

Crosslinking of Poly(Vinyl Chloride) with Bismaleic Compound. II. Rheological Behavior and Mechanical Properties of Crosslinked PVC

DAFEI ZHOU and MINWEI CHEN*

Box 289, East China University of Chemical Technology, Shanghai 200237, People's Republic of China

SYNOPSIS

In this study the rheological behavior of crosslinking PVC was studied. We carefully probed the effects of styrene and initiators on crosslink course and further verified PVC's crosslink mechanism suggested previously. St as auxiliary crosslinker was very important for PVC crosslink, no matter whether at lower temperature or at higher temperature, in the absence of initiator or in the presence of initiator. With higher decay temperature cumyl hydroperoxide (CHP) was a very appropriate initiator for PVC crosslinking. By controlling technological conditions, the crosslinked PVC with different cross density was obtained. We found that PVC with THF-insoluble fraction of about 7% had the best tenacity and maximum breaking energy. The tensile strength would increase as the gel-fraction content increased. By citing T. Kurauchi's ROF toughening theory, we satisfactorily explained the good ductility of crosslinked PVC with low cross density and the high fragility of over-crosslinked PVC. Because the motion of segments is hindered in thoroughly crosslinked PVC, its glass transition was so weak that we hardly found out T_g .

INTRODUCTION

Rheology of crosslinking poly(vinyl chloride) (PVC) is a new research area. By means of rheocord, we can study the crosslink courses and crosslinking mechanism of molten polymers. The theoretical basis is the Fox-Flory formula:

$$\eta_0 = K\bar{M}_w^\alpha \quad (1)$$

When shear rate ($\dot{\gamma}$) is very small,

$$\eta \approx \eta_0 = K\bar{M}_w^\alpha \quad (2)$$

For Rheocord System 40 employed in our experiments, the determined torque (TQ) is proportional to viscosity of molten poly mers:

$$\text{TQ} \propto \eta \approx K\bar{M}_w^\alpha \quad (3)$$

$$\text{TQ} \propto K\bar{M}_w^\alpha \quad (4)$$

Based on Eq. (4) we can trace the changes of PVC molecular weight in crosslinking by determining its melting viscosity.

Due to the formation of network structure, crosslinked PVC will have very different thermomechanical properties than uncrosslinked. Kurauchi and Ohta¹ suggested that rigid organic filler (ROF) could toughen ductile polymers, and ROF had the best toughening effect when ROF adhered very well with base polymer, even the strain of ROF could reach 400%. Based on Mises equation, $(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2 = 6k^2$, Inoue et al.^{2,3} replenished Kurauchi's theory. They suggested that the smaller ROF size, the better toughening effect. When ROFs approached infinity, the toughening effect would disappear, i.e., the overincrease of ROF's number and size was disadvantageous for toughening.

* To whom correspondence should be addressed. Present address: Chemical Engineering Department, Clarkson University, Potsdam, NY 13699, USA.

