Preparation and Structural Characterization of Nanocrystalline Poly(vinyl chloride)

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ABSTRACT: This article describes the development of novel nanocrystalline poly(vinyl chloride) (PVC) for potential applications in PVC processes and reports improvements in the mechanical properties and thermal resistance. Before the preparation of nanocrystalline PVC via jet milling, PVC was spray-treated and heat-treated to improve its crystallinity. The pulverization and degradation, morphology, crystalline structure, and melting-point changes of postmodified PVC during jet milling and the relationship between the distributions of the particle size and processing temperature were investigated. X-ray analysis and density testing indicated increased density and improved crystallinity. The crystalline region of nanocrystalline PVC was less than 80 nm, with a particle size distribution of 5–20 μm and a melting point of less than 128°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 563–569, 2004

Key words: poly(vinyl chloride) (PVC); modification; structure

INTRODUCTION

Poly(vinyl chloride) (PVC) is widely used in pipes and profiles because of its exceptional corrosion resistance, self-extinguishability, flame resistance, inexpensiveness, and recoverability. PVC products are restricted to environments not exceeding 80°C and to nonstructural applications because of their low strength, which is reduced by the —Cl substituent. As a result, PVC doorframes and windows must have a steel interior, and PVC pipes cannot convey hot water. Improved strength, rigidity, toughness, thermal resistance, and dimensional stability by nanocrystalline PVC will certainly extend the applications of PVC.

Many studies have been carried out to toughen and reinforce PVC.[1–3] Blends of PVC and thermoplastic elastomers show toughened impact properties, which are accompanied by deteriorated rigidity, stiffness, dimensional stability, and thermal resistance.[4,5] For inorganic particulate filler/PVC composites, the results are contrary to those of blending.[6,7] Another method is crosslinking.[8,9] Investigations have shown that crosslinked PVC has greatly improved thermal resistance and solvent resistance, but it is lacking in mechanical properties. Moreover, crosslinked PVC loses its recoverability, and this is harmful to the environment. It is thought that blending, filling, and crosslinking cannot satisfy high-performance plastic properties of strength, rigidity, toughness, and thermal resistance simultaneously.

Nanomaterials have received considerable attention in recent years. Inorganic nanoparticles are applied to the high-performance modification of plastics.[10–12] Interface adhesion between the polymer matrix and inorganic nanoparticles is strong enough to improve rigidity, toughness, thermal resistance, and processing properties simultaneously. However, inorganic nanoparticles tend to aggregate because of their high surface energy.[13,14] Consequently, this makes them hard to disperse in a polymer matrix on a nanometer scale, and this certainly reduces the properties of nanoparticle/plastic composites.

The crystallinity of typical PVC is under 5%. If the crystallinity is raised to a level greater than 30%, PVC can be used at elevated temperatures with enhanced strength, rigidity, and dimensional stability. Because the melting point of crystalline PVC is greater than 200°C, the processing temperature of PVC must also be over 200°C, and this results in the creation of HCl, which degrades PVC and makes crystalline PVC unsuitable.[12,15] This contradiction between crystallinity and processing must be settled.

PVC, with a melting point of 210°C and a crystallinity level of about 35%, is made by spray and heat treatments. Then, nanocrystalline PVC is prepared via jet milling. In the presence of nanocrystalline PVC as a self-plasticizer and self-nucleating agent, PVC can be

extruded easily, its mechanical properties reaching the standards of engineering plastics.

EXPERIMENTAL

Materials and equipment

PVC was provided by Sinopec Qilu Co., Ltd. (China), in the form of a powder with a weight-average molecular weight of 6.25×10^4. The syndiotacticity of PVC was 10–15%. The jet-milling treatment was conducted in a fluidized-bed opposed jet mill (Alpine Co., Germany).

Spray treatment

A nucleator solution was prepared by the 1:1 mixing of cyclohexanone and cyclohexane. An atomizer was adopted to spray-treat PVC during high-speed agitation to ensure that the PVC particles swelled. The boiling point of this mixed solvent was about 90°C.

Heat treatment

The PVC particle heat treatment was stopped after a 5-min residence time at a constant temperature of 110°C. During this procedure, the solvent inside the PVC particles volatilized. A temperature of 110°C was adopted for two reasons: the volatile temperature of the solvent had to be greater than 90°C, and the optimum crystallization temperature of PVC was 110°C.[16] The generating rate and nucleation rate were optimal at this temperature.

