

EFFECTS OF PHYSICAL CROSSLINKING ON PROPERTIES OF PLASTICIZED HIGH MOLECULAR WEIGHT PVC

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Abstract: A series of high molecular weight PVC (HMW - PVC) resin was synthesized by suspension process at various temperatures and compounded to prepare plasticized HMW - PVC. Plasticized HMW - PVC is physically crosslinked by microcrystallites and chain entanglements. The molecular weight and degree of crystallinity of PVC resin increase with decrease of polymerization temperature. More dense physical crosslinking networks are formed in plasticized PVC with the decrease of polymerization temperature of PVC resin. Plasticized HMW - PVC exhibits thermal reversible processability, but the gelation temperature and melt viscosity increase with increasing physical crosslinking density. Physical crosslinking also has great effects on the mechanical properties of plasticized HMW - PVC. The compression set and deformation decrease as molecular weight and crystallinity of PVC resin increase, but the softening temperature and tensile strength increase. The crosslinking network of plasticized HMW - PVC is more similar to the dissociable network of gels than to the permanent network of crosslinked rubber and is not stable under stretching at high stress.

Key words: PVC, physical crosslinking, molecular weight, crystallinity, chain entanglement, elasticity, processability

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INTRODUCTION

The mechanical properties of plasticized PVC are very strong even if the material is used well above its glass transition temperature (T_g). The flow and viscoelastic behavior are similar to that of a lightly crosslinked rubber. This has been the subject of much debate, but the most reasonable explanation is the presence of a physical crosslinking network consisting of microcrystallites (Brown et al., 1982; Ballard et al., 1987; Gilbert, 1994). However, conventional plasticized PVC has long been limited in its application in part. The limitations include low heat distortion temperature, poor elasticity, and extreme hardness dependence on temperature in comparison with crosslinked rubber (Brookman, 1988). This is caused by the lower physical crosslinking density of conventional plasticized PVC.

In order to improve the elasticity and the maximum application temperature of plasticized PVC, PVC can be chemically crosslinked by irradiation (Nethsinghe et al., 1988), polyfunctional nucleophile reagent (Hjertberg et al.,

1989) and silane (Kelner et al., 1993). The disadvantages of chemical crosslinking include acceleration of thermal degradation, decrease of processability or loss of thermal-reversible processability. Alternately, the elasticity and the maximum application temperature of plasticized PVC can be improved by using high molecular weight PVC (HMW - PVC) synthesized at low polymerization temperature (Brookman et al., 1993; Attwood et al., 1989). Plasticized HMW - PVC exhibits thermal-reversible processability and better elasticity properties than conventional plasticized PVC, which make it to be one kind of most important thermoplastic elastomers. Although there are many published patents on the synthesis and processing of HMW - PVC (Toyo Soda Mfg. Co. Ltd., 1985; Fukuda et al., 1987), the structure-property relationships of plasticized HMW - PVC were seldomly reported till now.

In this work, a series of HMW - PVC resins was synthesized at various polymerization temperatures, the nature of physical crosslinking in plasticized HMW - PVC and the influences of PVC structure on the properties of plasticized

HMW - PVC were investigated.

EXPERIMENTAL DETAILS

Synthesis of HMW - PVC resin

Suspension HMW - PVC resins were synthesized at various polymerization temperatures in a 5 - L autoclave by ourselves. Vinyl chloride monomer was of polymerization grade; Hydroxypropylmethylcellulose (HPMC, 65SH - 50) and partially hydrolyzed poly(vinyl alcohol) (PVA, KH20) were used as suspending agents; dicyclohexyl peroxy dicarbonate (DCPD) purified twice by methyl alcohol wash was used as initiator. The polymerization condition for synthesis of HMW - PVC resin is shown in Table 1.