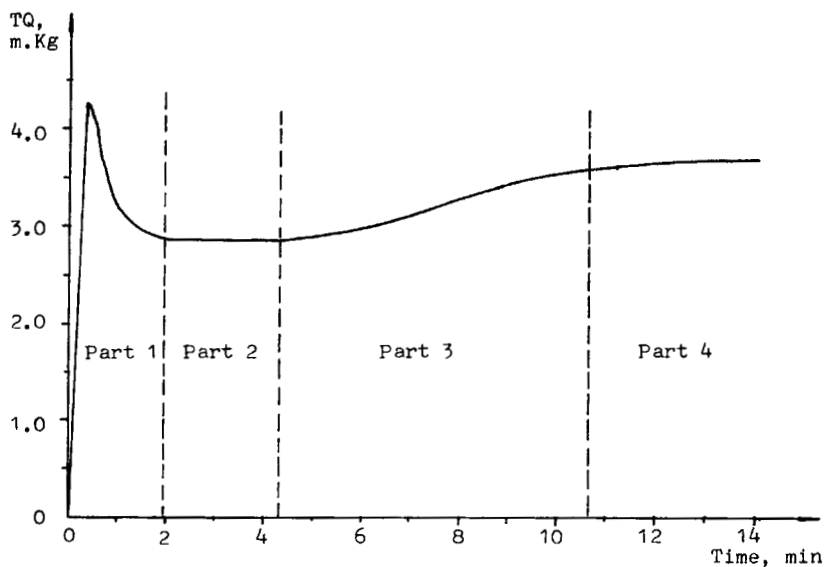


Figure 1 Rheological Behavior of Crosslinking PVC with St and 0.25% DCP at 170°C.

EXPERIMENTAL

Materials

All reagents and starting materials used were reagent grade and were used without any other purification.

Preparation of Samples

Samples of 100 phr PVC, 5 phr stabilizer (3PbO·PbSO₄·H₂O), and 6 phr BMC were well

mixed for rheological analysis by ball grinder. Samples for tensile measurement were prepared by molding homogeneously mixed PVC compound at 185°C for 12 min. The crosslinked PVC used in DSC was THF-insoluble.

Measurements

HaakeBuchler Rheocord System 40 accompanied by Rheomix 600 was employed to determine the vis-

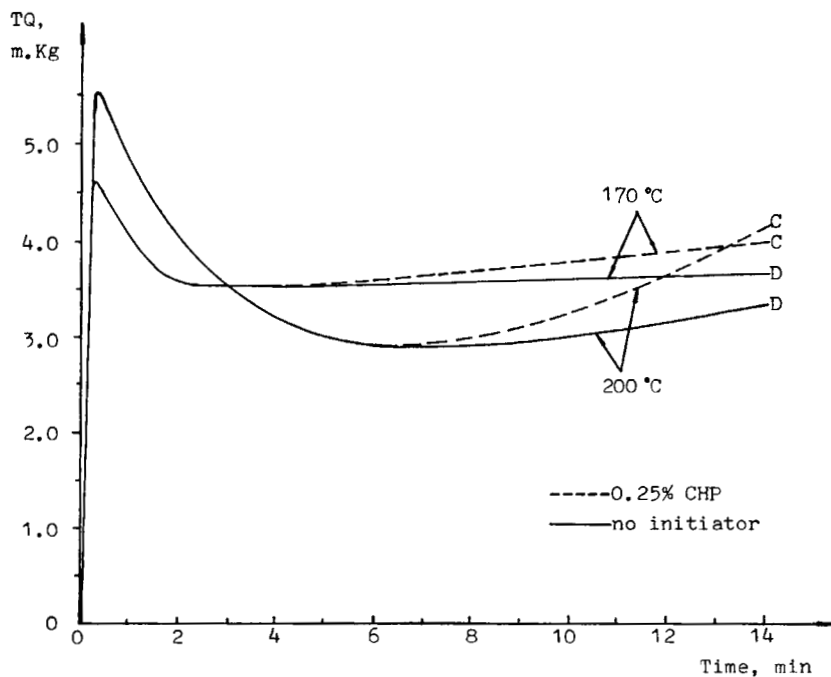


Figure 2 Rheological behavior of PVC in the absence of St.