Preparation of nanocrystalline PVC

Postmodified PVC was jet-milled in the fluidized-bed opposed jet mill, with three classifying gear speeds (3000, 6000, and 9000 rpm) and processing temperatures ranging from 5 to 20°C.

Testing and characterization

Scanning electron microscopy (SEM)

The samples were examined as a function of the classifying gear speed (3000, 6000, or 9000 rpm) at a constant temperature with a Hitachi (Tokyo, Japan) S2500 scanning electron microscope. Before the SEM examination, the surfaces were coated with a layer of a gold–palladium alloy.

X-ray analysis

Modified and unmodified PVC specimens were studied on a HZG4-PC X-ray diffraction analyzer, and then X-ray crystallinity was used to evaluate the improvement in the crystallinity.

Particle size distribution

The particle size distribution was determined with a BI-XDC particle size analyzer as a function of the temperature (5, 10, or 20°C) at a constant classifying gear speed. The size distribution curve displayed the particle size along the x axis and the percentage along the y axis. From these data, the average diameter of the different specimens was determined.

Differential scanning calorimetry (DSC)

The samples were initial PVC, jet-milled but unmodified PVC, and nanocrystalline PVC. The test was completed on a PerkinElmer differential scanning calorimeter at a heating rate of 20°C/min. The recorded scans were analyzed in terms of the melting point.

Fourier transform infrared (FTIR) spectroscopy

KBr and nanocrystalline PVC processed at different classifying gear speeds were thoroughly mixed and then pressed into thick films with a compression-molding machine between two Teflon sheets at 180°C, with a load of 10 tons, for 5 min. Finally, the samples were analyzed with a Nicolet (Madison, WI) 20DXB FTIR spectrometer. The changes in the band peak were connected to the microcrystalline structure of PVC as a function of the classifying gear speed.

Transmission electron microscopy (TEM)

TEM observations with a JEM-100CX II were used to evaluate the crystalline dimension and crystalline size distribution of nanocrystalline PVC. For TEM studies, a drop of a 1 wt % polymer solution in n-butanol was dried on a carbon-coated mica sheet to form a film. The film was then transferred to a copper grid and dried in a vacuum oven at 50°C for 24 h. The specimens were stained in ruthenium tetraoxide vapor for 5 h to improve the image contrast.

RESULTS AND DISCUSSION

Structure of PVC

PVC, for processing into a profile, is mostly synthesized by the suspension polymerization technique. This kind of polymerization makes PVC of a low crystallinity. The presence of crystallinity induces an increase in the fragility and a decrease in the impact properties. The polymerization is usually carried out at 50–70°C (lower than its glass-transition temperature of 80°C) to reduce the formation of crystallinity; this leads to a lower deterioration of the properties.

During suspension polymerization, when monomers react with PVC, porosity forms in the growing particles because PVC has a higher density than vinyl

Figure 1 SEM micrograph of a PVC particle.

TABLE I
Density of Modified and Unmodified PVC

	Specimen	
	Modified PVC	Unmodified PVC
Density (g/cm^3)	1.47	1.44

chloride. Water in the polymerization autoclave fluxes into the porosity thorough microvoids and cleavages in the surfaces of the growing particles, and further aggregation of growing particles ultimately results in a better formation of stable porosity. The effect becomes obvious with high-speed agitation and the impact of water against the porosity.

During the drying treatment, the nonreacted monomers move out from the primary particles, and PVC particles are formed, with their surface blown up because of vapor removal causing porosity.[17,18] Figures 1 and 2 present SEM micrographs of PVC particles and PVC primary particles, respectively. Figure 1 shows globular PVC particles, with much porosity in the surface. The micrograph corresponds to the previous descriptions. Figure 2 magnifies part of Figure 1. It shows that single PVC particles are made up of a multitude of primary particles. The small globular particles are the primary particles, aggregating to form PVC particles. The crystalline structure is inside the

primary particles, with a large protocrystalline region, which is of a high order and ultimately results in a high melting point and a high die strength. This is evident from its melting point of 210°C.

Crystallinity improvement of modified PVC

Table I summarizes the density changes of modified and unmodified PVC. A nucleator enters into PVC particles and acts as a crystal seed to induce the occurrence of heterogeneous nucleation. Heat treatment further induces it. The density of modified PVC increases because of the improved crystallinity and, therefore, the collapsed structure.

