Effect of Mechanochemical Degradation on Gelation and Mechanical Properties of PVC

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ABSTRACT: The effect of vibromilling or jet milling on gelation and mechanical properties of poly(vinyl chloride) (PVC) was studied through SEM, FTIR, DSC, and mechanical properties tests. The experimental results show that the size of the grain and apparent density of PVC are decreased. The grains become much more loosely aggregated and the crystallinity of PVC is decreased during milling. The extensional fracture of degraded PVC is obviously different from that of undegraded PVC, the tensile strength and degree of gelation of degraded PVC are increased as compared with undegraded PVC. The mechanical properties of PVC are improved quite a lot after blending it with a small amount of mechanochemically degraded PVC. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2273–2281, 1997

Key words: poly(vinyl chloride); mechanochemical degradation

INTRODUCTION

Poly(vinyl chloride) (PVC) is a semicrystalline polymer. The crystallinity of PVC is about 5–10%,[1] and its meltability during processing has great influence upon the properties of the product. The higher melting crystallites are in lamellated form and are formed during polymerization. The lower melting crystallites are in a fringed micelle form and are formed during processing under the influence of heat and shearing force.[2,3] The melting enthalpy of PVC crystallites recrystallized during cooling from processing temperature to room temperature is ΔH_A. The melting enthalpy of PVC crystallites unmelted during processing is ΔH_B. The degree of gelation of PVC during processing is $G = \Delta H_A/(\Delta H_A + \Delta H_B) \times 100\%$. The higher the value of G, the better the mechanical properties of the product.

Three methods are usually utilized for promoting gelation of PVC: addition of processing aids,[4] raising processing temperature and shear rate,[5] and modifying the granular structure of PVC and reducing its molecular weight.[6]

Imposition of critical stress on the polymer chain can cause the rupture of chain bonds. The effect of mechanochemical degradation on processability and properties of PVC has been studied.[7–10] The effect of vibromilling or jet milling on gelation and mechanical properties was studied in hopes of gaining an innovative route to raise the G value of PVC.

EXPERIMENTAL

Materials

Materials used were PVC-TK700 with a number average molecular weight ($\bar{M}_n$) of 4.49×10^4

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Table I Molecular Weight of Mechanochemically Degraded PVC

Sample	Vibromilling Temp. and Time (h)	Molecular Weight $\times 10^{-4}$
PVC-TK800 D5	Room temp., 5	4.92
PVC-TK800 D10	Room temp., 10	4.68
PVC-TK800 D20	Room temp., 20	4.46
PVC-TK800 D25	Room temp., 25	4.16
PVC-TK1300 D25	Room temp., 25	6.10

(China), PVC-TK800 with an $\bar{M}_n$ of 5.65×10^4 (Japan), and PVC-TK1300 with an $\bar{M}_n$ of 7.15 $\times 10^4$ (China).

Mechanochemical Degradation of PVC

This process was conducted in a vibromilling or a jet milling machine. The vibromilling was performed at 1340 rpm and 5 mm amplitude. The ratio of steel ball/PVC (by wt.) was 10 : 1, ball diameter was 14–18 mm, and the radical acceptor and heat resistant stabilizer were charged with PVC. Jet milling was conducted under a pressure of 0.92–0.93 MPa.

Measurement and Characterization

Molecular weight was measured by a Waters ALC/GPC liquid chromatograph. The solvent was THF, flow rate was 1.0 mL/min. The reference sample was polystyrene.

PVC crystallite was examined with a Nicolet 20 SXB FTIR. The effect of vibro- or jet milling on the crystalline structure of PVC was studied through the changes of the intensity of PVC crystalline absorption bands with time of vibro- or jet milling.

Morphology and extensional fracture morphology of PVC was observed through an X-650 scanning electron microscope.

Optical density was measured according to ASTM D1895-80.

Degree of gelation was measured with a Perkin–Elmer DSC-7 instrument. Heating rate was 20°C/min. PVC exhibits two endothermic peaks in the DSC heating curves. The area of the lower melting endotherm divided by the sum of the areas of the lower and higher melting endotherms is taken as a measure of the degree of gelation.

Stress–strain behavior was measured by an Instron 4302. The specimen had dimensions of 25 × 6.5 × 1 mm; tension speed was 20 mm/min. The sample was prepared by mixing the degraded PVC with a small amount of heat sta-

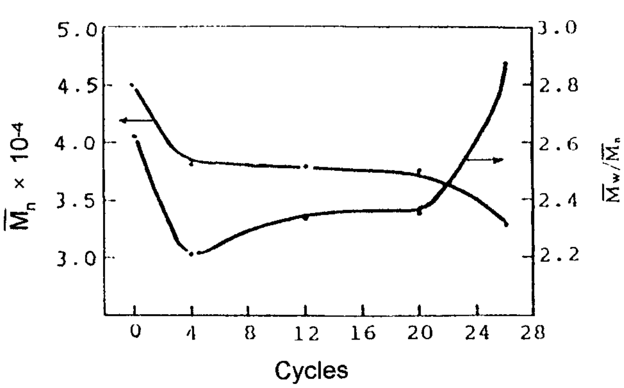


Figure 1 Effect of time of jet milling on molecular weight and its distribution of PVC.