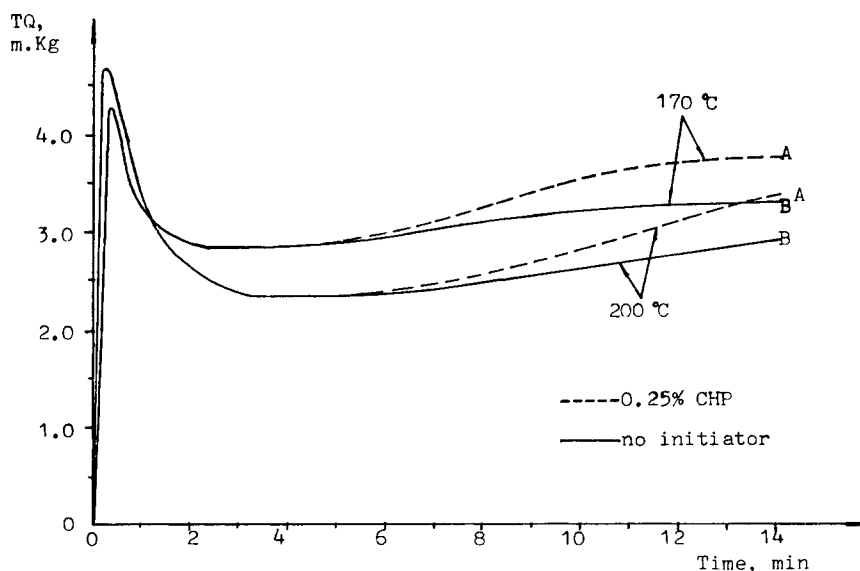


Figure 3 Rheological behavior of PVC in the presence of St.

cosity of molten PVC in crosslinking with low shear rate (rotational speed of rotor: 40 rpm). DuPont 1090 Interactive DSC was used to the thermal analysis of crosslinked PVC. The mechanical properties of crosslinked PVC were measured by means of AGA-2000 (Shimadzu, Japan).

RESULTS AND DISCUSSION

Rheological Behavior of PVC in Crosslinking

According to Fox-Flory formula [Eq. (2)], the viscosity of molten PVC will increase as the combination of PVC chains in the crosslinking course. Figure 1 shows the typical rheological behavior of PVC in crosslinking.

The rheological curve can be divided into four parts: melting section, equilibrium section, viscosity-increasing section; and PVC chain-broken section. Crosslinking reaction mainly takes place in the third part.

In part 2, M_w of PVC increases very little. This phenomenon can be explained as follows:

1. A lot of newborn PVC macroradicals and monomer radicals were most probably eliminated by foreign substances, i.e., induction period exists in crosslink of PVC.

2. In this part the dominant reaction is the produce of PVC macroradicals and grafting of BMC on PVC.

In the fourth section the increase of viscosity tends to slow down. It is because crosslinked PVC

chains will be broken by mechanical force and friction heat. In this section, TQ- t curve no longer reflects the crosslink course. Thus, we only study the rheological behavior of PVC in the third section.

Effects of St on Rheological Behavior

We have known that St can markedly promote the crosslink course of PVC, which is also confirmed by the rheology of crosslinking PVC (compare Figs. 2 and 3).

Comparing column A with column B, column C with column D of Table I, we can obtain a conclusion that DCP's existence will accelerate PVC crosslinking course. In the absence of St, temperature has a marked effect on PVC crosslink, which indicates that a part of PVC macroradicals is contributed by thermal degradation of PVC. In the presence of St, temperature has a very slight effect on crosslink of PVC. At this time a large portion of PVC macro-

Table I $(TQ)_{11}/(TQ)_{\text{equil}}$ of Molten PVC at Different Situation^a

Curve Mark ^b	A	B	C	D
170°C	1.27	1.14	1.07	1.00
200°C	1.28	1.15	1.18	1.06

^a $(TQ)_{11}$ means the torque of molten PVC at 11 min. $(TQ)_{\text{equil}}$ is the torque of molten PVC in equilibrium section.

^b It corresponds to Figs. 2 and 3.