An X-ray diagram of unmodified PVC has no obvious diffraction peak, and this is evidence of the low crystallinity of the PVC polymer (Fig. 3). In contrast, an X-ray diagram of modified PVC has two obvious diffraction peaks, and this is evidence of the crystallinity improvement.

Pulverization and degradation of PVC

In a jet mill, PVC particles rotate with a high-speed airflow and crash against one another, touch one another, and grind one another, thereby being pulverized into superfine particles in the fluidized bed.[19] The modification of PVC particles brings extended and perfect crystalline regions and increased fragility. The improved crystallinity makes the impact rigid particle to rigid particle, instead of soft particle to soft particle as before modification. This is different from the shear rupture of noncrystalline molecules during solid-state
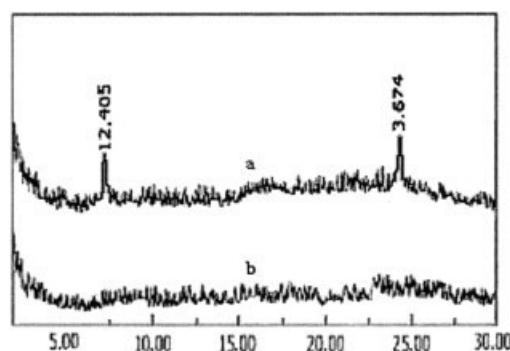

Figure 2 SEM micrograph of PVC primary particles.

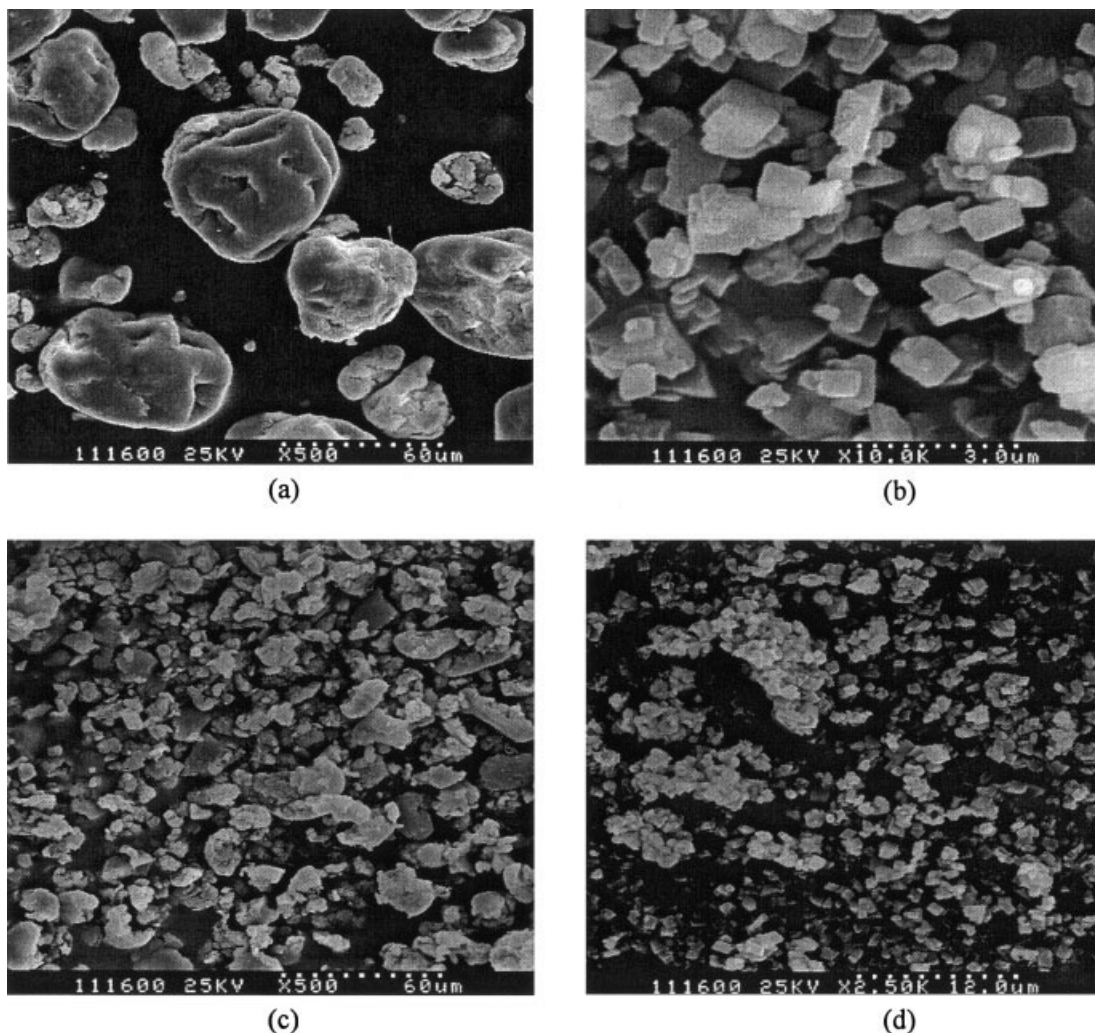**Figure 3** X-ray diagrams of (a) modified PVC and (b) unmodified PVC.