Table 1 Polymerization conditions for synthesis of HMW - PVC resin

Code	Polymn. temp. (°C)	DCPD (g/1000g VC)	Polymn. time (h)	Conversion (%)
R1	25	12.85	7.0	79.5
R2	30	1.85	20.3	77.5
R3	35	1.62	16.2	73.8
R4	36	1.81	13.1	78.4
R5	37	1.80	11.6	79.6
R6	40	1.77	7.4	83.5
R7	42.8	1.85	6.7	83.2
R8	45	1.74	6.7	80.2

Other grades of HMW - PVC, such as P2500, P4000 were supplied by the Second Chemical Factory of Beijing, China. S1000 PVC used for comparison was supplied by the Qilu Petroleum Chemical Co. China.

Characterization of HMW - PVC

The degree of polymerization (DP) of PVC resin was calculated from the viscosity of its dilute solution in nitrobenzene according to the National Standard of China GB/T 5761 - 93:

$$[\eta] = \frac{\sqrt{2}}{c} \cdot \sqrt{\eta_{sp} - \ln \eta_r}$$

$$DP = 500 \{ 10^{[\eta]/0.168} - 1 \}$$

The degree of crystallinity (X_c) of PVC resin was measured using Perkin-Elmer 7 type DSC. PVC resin (6.0 ~ 8.0 mg) was stored in sample cell and heated at a rate of 20°C/min in a nitrogen atmosphere to limit degradation. X_c of the PVC resin was calculated according to the

following equation:

$$X_c = \frac{\Delta H}{\Delta H_u} \times 100\%$$

in which ΔH is the fusion enthalpy of partially crystalline PVC resin measured by DSC, and ΔH_u is the fusion enthalpy of perfect crystalline PVC ($\Delta H_u = 10.5$ cal/g, Patterson et al., 1982).

Compounding

HMW - PVC (100 parts) were mixed with tribasic lead sulfate (3.0 ~ 5.0 parts) as stabilizer, lead stearate (1.0 part) and stearic acid as lubricant (0.5 parts), and a certain amount of di-(2-ethylhexyl phthalate) (DOP) as plasticizer. The resulting mixture was milled using a mill with two mixing rollers to produce plasticized PVC. The processing temperature and time were selected according to the molecular weight of PVC and the amount of DOP added.

Rheological properties of plasticized HMW - PVC

The rheological behavior of plasticized HMW - PVC powder was measured by a System - 90 Haake torque rheometer. The initial temperature of the mixing chamber was 165 °C, the speed of rotors 50 rpm and the charge weight 65.0 g. The rheological behavior of plasticized HMW - PVC was also characterized in the capillary rheometer after the first processing. A capillary with L/D = 40 was used, the shear rate and apparent viscosity were calculated without entrance and exit correction.

Mechanical properties of plasticized HMW - PVC

Plasticized HMW - PVC samples were prepared by compression molding and used to test mechanical properties. Heat-deformation measurement was carried out to evaluate the heat resistance and dimension stability of the material. The penetration value of a loaded probe was recorded using an instrument made by ourselves. The tip of the probe was flat, had surface area of 7.07 mm², and weight of 244.5 g (0.34 N/mm²); the heating rate was about 2 °C. Dumbbell shaped tensile pieces were cut in accord with the National Standard of China GB1040 - 79 and tested using an electrical tensile strength testing machine. Five specimens from the same formulation were tested and the obtained results were average. Test temperature was controlled at

24.0 ± 1 °C. The compression set was measured according to the Japanese Standard JIS K - 6301 (70°C, 22h).

RESULTS AND DISCUSSIONS

The nature of physical crosslinking in plasticized HMW - PVC

Polymer can be physically crosslinked by hydrogen bonds, chain entanglements, microcrystallites, and so on. The physical crosslinking of plasticized PVC was ascribed to crystallinity by most researchers (Nakajima, 1981; Acosta et al., 1971). Chain entanglements contribute much to the physical crosslinking in the plasticized HMW - PVC, since the density of chain entanglements increases as the molecular weight of PVC increases. The X_c and DP of various PVC resins synthesized at different temperatures are shown in Table 2.

