

Supramolecular Structure and Mechanical Properties of P(AN-AM-AA)/PVA Intermacromolecular Complex Formed Through Hydrogen Bonding

QI WANG, LINGYUN HE, JINGUI HUANG

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan Union University, Chengdu 610065, China

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ABSTRACT: In this article the supramolecular structure and mechanical properties of poly(acrylonitrile-acrylamide-acrylic acid)/poly(vinyl alcohol) [P(AN-AM-AA)/PVA] intermacromolecular complex formed through hydrogen bonding were studied by means of SEM, TEM, and mechanical property testing. The experimental results show that fibrous or network structure could be formed in P(AN-AM-AA)/PVA intermacromolecular complex, and this unique supramolecular structure endows the material with much superior mechanical properties to its constituents. The tensile strength of P(AN-AM-AA)/PVA complex is as high as 3 times that of PVA, and the Young's modulus of the complex is almost 6 times that of PVA. All the encouraging results demonstrate that intermacromolecular complexation among the polymers having complementary structures is an innovative strategy to reinforce polymer materials and, therefore, to prepare a new kind of microcomposites. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2089–2096, 1997

Key words: supramolecular structure; intermacromolecular complex; hydrogen bonding; mechanical property; microcomposite

INTRODUCTION

Fiber reinforced polymer composites have the comprehensive performances of their constituents.¹ The reinforcing fibers offer the high strength and modulus, and the polymer matrix provides the good physicochemical property, processability, and could transfer the stress. By means of compositing, light materials with compact structure, high strength, and good performances could be obtained. The challenging problems usually encountered in preparing fiber reinforced polymer composites with higher performances are the fiber-matrix adhesion, the dispersion of the fibers in the matrix, and the wet-

ting of the fibers by the resin. For many years great efforts have been made to solve these problems, for example: developing intensive mixing equipment to modify the dispersion of fibers in polymer matrix; selecting more polar polymers as the matrix to modify the wetting of fibers by the resins²; treating fibers with coupling agent³; or conducting polymerization of monomers on the fiber surfaces to establish chemical bonding across the interface, therefore enhancing the interfacial interactions between fibers and polymer matrix,⁴ etc. In recent years a new tendency in the polymer based composites research field is to develop microcomposites, especially focusing on "in situ composites" and "molecular composites."^{5–10} *In situ* composites are prepared through melt mixing of thermal liquid crystalline polymers with thermoplastics. The orientation structure of thermal liquid crystalline polymer during

Correspondence to: Q. Wang.

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Table I Characteristic IR Bands of PVA, P(AN-AM-AA), and P(AN-AM-AA)/PVA Complex

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

processing may act as the reinforcing agent. Because the order structures are formed *in situ* of the compositing procedure, these microcomposites are referred to as *in situ* composites. Molecular composites are prepared through solution mixing of liquid crystalline polymer with flexible polymer. The dispersion degree is almost in the molecular level. The rigid molecular chains of liquid crystalline polymers act as the reinforcing agent to produce the molecular composites with high modulus and high strength. In both *in situ* composites and molecular composites the reinforcing agents are the rigid chain fibrils of liquid crystalline polymers, which have much higher specific surface area and aspect ratio than that of the common fibers. These are able to solve the problems of fiber-matrix adhesion, dispersion of fibers in the matrix, and wetting of fibers by resins. The main obstacles for commercialization of such microcomposites are the difficulties in processing of the thermal liquid crystalline polymers, usually with quite high melting points; in matching the viscosity of thermal crystalline polymers with that of the common thermoplastics; or in finding the common solvent for the liquid crystalline polymers and flexible polymers; as well as the high cost of liquid crystalline polymers. It is still a big challenge to prepare microcomposites with high performance and low cost from the common polymers.