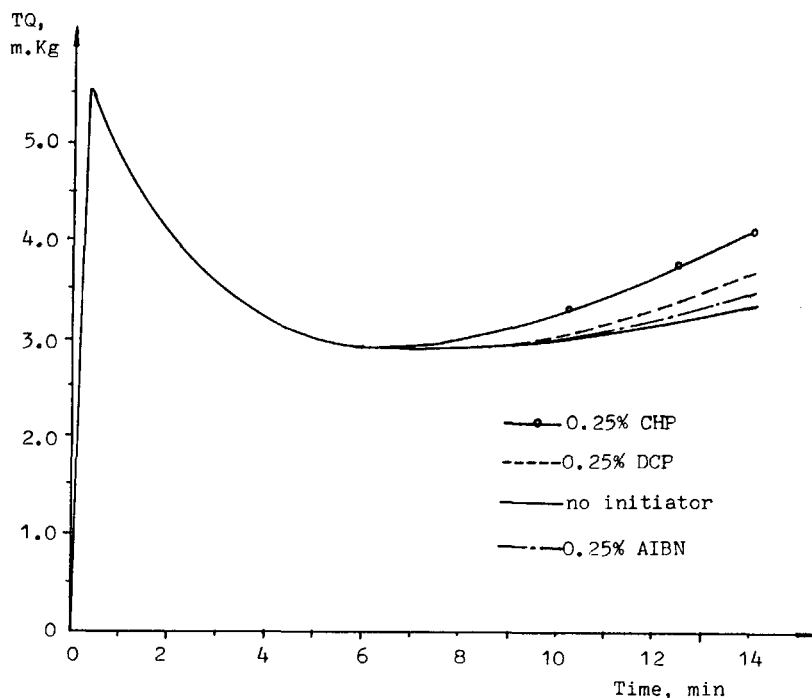


Figure 4 Effects of initiators on rheological behavior of PVC at 200°C (crosslinker: BMC; without St).

radicals is contributed by a disproportionate amount of St radicals and initiator radicals with PVC. The contribution of thermal degradation of PVC may be

omitted. All these experimental results satisfactorily support our previous crosslink mechanism.

As to the roles of St in PVC crosslinks, we can

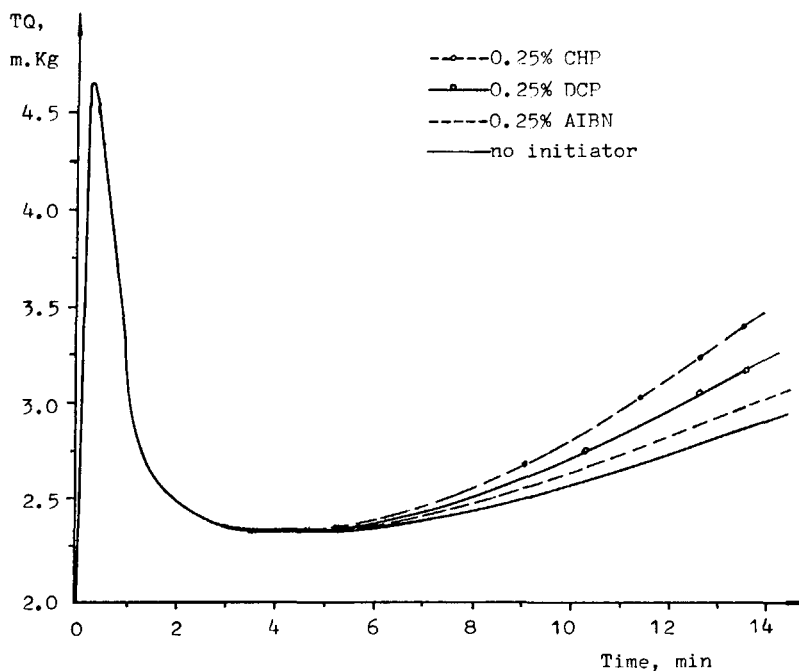


Figure 5 Effects of initiators on rheological behavior of PVC at 200°C (crosslinker: BMC; in the presence of St).

Table II $(TQ)_{14}/(TQ)_{\text{equil}}$ of Molten PVC at 200°C

Initiator	Without St	With St
CHP	1.40	1.45
DCP	1.25	1.35
AIBN	1.18	1.30
None	1.14	1.25

say that St is very important for PVC crosslink reaction, no matter whether at 170 or at 200°C, in the absence of DCP or in the presence of DCP. Styrene as auxiliary crosslinker to enhance BMC's grafting on PVC* is always very important.