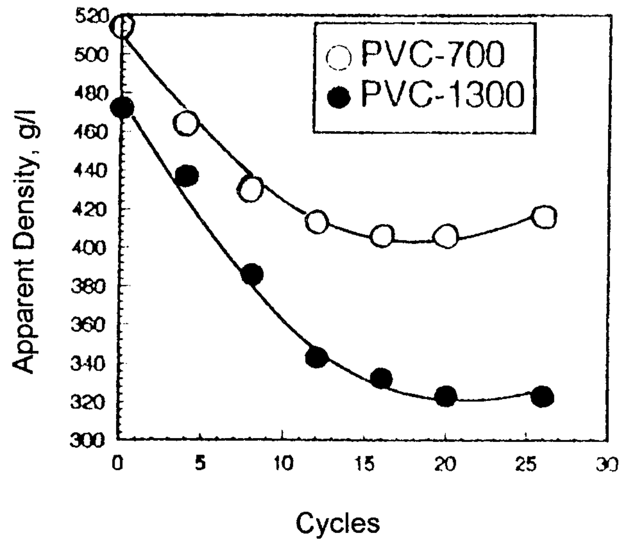
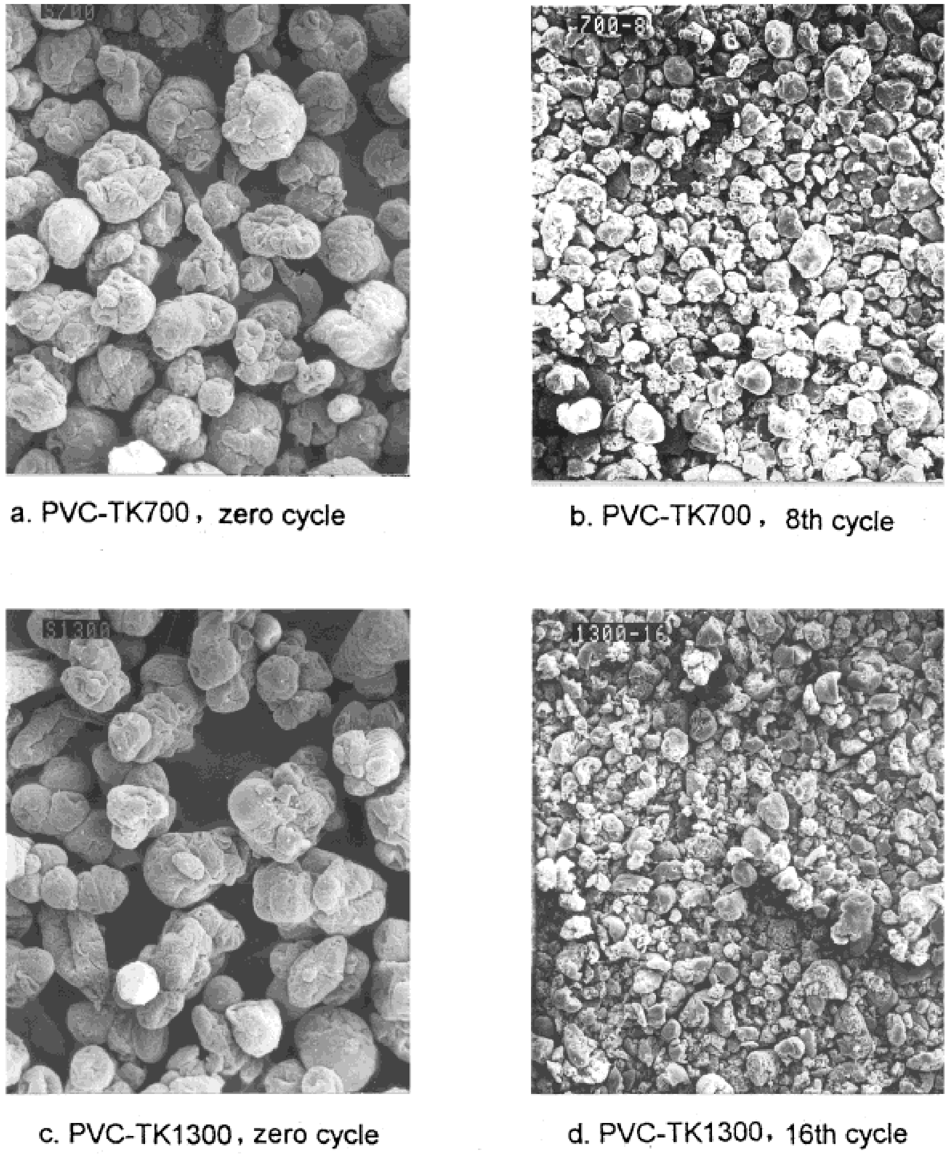


Figure 2 Apparent density of PVC after jet milling.