Table 2 shows that X_c and DP increase with decrease of polymerization temperature at the same time. It is general accepted that PVC crystallites are composed of syndiotactic segments (Gilbert, 1994). The probability of syndiotactic propagation of VC and syndiotacticity of PVC increase with decrease of polymerization temperature, which cause the increase of PVC resin X_c . On the other hand, PVC macromolecule radicals are mainly terminated by chain transfer to VC monomer and molecular weight of PVC is proportion to the reciprocal of the constant of chain transfer to monomer (C_M). C_M decreases and molecular weight increases as polymerization temperature decreases.

Table 2 Relationship between polymerization temperature and DP, X_c

Code	Polymn. temp. (°C)	DP	X_c (%)
R1	25	4914	11.00
R2	30	4044	10.18
R3	35	3069	9.62
R4	36	2910	—
R5	37	2753	—
R6	40	2253	9.34
R7	42.8	1980	—
R8	45	1775	9.07
S1000	≈ 57	985	7.93
P2500	≈ 38	2452	9.16
P4000	≈ 30	3945	10.6

The crystallinity in plasticized PVC was revealed by many investigators and was more complicated than PVC resin (Nakajima, 1981; Acosta et al., 1971; Bao et al., 1996). A part of the primary crystallites formed in the polymerization process will be fused during processing and re-crystallized to form secondary crystallites during cooling and storage. The secondary crystallites had noticeable effects on the formation of physical crosslinking of plasticized PVC. It shows that the crystallinity in plasticized PVC was influenced by the content of the plasticizer, processing temperature and time, cooling rate, and thermal treatments. More secondary crystallites were formed as the PVC molecular weight increased (or polymerization temperature decreased) (Bao et al., 1996).

Chain entanglements can be formed when the molecular weight of polymer exceeds the critical molecular weight for chain entanglements (M_{cr}). M_{cr} of PVC is about 6250 g/mol (Aharoni, 1986), General purpose PVC and HWM - PVC commonly form chain entanglements. A real polymer chain is composed of a number of Kuhn segments with length of l_k . The Kuhn chain is a random-flight chain. The joint between two continuous Kuhn segments is defined as the Kuhn node, which is a random-flight joint. Chain entanglements can only be formed at the Kuhn node points and the density of chain entanglements is proportional to the square of the number of Kuhn nodes. The number of Kuhn nodes increases as the molecular weight of PVC increases; the density of the chain entanglements increases then. The introduction of plasticizers to HMW - PVC will cause disentanglements of some chains. On the other hand, the mobility of PVC chains will increase as PVC is plasticized, which will favor formation of new chain entanglements.

According to the above results and discussion, a model of physical crosslinking in plasticized HMW - PVC is proposed and shown in Fig. 1.

In the above model, X presents the microcrystallite crosslinks, Y and Z present the trapped and temporary chain entanglements respectively. Trapped entanglements can only be disentangled after the fusion of microcrystallites and contribute more to the physical crosslinking, while the temporary entanglements are easy to be

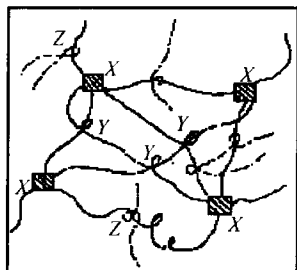


Fig. 1 The structure model of physical crosslinking of plasticized HMW - PVC

disentangled and contribute less to the physical crosslinking. Plasticized HMW - PVC exhibits low T_g , high chain mobility and has physical crosslinking networks consisting of microcrystallite and chain entanglements, so it displays rubber-like viscoelasticity at room temperature.

Effects of physical crosslinking on the rheological behavior of plasticized HMW - PVC

The rheological behavior of PVC is quite different from that of other polymers due to its special particle structure. Both gelation and melt flow behavior are important for study. The gelation behavior of plasticized PVC powder was determined by torque rheometer. Several parameters, such as the gelation time, maximum and equilibrium torque, gelation temperature are used to characterize the gelation character of plasticized PVC. The results are shown in Table 3. It can be seen that the gelation time, maximum

Table 3 Gelation parameters of different plasticized HMW - PVC (DOP = 50 phr)