In our laboratory, an innovative strategy (i.e., intermacromolecular complexation) was employed to develop a new kind of microcomposite. Inter-

macromolecular complexation occurring among the macromolecules having complementary structures through the secondary binding forces such as Coulomb forces, hydrogen bonding, van der Waals forces, charge transfer interactions etc.,¹¹ will confine the mobility of polymer chains. The combined complementary macromolecular chains may be twisted to form quite different supermolecular structure: a certain degree of orientation, twin molecular chain microfibrils, or network structures. These unique supermolecular structures may act as reinforcing agents and endow the materials with better properties than that of its constituents. Because these fibrous or network structures are formed *in situ* of blending and mixing and also reach the molecular level dispersion, the materials prepared in this way could be referred to as a new kind of *in situ* or molecular composites. The first system that we studied is poly(acrylonitrile-acryamide-acrylic acid)[P(AN-AM-AA)]/poly(vinyl alcohol) (PVA) intermacromolecular complex formed through hydrogen bonding. PVA is a widely used water-soluble polymer, from which vinylon fibers are made. It has excellent gas blocking ability and fairly good hygroscopicity, but its elasticity (modulus), strength, and dyeability are not good enough for high quality applications. Along the molecular chain of PVA there are many OH groups, the oxygens of which have a strong tendency to form hydrogen bonding with the hydrogen of carboxylic acid or amide groups. If we could prepare a copolymer that has adjustable complementary structure with PVA, hopefully we could modify PVA via complexing them through hydrogen bonding. For this purpose, we prepared a copolymer, P(AN-AM-AA), of which the AA group and AM group are the complementary structure to PVA. In our preceding articles^{12,13} we reported the preparation of P(AN-AM-AA) by means of alkaline hydrolysis of polyacrylonitrile (PAN) fibers followed by acidification, the formation, and characterization of P(AN-AM-AA)/PVA intermacromolecular complexation through hydrogen bonding. In this article we further study the supermolecular structure and the mechanical properties of P(AN-AM-AA)/PVA intermacromolecular complex formed through hydrogen bonding.

EXPERIMENTAL

Materials

PAN fibers were a product of Zibo Synthetic Fiber Factory (China). The composition was 90% AN,