Table II DSC Results of PVC-TK800 and PVC-TK800 D25

Sample, Proc. Temp., (°C)	ΔH_A (J/g)	ΔH_B (J/g)	G (%)
PVC-TK800 D25, 170	8.681	0.439	95.2
PVC-TK800, 185	5.882	0.905	86.7
PVC-TK800, 170	5.763	1.128	83.6



a. PVC-TK700, zero cycle

b. PVC-TK700, 8th cycle

c. PVC-TK1300, zero cycle

d. PVC-TK1300, 16th cycle

Figure 3 Scanning electron micrographs of jet-milled PVC (×100).

Table III DSC Results of Jet-Milled PVC

	Cycles	0	4	26
PVC-TK700	ΔH_A (J/g)	6.659	10.480	9.606
	ΔH_B (J/g)	0.513	0.110	0
	G (%)	92.8	98.9	100
PVC-TK1300	ΔH_A (J/g)	6.289	5.557	7.151
	ΔH_B (J/g)	1.171	0.619	0.609
	G (%)	84.3	90.0	92.2

Processing temperature was 170°C.

Table IV DSC Results of PVC-TK700/PVC-TK700-26 and PVC-TK1300/PVC-TK700-26 Blends

	ΔH_A (J/g)	ΔH_B (J/g)	G (%)
PVC-TK700/PVC-TK700-26			
60/0	6.659	0.513	92.8
60/5	8.914	0.400	95.7
60/20	7.400	0.302	96.0
PVC-TK1300/PVC-TK700-26			
60/0	6.289	1.171	84.3
60/5	8.607	0.522	94.3
60/20	8.088	0.417	95.1

Processing temperature was 170°C.

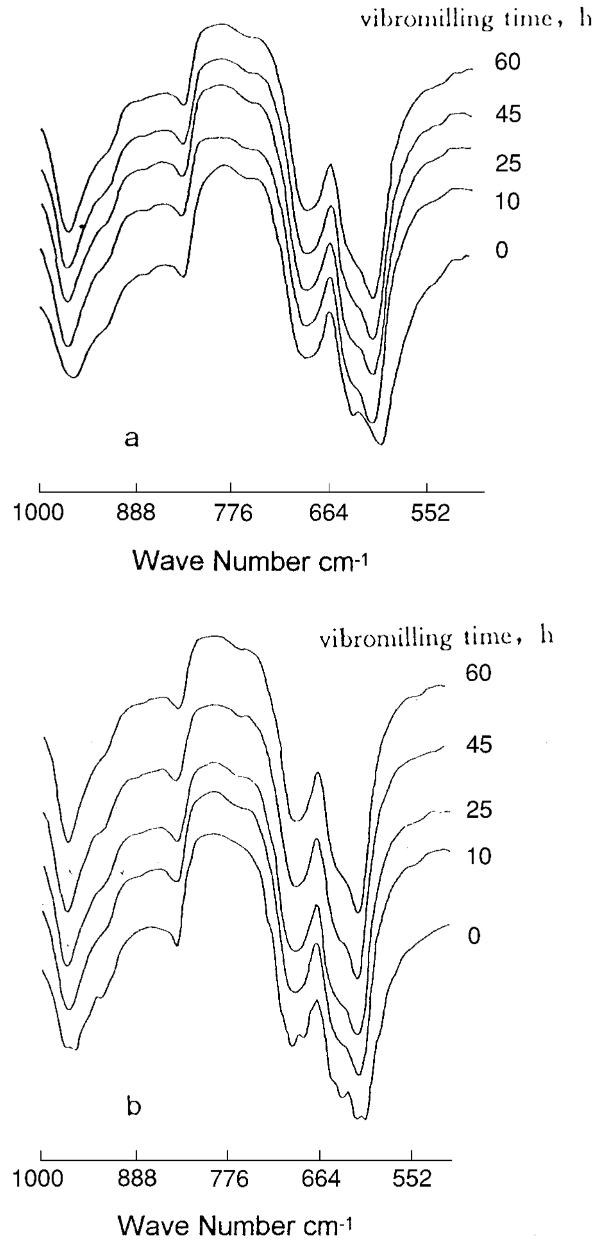


Figure 4 Effect of vibromilling time on FTIR spectra of (a) PVC-TK800 and (b) PVC-TK1300.

bilizer and stearic acid, then blended in a Brabender plasticorder at 170°C for a period of 10 min and compression molded at 185°C.

RESULTS AND DISCUSSION

Effect of Vibromilling or Jet Milling on Molecular Weight and Morphology of PVC

The data listed in Table I and Figure 1 show that the molecular weight of PVC decreases with time of vibromilling or jet milling. As shown in Figures 2 and 3, the size of PVC-TK700 and PVC-TK1300 grains and their apparent density are also decreased with time of jet milling.