Code of PVC	Gelation time (s)	Maximum torque (N·m)	Equilibrium torque (N·m)	Gelation temperature (°C)
S1000	12	14.35	5.72	172
R8	67	12.77	8.38	176
R7	120	12.84	9.31	177
R6	129	13.79	10.16	178
P2500	258	12.87	11.27	178
R5	300	12.91	12.15	179
R4	489	13.65	12.63	180

um and equilibrium torque, gelation temperature of plasticized PVC increase with molecular weight and crystallinity of PVC resin increasing. The gelation of PVC is a complicated process, including the breakage of PVC grains, agglomerates and primary particles, and the fusion of microcrystallites and disentanglements. More time and heat energy are required for gelation of plas-

ticized PVC as the molecular weight and crystallinity increase, which leads to the increase of gelation time and temperature. On the other hand, the microcrystallite and chain entanglements will not be wholly destroyed by processing, the physical crosslinking will partially remain in the PVC melt. For plasticized PVC, the melt viscosity increases with increase of molecular weight and crystallinity.

The melt flow behavior of plasticized HMW - PVC was characterized by the capillary rheometer. The dependence of shear rate ($\dot{\gamma}$) and apparent viscosity (η_a) on the shear stress (τ) for different plasticized HMW - PVC were obtained and shown in Fig. 2 and Fig. 3.

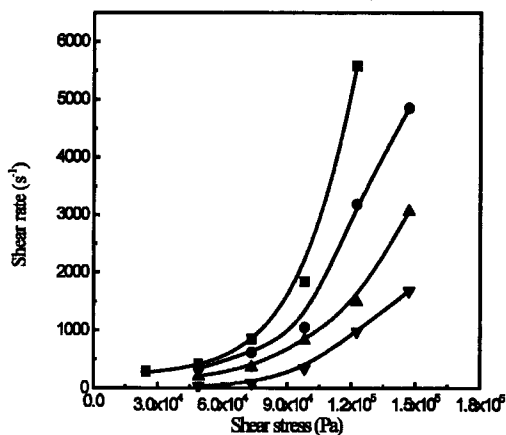


Fig. 2 $\tau \sim \dot{\gamma}$ relationships for different plasticized HMW - PVC (DOP = 80 phr, 190 °C)
■ R6; ● P2500; ▲ R3; ◆ P4000

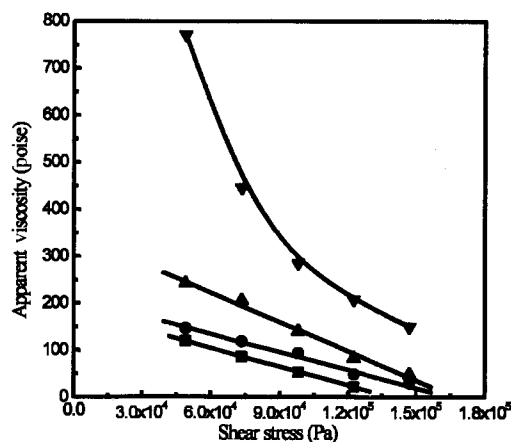


Fig. 3 $\tau \sim \eta_a$ relationships for different plasticized HMW - PVC (DOP = 80 phr, 190 °C)
■ R6; ● P2500; ▲ R3; ◆ P4000

It can be seen that γ increases and η_a decreases with the increase of τ for the same plasticized HMW - PVC and that γ decreases and η_a increases with the increase of molecular weight and crystallinity of PVC at the same τ . The density of residual physical crosslinking in plasticized HMW - PVC melts increases as molecular weight and crystallinity of PVC increase.

It can be concluded that physical crosslinking has great influences on the rheological behavior of plasticized HMW - PVC, and that plasticized HMW - PVC becomes more difficult to process as the molecular weight and crystallinity increase, but its processability is thermal reversible.

Effects of Physical Crosslinking on Mechanical Properties of Plasticized HMW - PVC

The mechanical properties of plasticized HMW - PVC, including the compression set, heat-deformation and tensile properties, are investigated in this study.