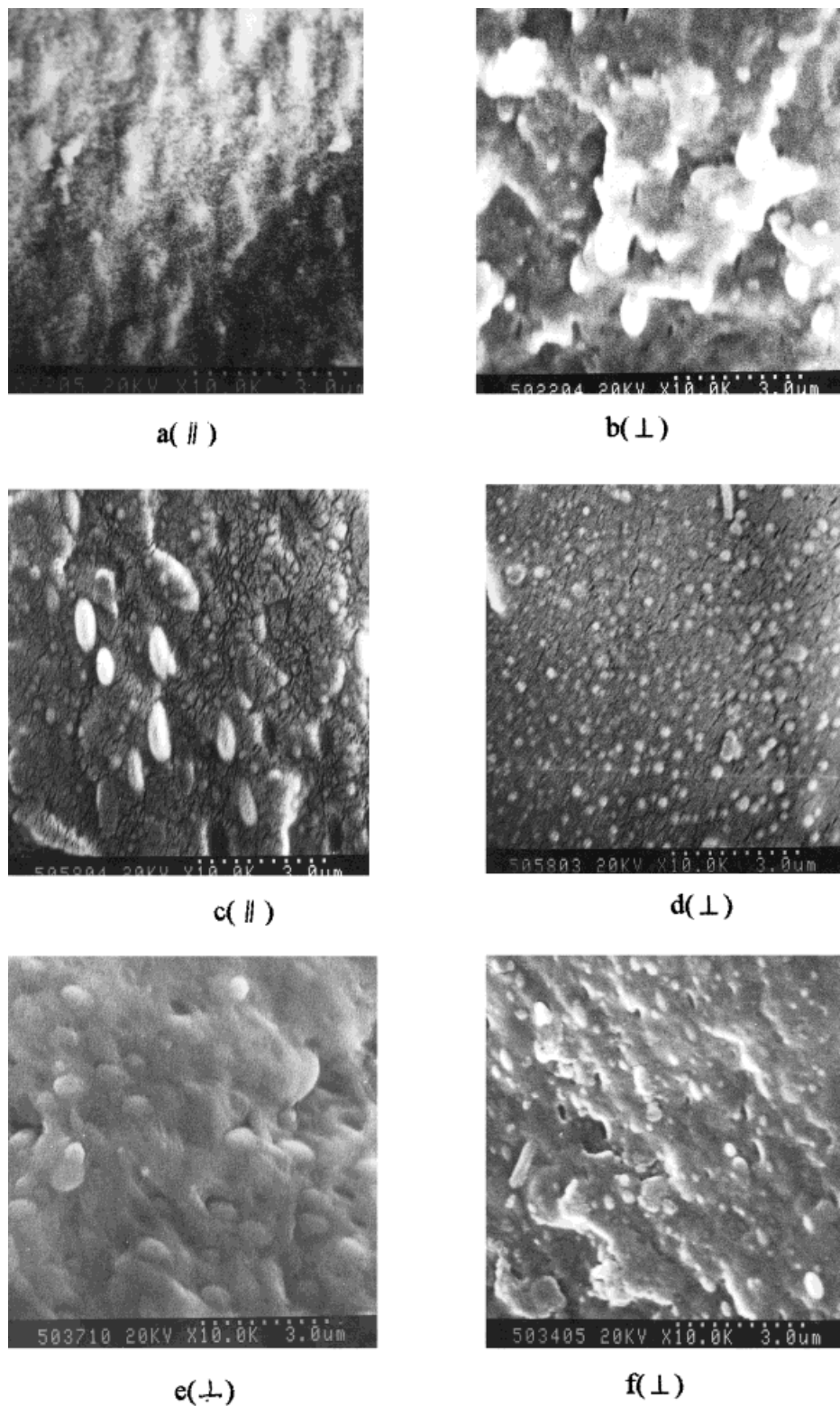


Figure 1 SEM micrographs of P(AN-AM-AA)/PVA complex with elongation of 5%: (a-d) brittle broken; (e-f) stretching broken.

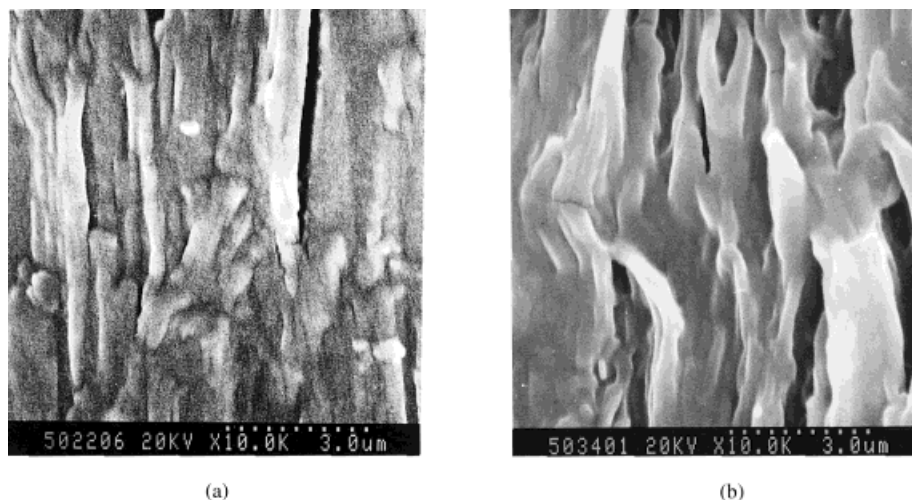


Figure 2 SEM micrographs of P(AN-AM-AA)/PVA complex with elongation of 700%: (a) brittle broken; (b) stretching broken.

9% methyl acrylate (MA), and 1% AA. PVA-1799 was a product of Sichuan Vinylon Factory (China). The degree of polymerization was 1700, degree of hydrolysis 99%, and it was soluble in hot water. PVA was purified by the following procedure: dissolved in water at 100°C, precipitated with ethanol, washed with water, then dried at 60°C to constant weight. KOH, CP, was from Chongqing Chemical Agent Factory (China) and HCl, AR, was from the Chemical Agent Factory of Deyang Miner Testing Center.

Sample Preparation

P(AN-AM-AA) was prepared by alkaline hydrolysis of PAN fibers followed by acidifying.^{7,14} The AA content in P(AN-AM-AA) was 36.8–56.8%, which was determined through a potentiometer.

P(AN-AM-AA) and PVA were 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 dried in a vacuum at 60°C.

Characterization

Tensile Properties

The tensile properties were tested by using an Instron 4302 Material Tester at a crosshead speed of 50 mm/min. Testing temperatures were 13, 40, 60, 85, and 120°C. All specimens were dried at 60°C for 4 h, then kept in an open environment

at room temperature for 24 h before testing. When the test temperature was higher than room temperature, the specimens were kept at that temperature for 30 min before testing.

