of the carboxylic acid group tends to dissociate which is unfavourable to the intermacromolecular complexation through hydrogen bonding. For intermacromolecular complexation of P(AN–AM–AA) with PVA through hydrogen bonding, the critical pH is 5.5. As shown in *Figure 7*, the optimum pH for complexation is 5.0–5.5.

Based on the above experimental results, the favourable conditions for the formation of the P(AN–AM–AA)/PVA complex through hydrogen bonding have been obtained as follows: acid content in P(AN–AM–AA): 41–46%; ratio of P(AN–AM–AA) to PVA: 1/20–1/10; pH value of the solution: 5.0–5.5.

CONCLUSION

P(AN–AM–AA), which has a complementary structure to PVA, could be prepared by alkaline hydrolysis of PAN fibres followed by acidifying. The formation of a P(AN–AM–AA)/PVA intermacromolecular complex through hydrogen bonding results in an increased pH of the solution and a broadening or positional drift of some characteristic bands of the *FT* i.r. spectra of the materials. The P(AN–AM–AA)/PVA complex is much superior to its constituents in thermal stability, and the intermacromolecular complexation of P(AN–AM–AA) with PVA confines the crystallization of PVA, broadening its crystalline process and lowering its melting

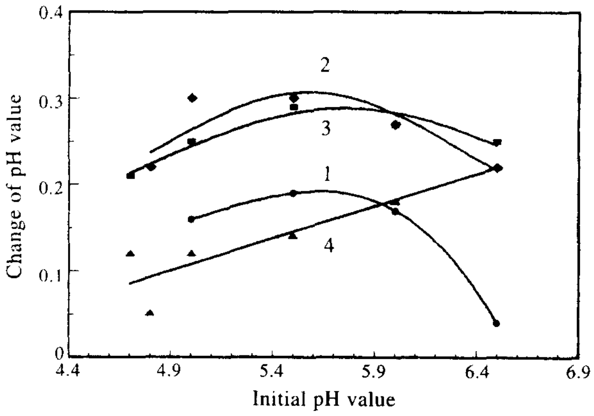


Figure 5 Influence of acid content of P(AN–AM–AA) on the complexation of P(AN–AM–AA) with PVA at different initial pH values of the solution. Acid content: (1) 36.8%; (2) 41.2%; (3) 45.8%; (4) 56.8%

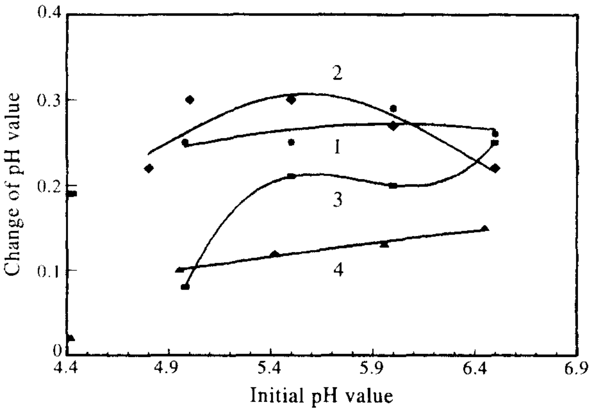


Figure 6 Influence of P(AN–AM–AA)/PVA ratio on the complexation of P(AN–AM–AA) with PVA at different initial pH values of the solution. P(AN–AM–AA)/PVA ratios: (1) 1/20; (2) 1/10; (3) 1/4; (4) 1/1

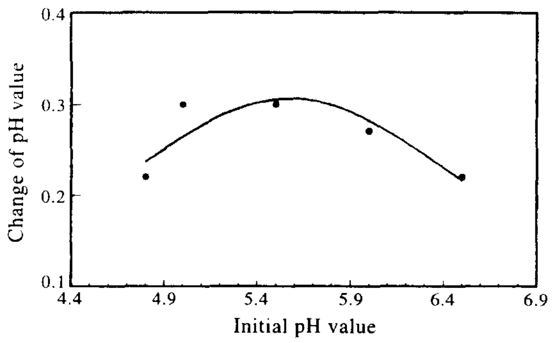


Figure 7 Influence of the initial pH of the solution on the complexation of P(AN–AM–AA) with PVA

point. Favourable conditions for formation of the P(AN–AM–AA)/PVA complex are: AA content of P(AN–AM–AA): 41–46%; ratio of P(AN–AM–AA) to PVA: 1/20–1/10; pH value of the solution: 5.0–5.5.

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