The compression set value can be used to evaluate the elasticity of plasticized HMW - PVC. The lower the compression set value, the better the elasticity. Fig. 4 presents the dependence of compression set on the molecular weight of PVC. It can be seen that the compression set decreases as molecular weight of PVC increases. The recoverable character from deformation can be taken as evidence that plasticized HMW - PVC has a network structure. The more dense physical crosslinking network can be formed as molecular weight and crystallinity of PVC increase, thus, the recover ability and rate are im-

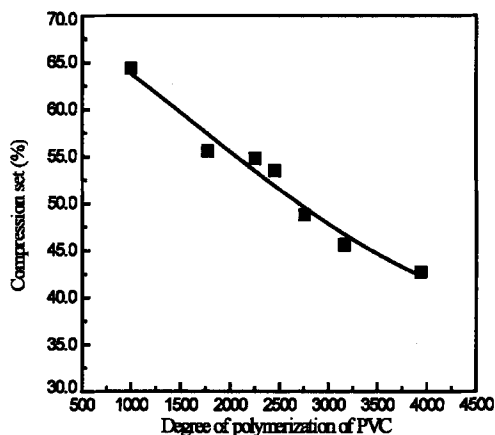


Fig. 4 Effect of DP on the compression set of plasticized PVC (DOP = 80 phr)

proved.

Heat-deformation behavior reflects the resilience, deformation resistance, hardness dependence on temperature of plasticized HMW - PVC. Heat-deformation curves for different plasticized PVC are shown in Fig. 5. It shows that the deformation (penetration) increases gently with the increase of temperature at lower temperature stage, but increases rapidly when temperature exceeds a critical value. This temperature is defined as the softening temperature (T_{soft}) of plasticized PVC and can be related to the maximum application temperature of plasticized PVC. It also shows that the penetration value decreases with the increase of molecular weight and crystallinity of PVC, since a more dense physical crosslinking network is formed for higher molecular weight and crystallinity PVC.

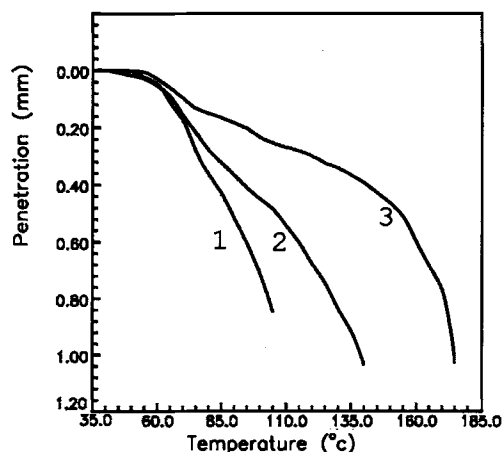


Fig. 5 Heat-deformation curves for different plasticized PVC (DOP = 80 phr)
1. S1000, 2. P2500, 3. P4000

In order to illustrate the influence of microcrystallite crosslinking on the heat-deformation behavior of plasticized HMW - PVC, plasticized P2500 PVC was annealed at 75 °C and 100 °C for about 1 h before the heat-deformation measurement respectively. The influences of annealing treatment on the heat-deformation behavior is shown in Fig. 6. It can be seen that the penetration value of annealed plasticized PVC increases slowly before a transition temperature and increases rapidly after this temperature. The transition temperature is higher than annealing temperature for about 15 °C. It showed that the microcrystallites formed in annealing treatment were fused at temperature higher than annealing tem-

perature for about 15 °C (Bao et al., 1996). So it can be concluded that the transition temperature is the melting temperature of microcrystallite formed at annealing treatment. Microcrystallite crosslinking has great effect on the heat-deformation behavior of plasticized HMW - PVC.

