Structure and Thermal Properties of Vinylidene Chloride/Acrylics Copolymers

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SYNOPSIS

A series of vinylidene chloride (VDC) copolymers with methyl acrylate (MA) or butyl acrylate (BA) as comonomer (not more than 10%) was prepared by free-radical suspension copolymerization. The effects of comonomer structure, copolymer composition, and reaction condition (such as polymerization temperature on crystallinity) and thermal properties (such as melting temperature and decomposition temperature) were investigated. All VDC/acrylics copolymers studied here are semicrystalline and have more than one crystalline structure. The melting temperature of MA/VDC copolymers is decreased progressively with increase in MA content. The decomposition temperature of MA/VDC copolymers is slight increased gradually with increase in MA content. MA/VDC copolymers have lower melting temperature compared with BA/VDC copolymers with same VDC composition. The melting temperature of VDC copolymers increases with increase in polymerization temperature and decomposition temperature of those is almost independent of polymerization temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The polymers with low gas and vapor permeability have widely been used for barrier packaging films and containers to protect foods, tea, beverage, and medicine from deteriorating decades.[1] The desirable barrier polymer materials should have very low permeability to gas, aroma, and vapor; high mechanical strength; and good processability.[2] Polyvinylidene chloride (PVDC) with high crystallinity has excellent gas and water vapor barrier properties.[3] However, the melting temperature (203°C) of PVDC is only slight lower than its decomposition temperature (213°C), causing rather difficult processing it into available forms. The most efficient method to improve its processability is to copolymerize VDC with a few percentages of other monomers such as acrylate and vinyl chloride. More comonomer content will lower the barrier property. Unfortunately, there is only few reports of detailed study on the thermal

properties and the processability of VDC copolymers.[3]

In the present study, the melting temperature, the end temperatures of melting endothermic peak, and decomposition temperature of VDC/acrylics copolymers were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) technique to investigate the effect of comonomer structure, copolymer composition, and polymerization process on the thermal properties and processability of VDC/acrylics copolymers and to develop favorable VDC/acrylics copolymer barrier materials.

EXPERIMENTAL

Materials

VDC (technical grade), methyl acrylate (reagent grade), and butyl acrylate (reagent grade) were all purified by distillation under normal and reduced pressure, respectively, before use. Benzoyl peroxide (BPO) and laurl peroxide (LPO) were technical

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grade and purified by repeat crystallization before use. Hydroxymethyl cellulose and hydroxypropyl methylcellulose were used as dispersing agent and supplied by Dow Chemical Co.

Preparation of Copolymers

The copolymerization was performed in the temperature range of 50–80°C in a 5-L stainless steel autoclave equipped with stirrer. VDC/MA mixtures or VDC/butylacrylate (BA) mixtures, de-ionized water, suspension agent, and initiator were charged into the autoclave. Methyl acrylate (MA) composition of the monomer feed was not more than 10%, and BA composition was not more than 7%. The weight ratio of water to monomers was about 1.5. BPO and/or LPO as initiators (0.02386 mol/L) and methyl cellulose and/or hydroxypropyl methylcellulose as suspension agents (1.5 g/kg monomers) were used. The process is similar to that is described in previous paper.[4]

Characterization of VDC Copolymers

DSC and thermogravimetry (TG) runs were made, respectively, on a Perkin-Elmer series 7 DSC instrument and a TD 230 thermogravimetric analysis instrument. Wide-angle X-ray diffraction (WAXD) measurements for VDC polymers were undertaken on a Philips X-ray diffractometer with CuKα radiation (λ = 0.154 nm).