The effect of vibro- or jet milling on PVC crystallite is examined through the changes of the intensities of crystalline absorption bands on FTIR spectra at 635, 604, and 1427 cm^{-1} and the amorphous absorption bands on FTIR spectra at 615 and 1435 cm^{-1} with milling time. As shown in Figures 4 and 5, the crystalline absorption bands become weaker and indistinct with time of milling and I_{615}/I_{635} and I_{1435}/I_{1427} increase with time of milling (Fig. 6), indicating the crystallinity of PVC is decreased during milling.

The mechanochemical degradation decreased the molecular weight of the PVC, loosened the aggregation of PVC grains, and decreased the crystallity of the PVC. The low molecular weight PVC prepared by mechanochemical degradation should have pretty good processability.

Effect of Vibro- or Jet Milling on Gelation and Mechanical Properties of PVC

The data listed in Table II and Figure 7 show that the higher the processing temperature, the lower the ΔH_B of PVC and the higher the ΔH_A and G. Both ΔH_A and G of PVC-TK800 D25 (PVC-TK800 vibromilled 25 h) are much higher than those of PVC-TK800, while the ΔH_B is much lower than that of PVC-TK800. The data listed in Table III and Figure 8 indicate that ΔH_B of PVC-TK700 and PVC-TK1300 decreased and their G increased with the time of jet milling. As shown in the data

Table V Effect of Time of Jet Milling on Mechanical Properties of PVC-TK700

Cycles	0	4	8	12	16	26
Yield strength (MPa)	63.8	67.3	66.2	67.8	68.1	69.1
Young's modulus (MPa)	3371	3712	3349	3366	3637	3365
Strength at break (MPa)	48.6	51.8	—	53.5	52.7	54.5

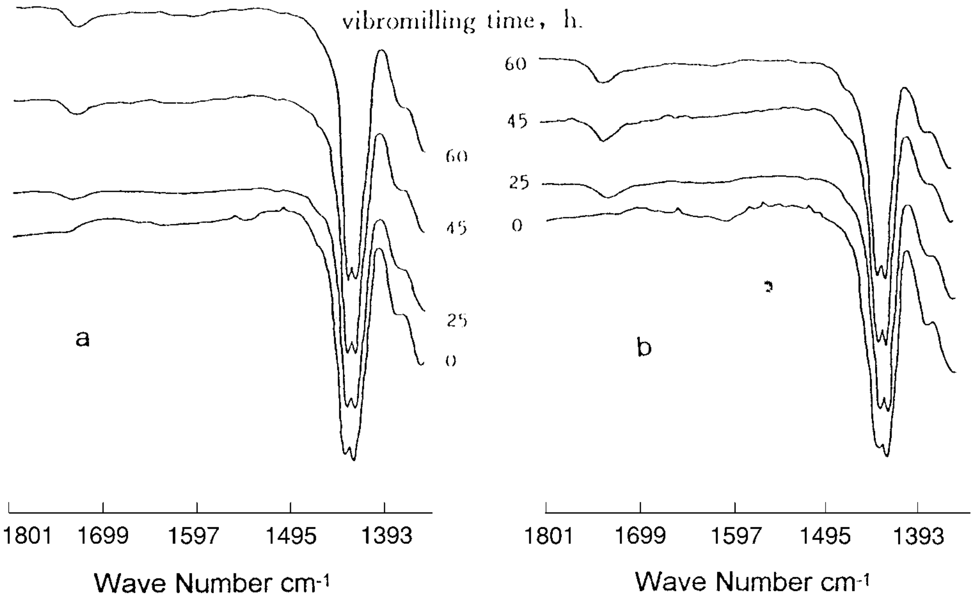


Figure 5 Effect of vibromilling time on FTIR spectra of (a) PVC-TK800 and (b) PVC-TK1300.