Effects of Initiators on Rheological Behavior

As the source of radicals, initiators play an important part in the crosslink of PVC, particularly in the absence of St and at lower temperature. Figures 4 and 5 indicate that effectiveness of initiators is $\text{CHP} > \text{DCP} > \text{AIBN}$. CHP is a high-temperature initiator. It has longer semidecay period (about 25 min at 200°C) than DCP, which has longer semidecay period (about 2 min at 200°C) than AIBN (ca. several seconds at 200°C). In the meantime we find that PVC can crosslink at high temperature even

though without St and initiators, which further verifies our previously raised crosslink mechanism that PVC will degrade into PVC* by heat and mechanical shearing, and PVC* will react with BMC to form network structure.

From the value of $(TQ)_{14}/(TQ)_{\text{equil}}$, we find that St makes initiators more unimportant, and CHP makes St more unimportant (Table II). According to our previous work, St and initiators only contribute a part of radicals at high temperature, respectively. Thus, in the presence of St, effects of initiators on crosslink speed are little than that in the absence of St (see columns 2 and 3 in Table I). In the presence of CHP, effects of St on crosslink speed are less than effects without any initiator (compare rows 2 and 5 in Table II). Because AIBN is a low-temperature initiator, it decays very fast at 200°C. Therefore, the effect of St on crosslink will be clearer in the presence of AIBN than in the presence of CHP.

Tensile Strength and DSC Analysis of Crosslinked PVC

We know that excessively crosslinked PVC is unpractical because of its fragility. Only when PVC has a definite cross density, PVC has excellent mechanical properties. Experimental results indicated

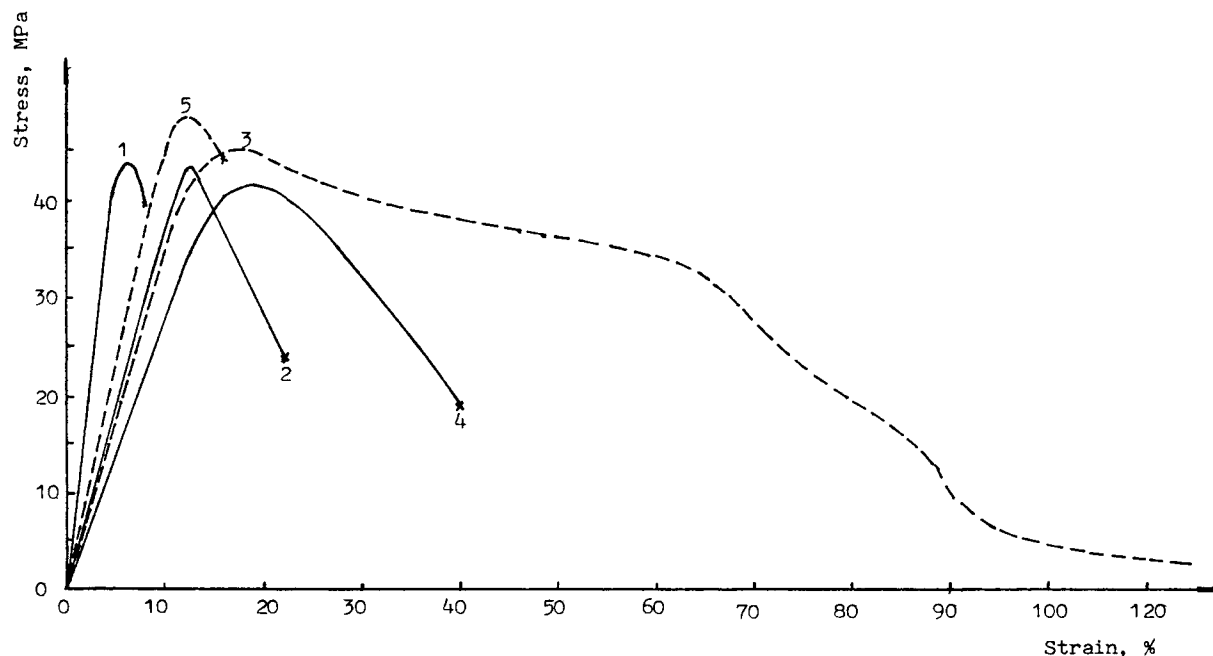


Figure 6 Stress-strain curves of PVC with different gel-fraction content, 1—0%; 2—4.10%; 3—7.05%; 4—13.75%; 5—58.38%.