SEM Observation

SEM was carried out with a Hitachi X-650 scanning electron microscope with an accelerating voltage of 100 kV. The stretched samples with elongation of 5 or 700% were put in liquid nitrogen and broken along or vertical to the drawing direction of the samples. The fracture surfaces of the broken samples and the stretched samples were vacuum coated with gold before observation.

TEM Observation

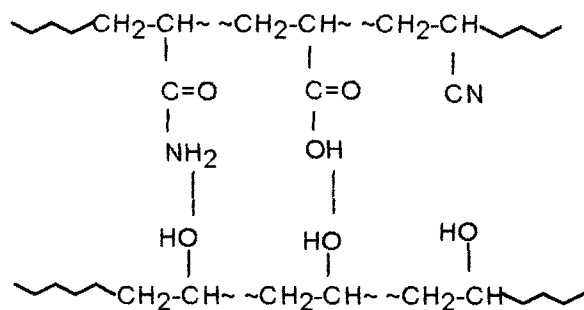
TEM was carried out with a JEM-100CX transmission electron microscope with an accelerating voltage of 80 kV. The samples with elongations of 5, 300, and 700% were quenched in liquid nitrogen, then cut into thin sections by an LKB microtome and stained by OsO₄ vapor to enhance contrast before observation.

RESULTS AND DISCUSSION

Supermolecular Structure of P(AN-AM-AA)/PVA Complex

The intermacromolecular complexes through hydrogen bonding are formed among the macromo-

lecular chains consisting of proton-donating or proton-accepting structures.¹¹ P(AN-AM-AA) has the complementary structure (i.e., AA group and AM group) to PVA. P(AN-AM-AA) could be prepared by means of alkaline hydrolysis of waste PAN fibers followed by acidifying.¹² The AM and AA content in P(AN-AM-AA) could be controlled by varying reaction conditions such as temperature, time, and alkaline amount added. It is well known that hydrogen bonding could occur between the hydrogen of the AM group and the AA group and the oxygen of the hydroxyl group. The proton of AA group has an especially strong tendency to form hydrogen bonds with the oxygen of the hydroxyl group. When the AA content in P(AN-AM-AA) reaches a certain value, a P(AN-AM-AA)/PVA intermacromolecular complex could be formed through hydrogen bonding, as shown in the following structure:



The formation of P(AN-AM-AA)/PVA complex results in a rising pH value of the solution, and a broadening or position drift of some characteristic bands of FTIR spectra of the materials.¹³ Table I compares some characteristic IR bands of PVA, P(AN-AM-AA), and P(AN-AM-AA)/PVA complex. The band broadening and decreasing wave numbers of ν_{OH} and ν_{NH} in P(AN-AM-AA)/PVA complex demonstrates the existence of a large amount of intermolecular hydrogen bonding.¹⁵ The weakening of the 2700–2500 cm^{-1} band shows that the self-association ν_{OH} band 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 wave numbers of ν bands in P(AN-AM-AA)/PVA complex decrease, and those of the δ bands increase, further confirming the formation of intermolecular hydrogen bonding.¹⁵ Furthermore, the P(AN-AM-AA)/PVA complex is much superior to its constituents in thermal stability, as confirmed by means of thermal analysis (TG, DSC).¹³