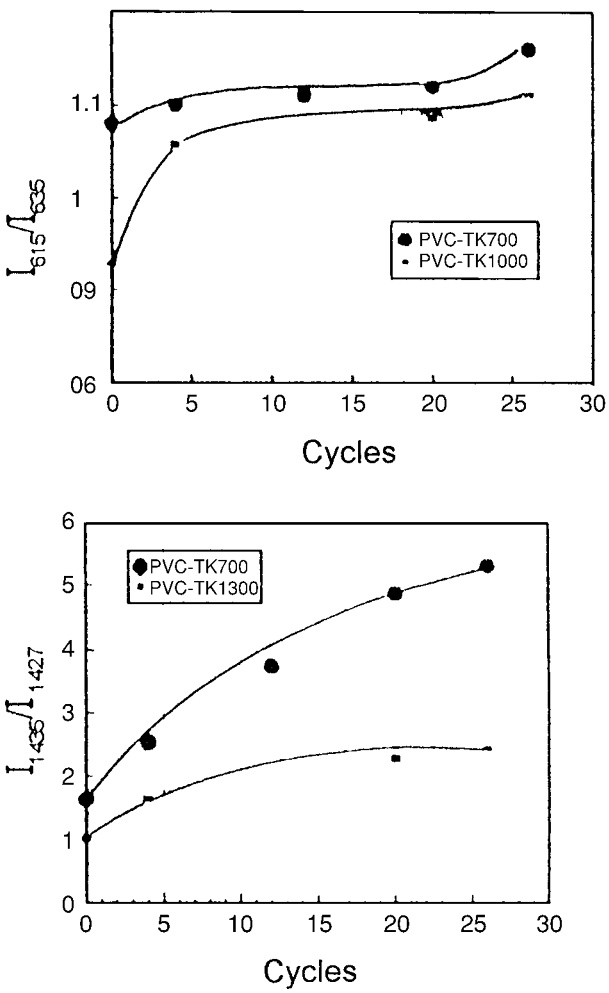


Figure 6 Effect of time of jet milling on I_{615}/I_{635} and I_{1435}/I_{1427}.

listed in Table IV and Figures 9 and 10, addition of a small amount of PVC-TK700-26 (PVC-TK700 jet milled 26 times) into PVC-TK700 and PVC-TK1300 greatly increased their degree of gelation and greatly decreased their ΔH_B. The results mentioned show that the milled PVC could be used as an innovative processing aid, fulfilling the idea of plasticizing PVC by itself.

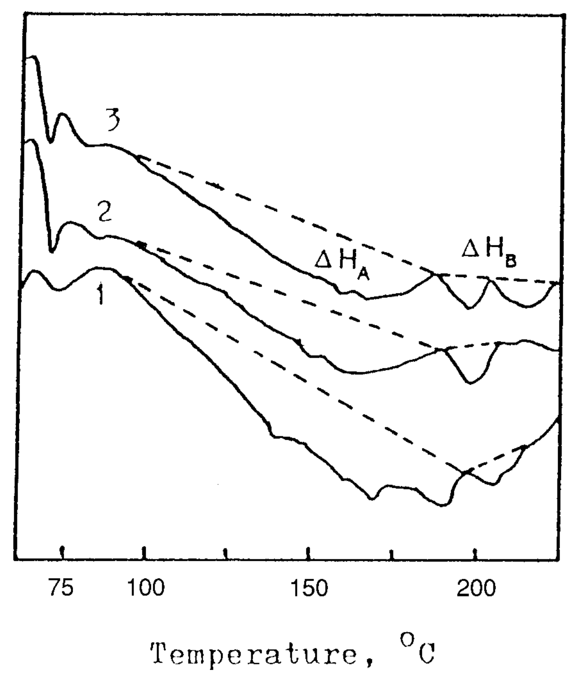


Figure 7 DSC curves of PVC: (1) PVC-TK800 D25, processing temp. 170°C; (2) PVC-TK800, processing temp. 185°C; (3) PVC-TK800, processing temp. 170°C.

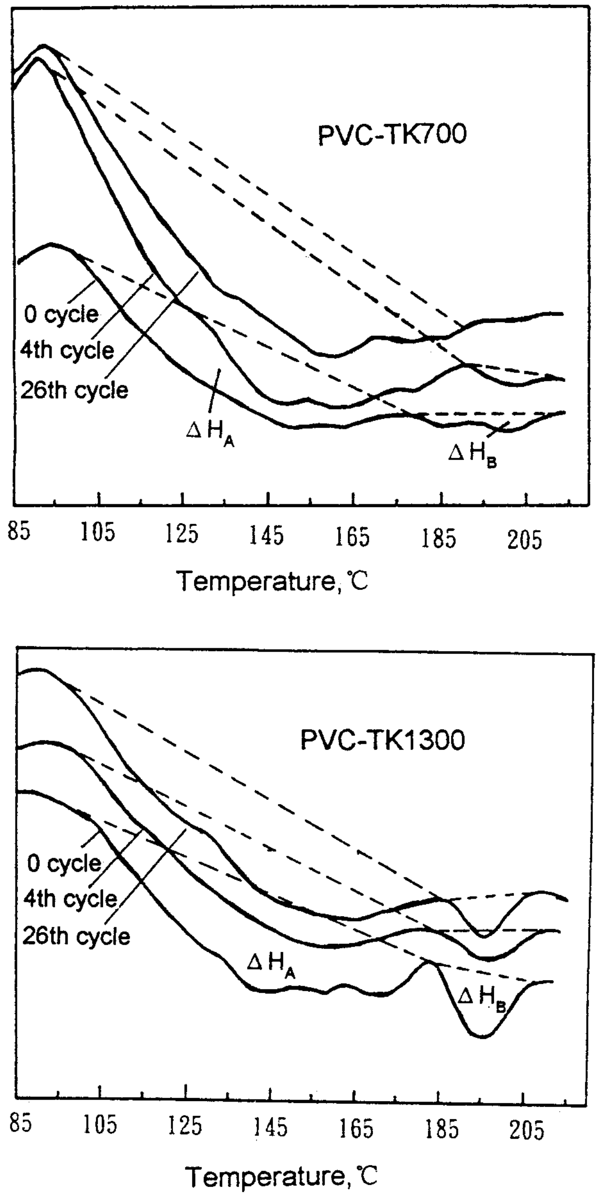


Figure 8 Effect of time of jet milling on DSC curves of PVC.