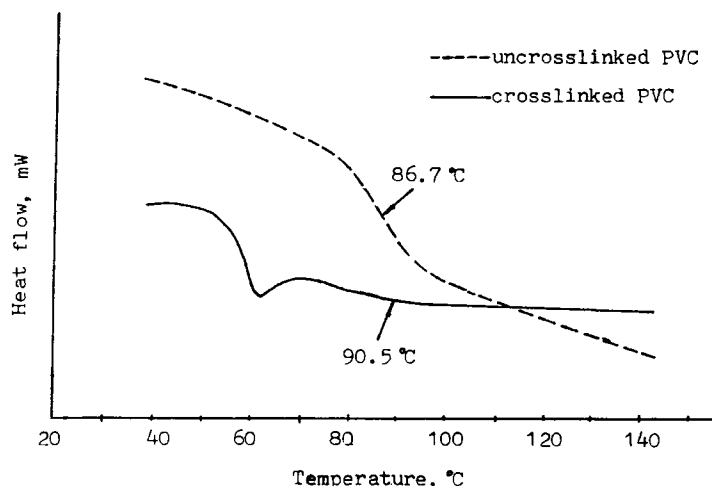


Figure 7 DSC curves of PVC.

that many factors, such as crosslink time, temperature, initiators, and the dosage of crosslinker and auxiliary crosslinker, affected crosslink speed and cross density of PVC. So we can obtain practical products through controlling ingredient dosage and technological conditions.

Crosslink can slightly increase tensile strength of PVC (see Fig. 6), and when the gel-fraction content is 7.05%, crosslinked PVC has the best tenacity and largest breaking energy. According to ROF (rigid organic filler) toughening theory raised by Kurauchi, and Ohta, the brittle polymer particles dispersed in ductile polymers can toughen base polymer. In the present system the crosslinked part mainly consisting of BMC, St, and a few PVC segments can be regarded as ROF that is well-dispersed in PVC. Inoue et al.^{2,3} pointed out that the smaller the size of ROF, the better the effect of toughening.

When the gel-fraction is less than 5%, ROF is too few to appear its toughening effect.

When PVC has appropriate cross density (gel-fraction: about 7%), the size of ROF is very small, and the number of ROF is enough to reflect its toughening effect.

When cross density is too high (gel-fraction > 50%), the size of ROF becomes too large to give any play to toughening PVC. If PVC is thoroughly crosslinked, it will be too fragile to be used as structure material.

The DSC curve of crosslinked PVC displays that the motion of PVC segments is hindered by crosslink structure, and T_g (90.5°C) is higher than original PVC (86.7°C) (Fig. 7). The glass transition tends to disappear.

CONCLUSIONS

By having studied rheological behavior of crosslinking PVC, we further verified the crosslink mechanism raised in our previous study. Styrene is a very effective auxiliary crosslinker in crosslink of PVC. It can markedly promote crosslinking proceeding. As a high-temperature initiator, CHP is a very suitable initiator for PVC crosslinking. After having been crosslinked, PVC will have very different thermomechanical properties from original PVC. Based on ROF toughening theory, we have satisfactorily explained why the PVC with gel-fraction content of about 7% has the best tenacity and maximum breaking energy. When PVC is thoroughly crosslinked, it is so fragile that it cannot be used as structure materials. Its glass transition tends to disappear.

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REFERENCES

1. T. Kurauchi and T. Ohta, *J. Mat. Sci.*, **19**, 1699-1709 (1984).
2. K-K Koo, T. Inoue, and K. Miyasaka, *J. Polym. Eng. Sci.*, **25**, 741 (1985).
3. J. C. Angola, Y. Fujita, T. Sahai, and T. Inoue, *J. Polym. Sci. Polym. Phys.*, **26**, 807-816 (1988).

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