RESULTS AND DISCUSSION

Copolymer Composition and Thermal Behavior of VDC/Acrylics Copolymers

Two sets of radical polymerization samples with different MA content prepared; respectively, at 50 and 80°C were studied. Figure 1 is DSC heating scans of some representative examples. PVDC has two melting endothermic peaks at 203 and 180°C, respectively, in DSC heating scan. VDC copolymer with 5% MA prepared at 50°C has two melting endothermic peaks at, respectively, 171 and 156°C, whereas that at 80°C has only one melting endothermic peak at 167°C. Crystallinity of PVDC originates from the high symmetry of molecular chain segment. MA chain segment with low symmetry and bulky side substitute (— COOCH₃) hinder crystal growing and result in crystal grating defect. Hence, the melting temperatures of and melting heats of
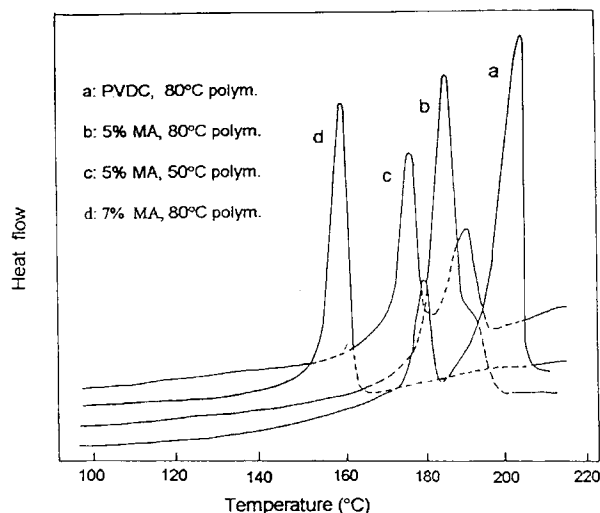

Figure 1 DSC heating scans of some representative examples.

VDC/MA copolymers are lower compared with those of PVDC.

Table I is the melting properties of PVDC and VDC/acrylics copolymers. Figure 2 is the plot of melting temperature against acrylics content of VDC copolymers. Table I and Figure 2 show that the melting temperatures of MA/VDC copolymers decrease with increase in MA content. VDC polymers with lower MA content have two melting endothermic peaks, and the ratios of the melting heat at higher temperature peak to that at lower temperature peak decrease gradually as MA content increases. This is because VDC polymers have more than one crystalline structure, and there is also crystal grating defect in some crystalline structure. PVDC has relatively low crystal grating defect, resulting in that its strength of melting endothermic peak at lower temperature in much weaker than that at higher temperature. With increase in MA content, crystals grating defect of MA/VDC copolymers increase gradually due to MA chain segment with low symmetry and bulky side substitute (— COOH₃) hinder crystal growing; hence, their strengths of melting endothermic peak at higher temperature decrease progressively with increase in MA content. When MA content to a specified content, crystal phase of MA/VDC copolymer is mainly composed of unite cell with more crystal grating defect, causing only one melting endothermic peak in DSC heating scans.

This can be explained by the results of WAXD investigation for MA/VDC copolymers. Figure 3 is WAXD measurements for MA/VDC copolymers. PVDC has four types of crystalline structures. The

Table I The Melting Properties of PVDC and MA/VDC Copolymers

Sample	Polym. Temp. (°C)	Peak Number	Melting Endothermic Band 1		Melting Endothermic Band 2	
			Temp. (°C)	ΔH Fraction (%)	Temp. (°C)	ΔH Fraction (%)
PVDC	80	2	180	16.5	203	83.5
3% MA	80	2	172	57.0	187	43.0
5% MA	80	1	167	100		
7% MA	80	1	162	100		
10% MA	80	1	152	100		
3% MA	50	2	162	33.2	184	66.8
5% MA	50	2	156	59.7	171	40.3
7% MA	50	1	151	100		
10% MA	50	1	140	100		
3% BA	80	2	173	45.3	191	54.7
5% BA	80	2	170	72.6	180	27.5

diffraction angles (2θ) of the highest crystal diffraction intensities of four crystalline structures are, respectively, at 15.8, 24.5, 25.5, and 32.0°, and diffraction intensities decrease progressively with increase in diffraction angle. Except diffraction peak becoming broad and diffraction intensity becoming weak, WAXD cure of VDC copolymer with 3% MA is similar to that of PVDC. With increase in MA content, the number of the crystal diffraction peak of MA/VDC copolymer becomes three, the two diffraction peaks of the VDC copolymers at 24.5, 25.5° become one broad and weak. Furthermore, each WADX diffraction peak of VDC copolymers becomes broad, and the diffraction intensity becomes weak as MA content increases due to MA chain segment with low symmetry and bulky side substitute ($-COOCH_3$) hinder crystal growing.