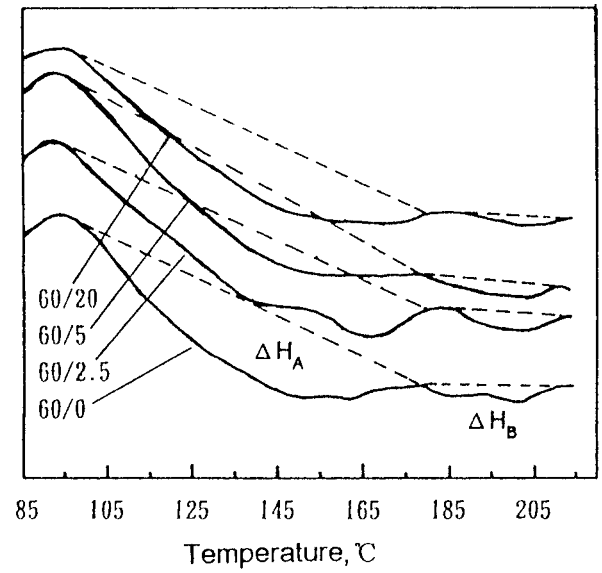


Figure 9 DSC curves of PVC-TK700/PVC-TK700-26 (PVC-TK700-26: PVC-TK700 jet milled 26 times).

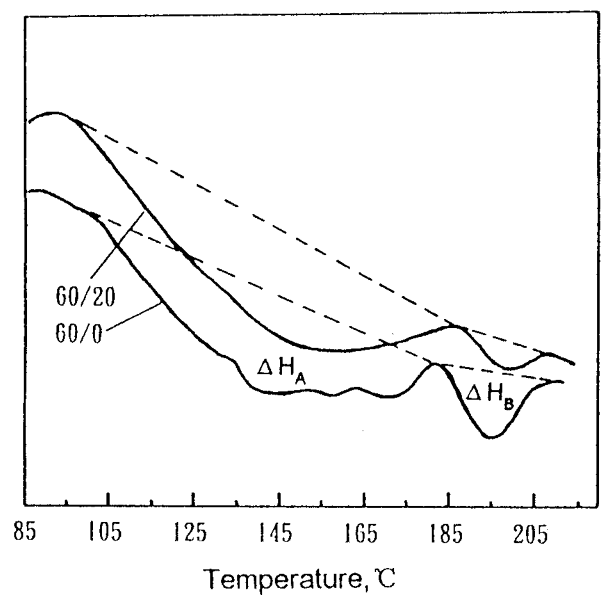


Figure 10 DSC curves of PVC-TK1300/PVC-TK700-26.

Table VI Effect of Time of Jet Milling on Mechanical Properties of PVC-TK1300

Cycles	0	4	12	20	26
Yield strength (MPa)	65.7	66.1	66.2	66.4	—
Young's modulus (MPa)	3127	3382	3347	3420	3780
Strength at break (Mpa)	43.2	56.6	—	56.2	64.7

Table VII Mechanical Properties of Degraded and Undegraded PVC

Sample	Yield Strength (MPa)	Strength at Break (MPa)	Elongation at Break (%)
PVC-TK800	70.0	49.9	228.6
PVC-TK800 D25	75.2	57.3	211.1
PVC-TK1300	65.7	43.2	162.7
PVC-TK 1300 D25	77.9	57.0	214.4

Table VIII Mechanical Properties of PVC-TK1300/PVC-TK800 D25 Blends

Sample	Yield Strength (MPa)	Strength at Break (MPa)	Elongation at Break (%)
PVC-TK1300	65.7	43.2	162.7
PVC-TK1300/PVC-TK800 D25 (80/20)	73.1	58.6	234.0
PVC-TK1300/PVC-TK800 (80/20)	72.1	49.3	102.9