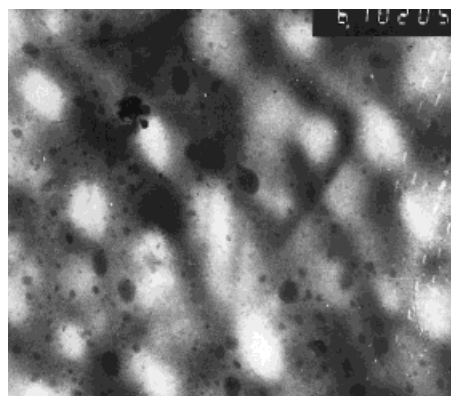
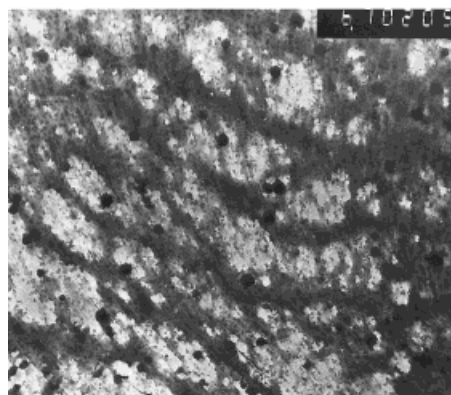
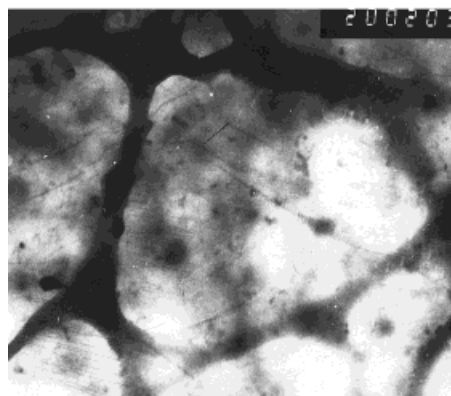
a. ($\times 6700$)b. ($\times 6700$)c. ($\times 20000$)

Figure 3 TEM micrographs of P(AN-AM-AA)/PVA complex with different elongations: (a) 5%; (b) 300%; (c) 700%.

As mentioned before, the complexation of macromolecules with complementary structures through the secondary binding forces could confine the mobility of the molecular chain, resulting in quite different supermolecular structure to

that of its constituents. For example, Tsuchida¹¹ pointed out that fibril and network structure could be formed in polyelectrolyte complex through Coulomb forces via pairing of the oppositely charged chains. Wang and Xu¹⁶ reported that the complexation of poly(methyl methacrylate-methacrylic acid) [P(MMA-MAA)] with poly(ethylene oxide) (PEO) suppresses the crystallization of PEO, forming certain ordered fibrous or network structures. A similar phenomenon is expected to take place in the system of P(AN-AM-AA)/PVA. As shown in the above structure, the combining of the complementary structure of the macromolecular chains, or the complexation of P(AN-AM-AA) with PVA through the strong secondary binding force (i.e., hydrogen bonding), may confine the mobility of polymer chains, resulting in paired segments or paired chains, which could be twisted together to form twin-chain microfibrils or further to form network structures. This unique supermolecular structure of P(AN-AM-AA)/PVA complex was examined through electron microscope observation. Figure 1 is the SEM photos of P(AN-AM-AA)/PVA complex with low drawing ratio ($\sim 5\%$). Figure 1(a-d) shows the morphology of the surface of the brittle broken sample, and Figure 1(e, f) shows the surface of the stretching broken sample. The sign \perp denotes a surface broken vertically to the drawing direction, and the sign \parallel denotes a surface broken parallel to the drawing direction. It can be clearly seen that in P(AN-AM-AA)/PVA complex many rodlike or microfibrils are formed, which may orient along the stretching direction of the sample and distribute evenly in the matrix. No obvious holes were observed between the rodlike or fibrous structures and the matrix, demonstrating a good interfacial adhesion and interfacial wetting. The advantages of the complex fibrils such as small diameter, even dispersion, good interfacial adhesion and wetting, etc., make the complex fibrils good reinforcing agents for the matrix. Figure 2 shows that when the drawing ratio is increased to 700%, the orientation of the

complex fibrils along the drawing direction becomes more obvious and the aspect ratio of the fibrils greatly increases.

The fibrous or network structure of P(AN-AM-AA)/PVA complex could be further confirmed through TEM observation (Fig. 3). It should be noted that with an increase in drawing ratio (from 5 to 300%, and to 700%) the orientation of the fibrils and the network structure become more and more obvious.