Figure 4 SEM micrographs of (a) unpulverized PVC, (b) PVC pulverized at 3000 rpm, (c) PVC pulverized at 6000 rpm, and (d) PVC pulverized at 9000 rpm.

grinding.[20,21] At the same time, internal stress also appears in the PVC molecules, inducing local degradative reaction. Pulverization and degradation give PVCs of different structures and properties.

Effect of jet milling on the particle morphology of nanocrystalline PVC

Figure 4 illustrates the variations of superfine PVC particles at different classifying gear speeds. The higher the speed is, the smaller the dimension is. At 9000 rpm [Fig. 4 (d)], most PVC particles pulverize into microparticles with a particle size of about 10 μm, accompanied by slight aggregation on account of the high surface energy. A higher speed, with higher frequency jet milling, produces more of a chance for pulverization, and this results in smaller dimensions of the PVC particles. However, the particle size does not follow a linear relationship with the speed. The pulverization efficiency is highest at 3000 rpm, with

the particle size decreasing from 160 to 50 μm and reaching 20 μm at 6000 rpm and 10 μm at 9000 rpm. This can be explained as follows: the initial PVC particle is large and has a high kinetic energy at a constant classifying gear speed; the modification increases the crystallinity and fragility. All of this makes the post-modified PVC particle easy to pulverize. After several impacts, one particle breaks into several smaller particles. Each smaller particle is small and thus has a low kinetic energy at the same speed; this makes pulverization difficult. The smaller the particle size is, the more obvious the phenomenon is. That is, the particle size is not always inversely proportional to the classifying gear speed.

Figure 5 presents a magnified SEM micrograph of a PVC particle pulverized at 9000 rpm. The particle has been pulverized internally, assembled by many loose microparticles, changing from a spherical shape to a flake; this indicates that the inner crystal structure has
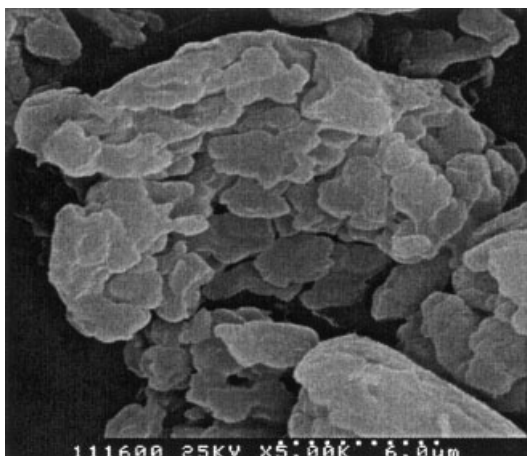
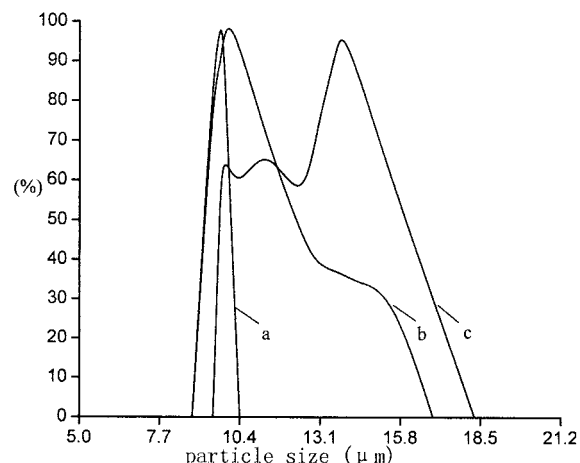**Figure 5** Magnified SEM micrograph of a PVC particle pulverized at 9000 rpm.