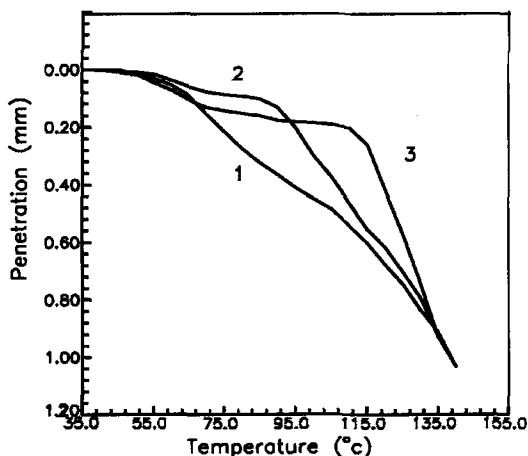


Fig. 6 Heat-deformation curves for plasticized P2500 PVC (DOP = 80 phr)
1. No annealing, 2. Annealing at 75 °C,
3. Annealing at 100 °C

The typical stress-strain curves of plasticized PVC shown in Fig. 7 resemble those of rubber and thermoplastic elastomer, and have the characteristics of a three-dimensional network. Effects of molecular weight of PVC on the tensile strength of plasticized HMW - PVC are shown in Fig. 8.

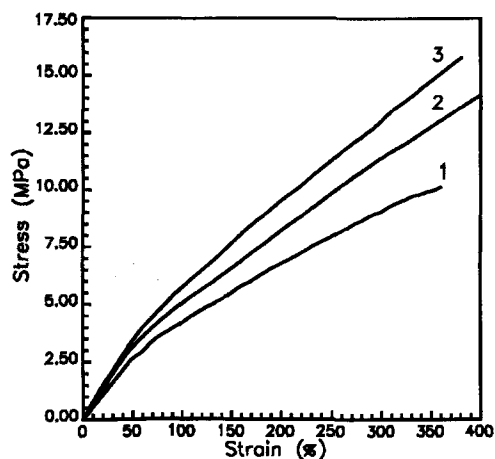


Fig. 7 The stress-strain curves for different plasticized PVC (DOP = 80 phr)
1. S1000, 2. P2500, 3. P4000

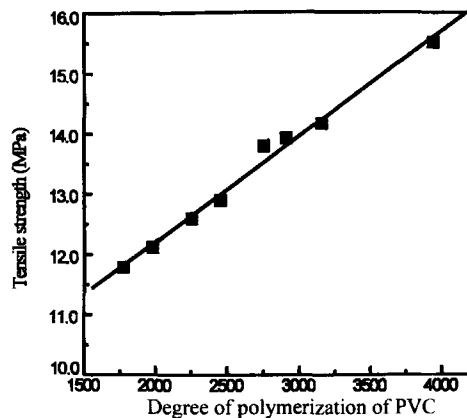


Fig. 8. Effect of DP of PVC on the tensile strength of plasticized HMW - PVC (DOP = 80 phr)

It can be seen that the tensile strength increases as molecular weight of PVC increases. It was found that the tensile strength of crosslinked rubber increased with the increase of molecular weight, followed by a leveling off to an equilibrium value (Pezzin et al., 1968). The different tensile strength-molecular weight relationships of plasticized PVC and crosslinked rubber are resulted from the nature of the crosslinking network. The physical crosslinking network of plasticized PVC is more similar to the dissociable network of gels than to the permanent network of rubber. The network crosslinks (microcrystallites or entanglements) of plasticized PVC are not stable under stretching at higher stresses.

CONCLUSIONS

High molecular weight PVC (HMW - PVC) resin was prepared at low polymerization temperature in the suspension process. It shows that molecular weight and degree of crystallinity of PVC resin increase as polymerization temperature decreases. The physical crosslinking of plasticized HMW - PVC is contributed by microcrystallites and chain entanglements. The physical crosslinking density increases with increase of the molecular weight and crystallinity of PVC resin. Physical crosslinking networks have great effects on the processability, elasticity, heat-deformation and tensile properties of plasticized HMW - PVC. The gelation temperature and melt viscosity of plasticized HMW - PVC increase with the increase of physical crosslinking density. The compression set and deformation de-

crease with increase of molecular weight and crystallinity of PVC. On the contrary, the softening temperature and tensile strength increase with the increase of molecular weight and crystallinity of PVC. The results can be interpreted by the great effect of physical crosslinking as molecular weight and crystallinity of PVC increase.

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