Mechanical Properties of P(AN-AM-AA)/PVA Complex

The unique supermolecular structure (i.e., fibrous or network structure) formed in P(AN-AM-AA)/PVA complex could endow the material with much superior mechanical properties to its constituents. Table II compares the mechanical properties of P(AN-AM-AA), PVA, and P(AN-AM-AA)/PVA complex. P(AN-AM-AA) is brittle and cannot be stretched at all. The Young's modulus of PVA is 0.442 GPa, and its tensile strength is 31.4 MPa. But for P(AN-AM-AA)/PVA complex, the Young's modulus reaches 2.637 GPa, as high as 6 times that of PVA. Its tensile strength increases to 89.79 MPa, almost 3 times that of PVA. These encouraging experimental results demonstrate that it is possible to enhance the mechanical properties of materials by means of the unique supermolecular structure formed in intermacromolecular complex, and therefore, to prepare a new kind of microcomposite. Similar to the materials reinforced by common fibers or liquid crystalline polymer fibrils, the elongation at break of the material reinforced by intermacromolecular complex through hydrogen bonding also decreases.

The factors affecting the mechanical properties of P(AN-AM-AA)/PVA complex were also investigated.

Table III shows the effect of acid content of P(AN-AM-AA) on the properties of P(AN-AM-AA)/PVA intermacromolecular complex. It could

Table II Mechanical Properties of P(AN-AM-AA), PVA, and P(AN-AM-AA)/PVA Complex

Samples	Tensile Strength (MPa)	Young's Modulus (GPa)	Break Elongation (%)
PVA	31.4	0.442	126.10
P(AN-AM-AA)	Brittle		
P(AN-AM-AA)/PVA complex	89.79	2.637	5.14

Table III Effect of Acid Content of P(AN-AM-AA) on Mechanical Properties of P(AN-AM-AA)/PVA Complex

AA Content (%)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
36.8	49.85	3.858	0.6
41.2	56.99	3.034	3.05
45.8	89.79	2.637	5.14
56.8	40.16	2.137	12.62

be seen that when the AA content is 41.2–45.8%, the material has higher tensile strength, because this composition favors the formation of P(AN-AM-AA)/PVA intermacromolecular complex.¹³ On the other hand, the Young's modulus of the complex decreases with the increase of AA content, probably due to the fact that the water absorbency of the material increases with the increase of AA content and the water absorbed may act as a plasticizer for the material, resulting in the decrease of modulus as well as the increase of elongation at break of the material. This is a phenomenon that could be observed in many plasticized polymer materials.

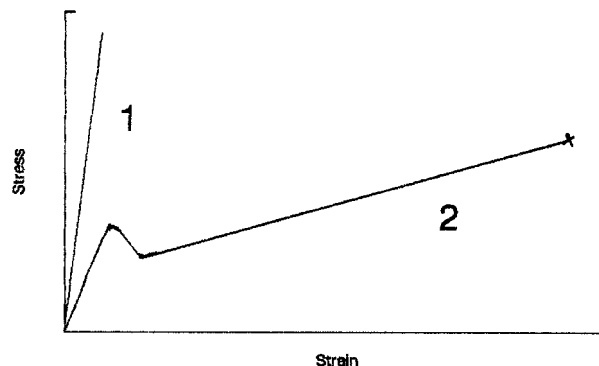
Table IV shows the effect of the ratio of P(AN-AM-AA) to PVA on the mechanical properties of P(AN-AM-AA)/PVA complex. Obviously, when the ratio of P(AN-AM-AA) to PVA is 1 : 10, the material has better mechanical properties; when the ratio of P(AN-AM-AA) to PVA is higher than 1 : 4, the material exhibits brittle behavior and cannot be stretched at all.

Table IV Effect of Ratio of P(AN-AM-AA) to PVA on Tensile Properties of P(AN-AM-AA)/PVA Complex

Ratio of P(AN-AM-AA) to PVA	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
1 : 20 ^a	52.00	2.452	25.07
1 : 10	56.90	3.034	3.05
1 : 4		Brittle	
1 : 1		Brittle	
1 : 20 ^b	55.44	2.589	40.77
1 : 10	89.79	2.637	5.14
1 : 4		Brittle	
1 : 1		Brittle	

^a AA content of P(AN-AM-AA) was 41.2%.

^b AA content of P(AN-AM-AA) was 45.8%.