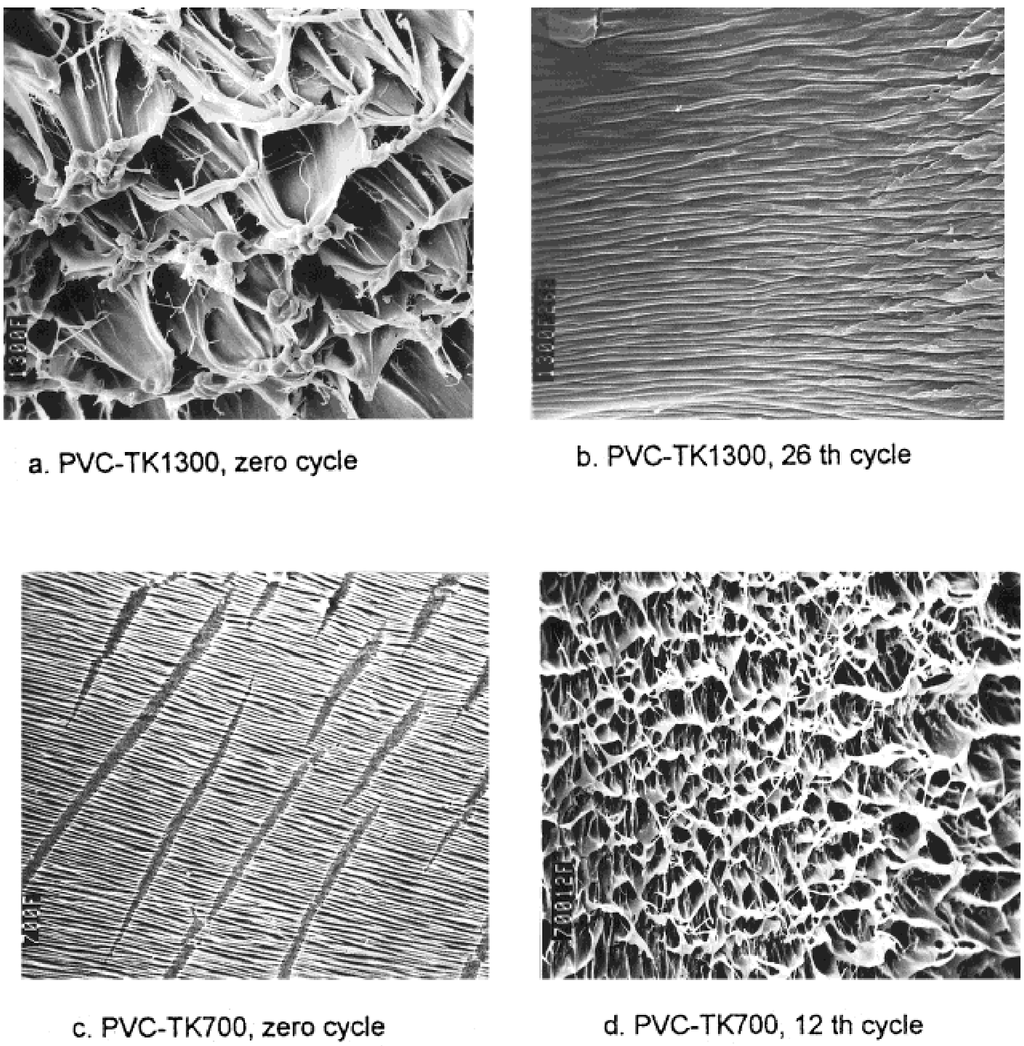
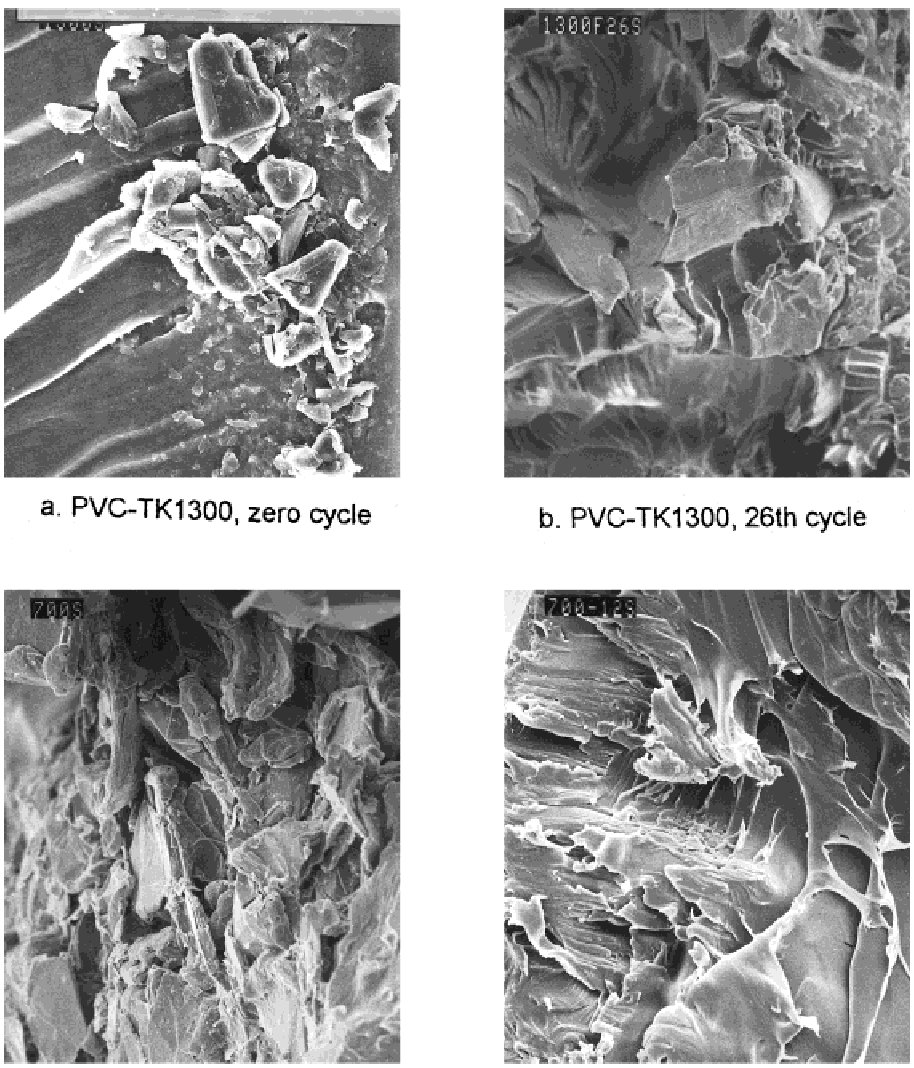