Figure 6 Centralized distribution at processing temperatures of (a) 5, (b) 10, and (c) 20°C.

been broken greatly. It can be deduced that an extended jet-milling time leads to superfine PVC particles with smaller volumes and higher degrees of damage.

Effect of the processing temperature on the particle size distribution of nanocrystalline PVC

Table II shows data from BI-XDC representing the variations of the PVC particle size distribution as a function of the processing temperature. Figure 6 shows the centralized distribution at different processing temperatures.

a, b, and c in Table II correspond to PVC particles pulverized at processing temperatures of 5, 10, and 20°C, respectively. Curves a–c in Figure 6 are selected regions from the particle size distribution curves that show the centralized distribution.

From a comparison of the curves and data, we can surmise that, with an increase in the processing temperature, the average particle size and maximum particle size increase, but the specific surface area decreases. Centralized distribution maxima lie at 9.8, 10.0, and 13.5 μm, corresponding to 5, 10, and 20°C, respectively. The lowest temperature provides the most uniform distribution. This result is associated with the better toughness due to the active movement

of PVC molecules at higher temperatures and the resultant poor pulverization efficiency.

Effect of jet milling on the microcrystals of nanocrystalline PVC

The effect of jet milling on microcrystals can be detected through FTIR. Spectra in the 600–700-cm^{-1} region are shown in Figure 7(a–c) for 0, 6000, and 9000 rpm, respectively. The band at approximately 690 cm^{-1} accounts for the isotactic C—Cl stretching vibration. The band at about 635 cm^{-1} is the absorption band of the crystal region and accounts for the syndiotactic C—Cl stretching vibration. A high degree of crystalline order results in a strong band at 635 cm^{-1}. After jet milling, the peak at about 635 cm^{-1} decreases with an increase in the classifying gear speed; this means a low degree of crystalline order. This confirms that jet milling destroys the microcrystals of crystalline PVC.

Effect of jet milling on the melting point of nanocrystalline PVC

The DSC spectral analysis results are shown in Figure 8 and represent the variations of the melting temperatures of different specimens. Curves a–c correspond

TABLE II
Variation of PVC Particle Size Distribution

	<5 μm (%)	<10 μm (%)	<15 μm (%)	Average particle size (μm)	Maximum particle size (μm)	Specific surface area (μm)	Centralized distribution (μm)
a	27	42	92	9.38	17	0.481	9.8
b	10	44	86	9.70	20	0.457	10.0
c	16	36	72	10.75	23	0.426	13.5
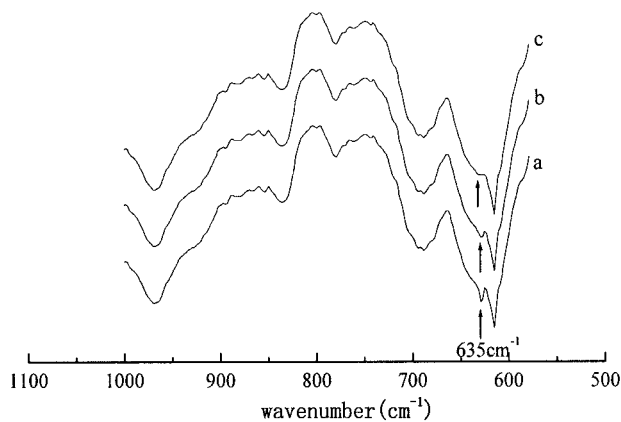
Figure 7 FTIR spectra of PVC pulverized at a classifying gear speed of (a) 0, (b) 6000, or (c) 9000 rpm.

Figure 9 TEM micrograph of nanocrystalline PVC.

to specimens of nanocrystalline PVC, initial PVC, and unmodified but jet-milled PVC, respectively. The melting point decreases from 210 to 128°C, but the melting point of unmodified PVC is still about 200°C, which is negligible. The melting point of the polymer corresponds to the degree of crystalline order. The higher the crystal defect is, the lower the melting point is. The decreased melting point confirms that jet milling destroys the crystal region. However, the previous modification is a fatal factor, and this can be proved by the unmodified but jet-milled PVC

The low melting point enables nanocrystalline PVC, a self-plasticizer, to improve processing properties. Moreover, the crystal nucleus cannot melt during processing, acting as a nucleating agent to induce PVC to crystallize. The improved crystallinity leads to excellent mechanical properties.