**Figure 4** Effect of temperature on the shape of stress-strain curves of P(AN-AM-AA)/PVA complex: (1) 13°C; >40°C.

Hydrogen bonding energy is about 10–40 kJ/mol, much smaller than that of chemical bonding. Hydrogen bonding is sensitive to temperature. Therefore, temperature has a great effect on the mechanical properties of intermacromolecular complex formed through hydrogen bonding. Figure 4 compares the stress-strain curves of P(AN-AM-AA)/PVA complex at different temperatures. The figure shows that temperature has a great influence on the shape of stress-strain curve. At room temperature, the curve shows the characteristics of a rigid material (i.e., small strain and high modulus) and at higher temperature the curve shows the characteristics of a tough material (i.e., large elongation and low modulus). This is because with an increase of temperature, the hydrogen bonding of P(AN-AM-AA)/PVA complex is weakened and the matrix is softened. In addition, a yield point appears on the stress-strain curve because the orientation structure of the complex during stretching aids in keeping better mechanical properties at higher temperature.

Table V further demonstrates the effect of temperature on the mechanical properties of P(AN-AM-AA)/PVA complex. With an increase of temperature, the modulus and tensile strength of the complex decrease remarkably, mainly due to the weakening of the intermolecular hydrogen bonding at high temperature, while the elongation of the complex increases. The glass transition temperature of PVA is around 85°C; when the temperature is higher than that temperature, the elongation at break of the complex increases greatly.

CONCLUSION

The unique supermolecular structure (i.e., the fibrous or network structure) of P(AN-AM-AA)/

Table V Effect of Temperature on Mechanical Properties of P(AN-AM-AA)/PVA Complex

	13°C	40°C	60°C	85°C	120°C
Young's modulus (GPa)	2.637	0.448	0.278	0.130	0.145
Tensile strength (MPa)	89.79	32.63	22.61	19.81	10.52
Elongation at break (%)	5.14	149.02	232.32	676.06	630.44

PVA intermacromolecular complex may act as an effective reinforcing agent for the matrix, resulting in great enhancement of modulus and tensile strength. The AA content of P(AN-AM-AA), the ratio of P(AN-AM-AA) to PVA, and temperature affect the strength of intermolecular hydrogen bonding and, therefore, have great influence on the mechanical properties of the complex. Intermacromolecular complexation through the secondary binding forces, in our case the intermolecular hydrogen bonding, is a convenient and effective way to prepare an innovative microcomposite.

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REFERENCES

1. A. A. Berlin, S. A. Volfson, N. S. Enikopian, and S. S. Negmatov, *Principles of Polymer Composites*, Springer-Verlag, Berlin, 1986.
2. A. A. Tager and S. Jushkova, in *Theses of Natural Science Technology Conference of Filled Polymer Materials*, NHTEKHIM, Moscow, 1982, p. 20.
3. E. P. Plueddmann, *Silane Coupling Agents*, Plenum, London, 1982.
4. Q. Wang, S. Kaliaguine, and A. Ait-Kadi, *J. Appl. Polym. Sci.*, **44**, 1107 (1992).
5. X. Xu, Ed., *Polymer Materials Science*, Science Press, Beijing, 1994, p. 63.
6. J. He and W. Pu, *J. Composites*, **9**(4), 53 (1994).
7. B. Zhang and S. Wang, *Acta Polym. Sinica*, **2**, 211 (1994).
8. D. Dutta, H. Fruitwala, A. Kohli, and R. A. Weiss, *Polym. Eng. Sci.*, **30**, 1005 (1990).
9. D. J. Craziano and M. R. Mackley, *Mol. Cryst. Liq. Cryst.*, **106**, 73 (1984).
10. N. O. Field and S. S. Song, *J. Polym. Sci., Part A-2*, **22**, 102 (1984).
11. E. Tsuchida and K. Abe, *Adv. Polym. Sci.*, **45** (1982).
12. Q. Wang, L. He, and Y. Zhang, *J. Functional Polym.*, **9**, 78 (1996).
13. L. He and Q. Wang, in *Abstracts of the 36th IUPAC International Symposium on Macromolecules*, August 4-9, 1996, Seoul, Korea, p. 338.
14. M. Kopic, *J. Macromol. Sci. Chem.*, **A24**, 17 (1987).
15. D. Shen, *Application of IR Spectrometry in Polymer Research* [in Chinese], Science Press, Beijing, 1982.
16. Q. Wang and X. Xu, *Science in China (Eng.)*, Series B, **34**(12), 1409 (1991).