Figure 11 SEM of extensional fractured surface of jet-milled PVC-TK1300 and PVC-TK700 (×1500).

Data listed in Tables V–VII show that the yield strength and the strength at break of milled PVC is higher than those of unmilled PVC, in spite of the fact that the molecular weight of the milled sample is lower than that of the unmilled one. The yield strength, strength at break, and elongation at break of PVC increased quite a lot after blending it with a small amount of milled PVC (Table VIII).

Extensional Fracture Morphology of PVC

The phenomenon of stress whitening of higher molecular weight PVC usually is more obvious than that of lower molecular weight PVC. Figure 11 shows that the stress whitening phenomenon on the extensional fractured surface of PVC-TK1300 [Fig. 11(a)] disappeared after jet milling [Fig. 11(b)]. The stress whitening phenomenon of the extensional fractured surface of PVC-TK700 becomes indifferent after jet milling [Fig. 11(c, d)]. Figures 12 and 13 are the liquid nitrogen frozen fracture surface perpendicular to and parallel to the extension direction, respectively. As shown in these figures, many unmelted PVC particles are present on the fractured surface of unmilled PVC; however, the milled PVC does not have these. This is why the degree of gelation



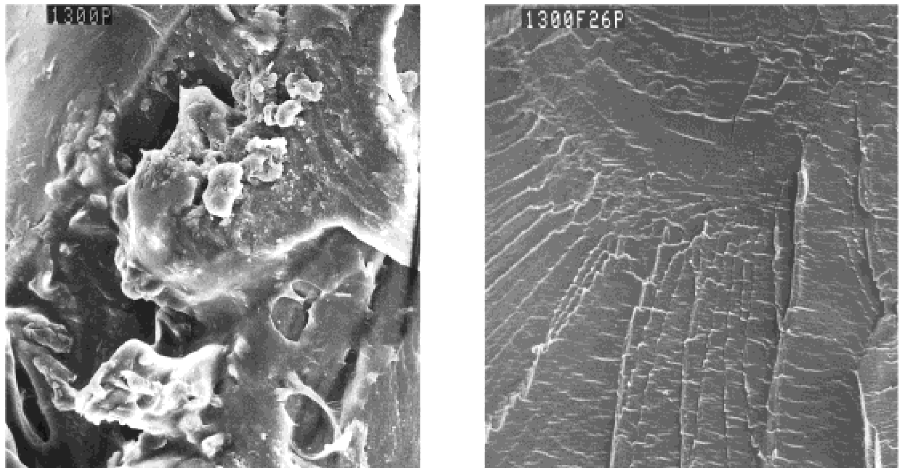
a. PVC-TK1300, zero cycle

b. PVC-TK1300, 26th cycle

c. PVC-TK700, zero cycle

d. PVC-TK700, 12th cycle

Figure 12 SEM of liquid nitrogen frozen fractured surface perpendicular to extension direction of jet-milled PVC-TK1300 and PVC-TK700 (×500).



a. PVC-TK1300, zero cycle b. PVC-TK1300, 26 th cycle

Figure 13 SEM of liquid nitrogen frozen fractured surface parallel to extension direction of jet-milled PVC-TK1300 ($\times500$).

of milled PVC and its mechanical properties are higher and better than those of unmilled PVC.

CONCLUSIONS

After vibro- or jet milling, the molecular weight of PVC is decreased somewhat and the intensity of its FTIR crystalline absorption band becomes indistinct, whereby the processability, degree of gelation, and mechanical properties of PVC are improved quite a lot as compared with those of unmilled PVC.

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