Structure of nanocrystalline PVC

Figure 9 presents a TEM micrograph of a pulverized PVC particle. The little black points represent the crys-
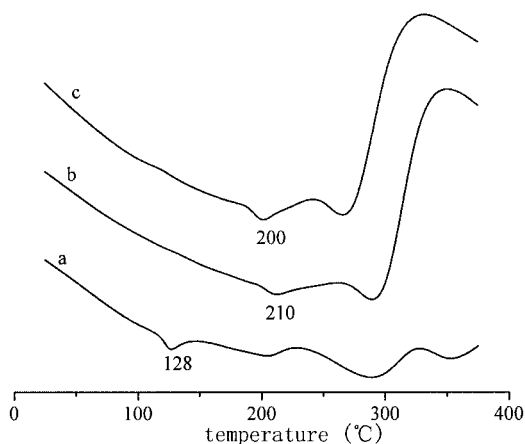
tal regions of nanocrystalline PVC, with diameters of less than 80 nm. These fine and uniformly distributed crystal regions have a nucleation effect.

CONCLUSIONS

On the basis of the structure of PVC, a novel nanocrystalline PVC has been successfully prepared for potential applications in PVC processes, showing improvements in the mechanical properties and thermal resistance. It is evident from X-ray diagrams that the crystallinity of PVC is increased after modification, and this results in easier pulverization during jet milling and ultimately nanometer crystal regions. The effect of jet milling on the particle morphology shows that a higher classifying gear speed produces smaller PVC microparticles, but the particle size does not follow a linear relationship with the speed. The melting point of nanocrystalline PVC is 128°C, which enables it to be a self-plasticizer to improve the processing properties and to be a self-nucleating agent to induce PVC to crystallize; consequently, the mechanical properties and thermal resistance of PVC products can be improved. The appearance of nanocrystalline PVC settles the contradiction between crystallinity and processing.

Figure 8 DSC spectra of (a) nanocrystalline PVC, (b) initial PVC, and (c) unmodified but jet-milled PVC.

References

1. Nakamura, Y.; Kanbe, M.; Takekuni, E.; Iida, T. Compos Interface 2001, 8, 367.
2. Crawford, E.; Lesser, J. Polymer 2000, 41, 5865.
3. Mishra, S.; Perumal, G. B.; Naik, J. B. Polym Plast Technol 1997, 36, 489.
4. Chan, C. M.; Zhu, S. H.; Wong, S. C.; Mai, Y. W. Polym Eng Sci 1999, 39, 1998.
5. Braun, D.; Bohringer, B.; Eidam, N.; Fischer, M.; Kommerling, S. Angew Makromol Chem 1994, 216, 1.
6. Nakamura, Y.; Okabe, S.; Yoshimoto, N.; Iida, T. Polym Polym Compos 1998, 6, 407.

7. Wiebking, H. E. Soc Plast Eng 1995, 4112.
8. Yanez-Flores, I. G.; Ibarra-Gomez, R.; Rodriguez-Fernandez, O. S.; Gilbert, M. Eur Polym J 2000, 36, 2235.
9. Xu, C.; Fang, Z.; Zhong, J. Angew Makromol Chem 1993, 212, 45.
10. Wang, H.; Mei, M.; Jiang, Y.; Li, Q.; Zhang, X.; Wu, S. Polym Int 2002, 51, 7.
11. Vollenberg, P. H. T.; Heikens, D. Polymer 1989, 30, 1656.
12. Ruckenstein, E.; Yuant, Y. Polymer 1997, 38, 3855.
13. Cavicchi, R. E.; Silsbee, R. H. Phys Rev Lett 1984, 52, 1453.
14. Ball, P.; Garwin, L. Nature 1992, 355, 761.
15. Bisi, M.; Nicolella, C.; Palazzi, E.; Rovatti, M.; Ferraiolo, G. Chem Eng Technol 1994, 17, 67.
16. Gilbert, M.; Ansari, K. E. J Appl Polym Sci 1982, 27, 2553.
17. Liu, X. M. Modification and Processing of Rigid PVC; Chinese Light Industry Press: Beijing, 1998; p 78.
18. Hua, Y.; Huang, Y.; Siqin, D. J Vinyl Technol 1994, 16, 235.
19. Li, F. S. Application and Manufacture Technology of Special Superfine Power; National Defense Industry: Beijing, 2002; p 28.
20. Guo, S. Y.; Xu, X. Polym Mater Sci Eng 1993, 6, 106.
21. Guo, S. Y.; Xu, X. Polym Mater Sci Eng 1995, 2, 81.