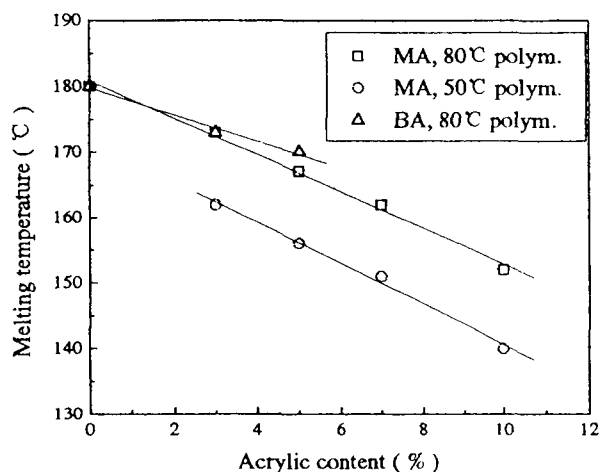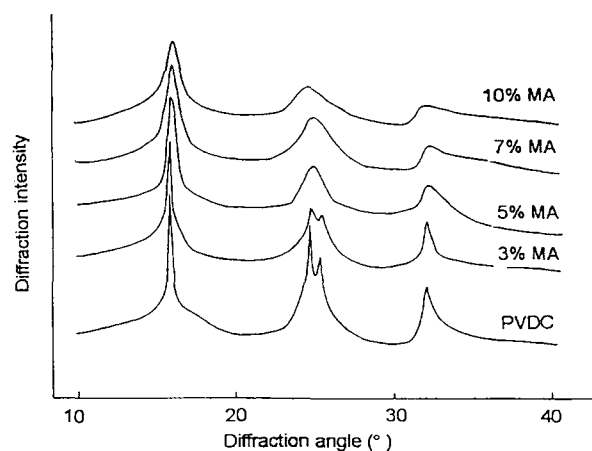Figure 4 is the plot of melting heat (ΔH) against acrylics content of VDC copolymers. The melting heat of MA/VDC copolymers is controlled by their crystalline fraction and crystalline structure. MA chain segment with bulky side substitute ($-COOCH_3$) hinders crystal growing and results in crystal grating defect and crystalline fraction lowering. As a result, the melting heats of MA/VDC copolymers decrease progressively with increase in MA content.

Figure 5 is TG runs of PVDC and VDC copolymers with 7% MA. The difference between their TG cures is subtle. TG cures of the other VDC/acrylics copolymers are similar to them. PVDC slight decomposes, gives out hydrogen chloride, and makes resin colors changing at below 200°C. VDC copolymer with 7% MA do almost not decompose below 210°C due to MA stabilization.

Figure 2 The plot melting temperature against acrylics content of VDC copolymers.

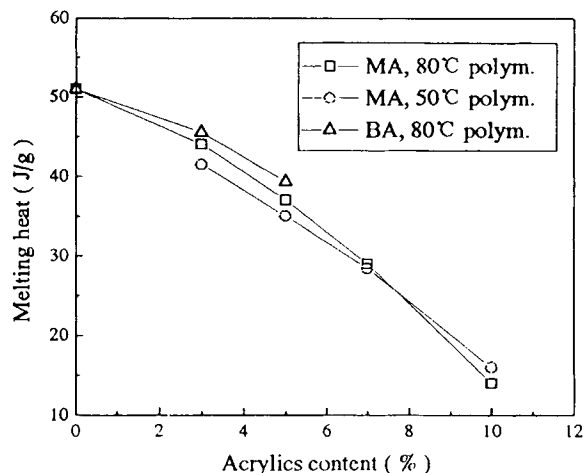**Figure 3** WAXD cures of MA/VDC copolymers.

Figure 4 The plot of melting heat (ΔH) against acrylis content of VDC copolymers.

Figure 6 The plots of thermal properties of VDC copolymers against MA content.

Figure 6 is the plots of thermal properties of MA/VDC copolymers versus MA content. T_{offset} and T_i are, respectively, the end temperature of melting endotherm and the start temperature of decomposition, and ΔT is their difference. The end temperatures of melting endotherm of PVDC and VDC/acrylics copolymers were determined by DSC measurements, and the start temperatures of decomposition were determined by TGA. The end temperatures of melting endotherm of MA/VDC copolymers decrease considerably with increase in MA content, and the start temperatures of decomposition of those increase slight as MA contents increase progressively. Consequently, the difference between the start temperature of decomposition and the end temperatures of melting endotherm increases grad-
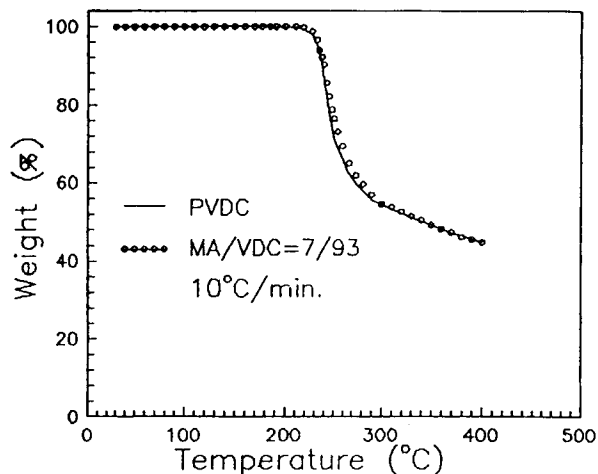
ually with increase in MA content and results in not only a processing temperature decrease but also the ranges of processing temperatures increase as MA content increase.

Comparison of BA/VDC Copolymers and MA/VDC Copolymers

Figure 7 is the plots of thermal properties of BA/VDC copolymers versus BA content. The effect of BA composition on the thermal properties of VDC copolymers is similar to that of MA composition. Processing temperatures of BA/VDC copolymers are considerably decreased gradually with increase in BA content, and the ranges of processing temperatures are greatly increased progressively as BA content increase.
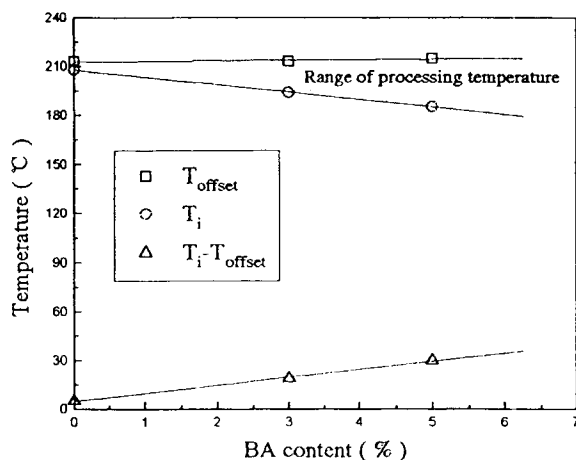

Figure 5 Thermogravimetry (TG) runs of PVDC and VDC copolymers with 7% MA.

Figure 7 The plots of thermal properties of VDC copolymers against BA content.

Table II is the comparison of MA/VDC copolymers thermal properties and BA/VDC copolymers thermal properties. BA/VDC copolymers have both higher crystalline fraction (determined by melting heat) and higher melting temperature than MA/VDC copolymers with same VDC content. These facts indicate that the ability of BA to impede crystal growing is weaker that of MA. The processability of BA/VDC copolymers is lower than that of MA/VDC copolymers with same VDC content. More BA than MA is needed to improve the processability of BA/VDC copolymers and VDC polymers. However, BA/VDC copolymers have higher gas and vapor permeability than MA/VDC copolymers.[5] In other words, MA is better comonomer for VDC copolymers, as barrier polymer materials, than BA.

Polymerization Temperature and Thermal Behavior of VDC/Acrylics Copolymers

From abovementioned experimental data and discussion, one can see that polymerization temperature has some effect on melting behavior of VDC/acrylics copolymers. MA/VDC copolymer with 7% has both favorable processability as abovediscussed and excellent barrier properties to oxygen and water vapor[6]; therefore, the effect of polymerization temperature on its thermal behavior was investigated in detail.

Figure 8 shows DSC heating scans of VDC copolymers with 7% MA prepared at various temperatures. Riser and Witnauer[7] reported that crystalline rate of VDC copolymers is increased with increase in temperature in the range of 50–80° with 7% MA.

MA/VDC system is where polymerization and crystallite take place at same time. The mobility of chain segment and crystalline rate of VDC copolymers with 7% MA are both increased as temperature results in that the crystal grating defect of the copolymers prepared at higher temperature is less than that at lower temperature. In other words, the normality of the crystal phase of the copolymers in-
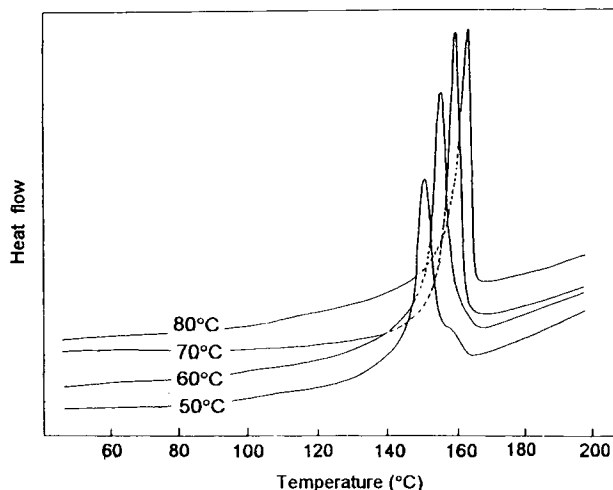

Figure 8 DSC heating scans of VDC copolymers with 7% MA.

crease with increase polymerization temperature. Hence, melting temperature of the copolymers increases as polymerization temperature increase at the temperature range of 50–80°C and can be described in eq. 1.

$$T_m = 0.3535T + 133.32°C \quad (T = 50\text{--}80°C) \quad (1)$$

where T_m and T are, respectively, the melting temperature of the copolymers and polymerization temperature.

Figure 9 plots of polymerization temperature against melting temperature, the onset temperature and offset temperature of melting endothermic peak, and the initiation temperature of MA/VDC copolymer decomposition. Although the onset temperatures of melting endothermic peak increase as polymerization temperature of MA/VDC increase, the offset of melting endothermic peak and the initiation temperature of MA/VDC copolymer decomposition are independent of polymerization temperature. Hence, the processing temperature and its range are independent of polymerization temperature. In other

Table II The Comparison of MA/VDC Copolymers Thermal Properties and BA/VDC Copolymers Thermal Properties

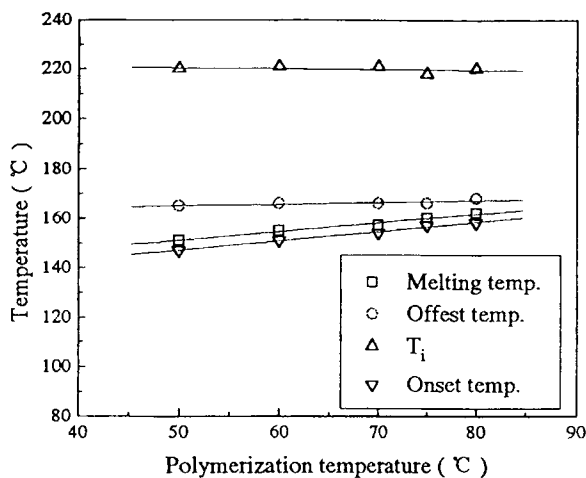| Sample	Polym. Temp. (°C)	Melting Heat (J/g)	T_{offset} (°C)	T_i (°C)	ΔT (°C)
PVDC	80	51	208	213	5
3% MA	80	45	190	213	23
5% MA	80	38.0	180	217	37
3% BA	80	46.5	195	213	18
5% BA	80	40.1	186	215	29

Figure 9 The plots of the thermal properties of VDC copolymers with 7% MA.

words, the processability of MA/VDC copolymers is almost not controlled by polymerization temperature.

CONCLUSIONS

VDC copolymers with 3–10% MA are semicrystalline polymers, and the crystal phases consist of more than one crystalline structure same as PVDC. VDC copolymers with low MA content have two melting endothermic peaks, and those with low MA content have only one melting endothermic peak. The melting temperatures of MA/VDC copolymers increase gradually as MA increases. The end temperatures of the melting endothermic peak of MA/VDC copolymers are considerably decreased with increase in MA content, whereas the decomposition temperatures of VDC copolymers are slightly increased gradually with increase in MA content. The processing temperatures of MA/VDC copolymers are gradually decreased with increase in MA content, and the range of processing temperatures of those is gradually increased as MA content increases. BA/VDC copolymers have lower processability than MA/VDC copolymers with same VDC content. The melting temperatures of VDC copolymers with 7% MA increase gradually as polymerization temperature increase in the range of 50–80°C, and their decomposition temperatures and offset temperatures are almost independent of polymerization temperature. The effect of polymerization temperature on the processability of VDC copolymers with 7% MA is relatively low.

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