Peroxide Crosslinking of Rigid Poly(vinyl chloride)

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ABSTRACT: The optimum conditions for crosslinking rigid poly(vinyl chloride) with trimethylolpropane trimethacrylate (TMPTMA) and peroxide have been examined. The extent of crosslinking was measured by determining gel content by Soxhlet extraction in tetrahydrofuran. Mechanical properties were measured at 130°C and dynamic viscoelastic measurements were carried out to detect changes in the glass transition temperature (T_g). It was found that 15 phr of TMPTMA and 0.3 phr of peroxide were optimum concentrations for maximizing the extent of crosslinking, tensile strength, and T_g. The lower molding temperature of 170°C was preferred to minimize thermal degradation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2904–2909, 2007

Key words: poly(vinyl chloride); peroxide; crosslinking; mechanical properties; trimethylolpropane trimethacrylate

INTRODUCTION

Crosslinking of poly(vinyl chloride) (PVC) and other thermoplastics has long been used as an effective way of improving mechanical properties at elevated temperatures. For example, radiation crosslinking of plasticized PVC in the presence of polyfunctional monomeric additives has been employed in the manufacture of wire and cable insulation to improve strength and abrasion resistance.[1] Of the various polyfunctional monomers used in these systems, methacrylates and acrylates were found to be the most efficient.

More recently, chemical crosslinking of PVC has been investigated. Hydrolytic crosslinking using either mercapto- or aminosilane grafted onto PVC has been successful in plasticized formulations.[2–6] However, good results are harder to achieve in rigid PVC systems. Kelnar and Schatz[7,8] have studied the crosslinking of rigid PVC using mercaptosilane. Although a high crosslinked density could be achieved, it was found to be a much slower process than crosslinking of plasticized PVC. This is because of the reduced rate of permeation of water in rigid PVC compared with plasticized PVC and hence a slower hydrolysis reaction. Aminosilane crosslinking of rigid PVC has been investigated by Gilbert and Garcia-Quesada.[9] They reported a significant improvement in tensile strength above the glass transition temperature, but also found deterioration in thermal stability. This is due to the reactivity of the amine group in abstracting HCl and hence initiating dehydrochlorination.

The use of peroxide for crosslinking rigid PVC has been studied by Garcia-Quesada and Gilbert.[10] They added a trifunctional monomer trimethylolpropane trimethacrylate (TMPTMA) to the PVC. TMPTMA has the formula $CH_3CH_2C(CH_2—O—CO—CCH_3=CH_2)_3$ and is compatible with PVC. It has been used extensively in previous studies of radiation crosslinking of PVC[1,11] and found to be highly effective. During peroxide crosslinking, elevated temperature is required to initiate the reaction. The TMPTMA undergoes rapid polymerization followed by grafting on to the PVC chains and subsequent crosslinking. In their studies, Garcia-Quesada and Gilbert found that as little as 0.5 parts of peroxide per hundred parts of PVC (phr) gave significant property improvements. However, there was found to be evidence of thermal degradation.

The current study aims to investigate the optimum formulation and processing temperature for producing peroxide crosslinked PVC using TMPTMA as the trifunctional monomer. The resulting polymers have been characterized in terms of their crosslinked density, color, glass transition temperature, and tensile properties. The optimum conditions are determined to maximize crosslinked density and tensile strength, while minimizing thermal degradation.

MATERIALS AND PROCESSING

The formulations used in this study are shown in Table I. Concentrations are expressed as parts per hundred parts of resin (phr). The PVC resin was suspension grade Evipol SH6030, supplied by Ineos Vinyls, and

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TABLE I
Formulations

Chemical type	Ingredient	Concentration [Parts per hundred parts of polymer (phr)]
Poly(vinyl chloride)	Evipol SH6030	100
Thermal stabilizer	Tribasic lead sulfate	7
Acrylic processing aid	Paraloid K120N	1.5
Lubricant – Fatty alcohol	Loxiol G53	1.2
Lubricant – Fatty alcohol	Loxiol G52	0.4
Lubricant – Poly(ethylene) wax	Hoechst PE 190	0.2
Tri-functional monomer	TMPTMA	0, 5, 10, 15 (According to plan)
Peroxide	Trigonox 29-C75	0, 0.3, 0.6 (According to plan)

has a *K*-value of 60. The molecular weight of PVC is expressed in terms of its *K*-value, which is a measure of the relative solution viscosity of the polymer. A *K*-value of 60 is equivalent to a weight–average molecular weight of about 64,000.[12] The thermal stabilizer used was tribasic lead sulfate (TBLS). The acrylic processing aid, Paraloid K120N, was supplied by Rohm and Haas. The lubricants used were fatty alcohols, Loxiol G52 and G53, from Echem and a poly(ethylene) wax, PE 190, from Hoechst. The trifunctional monomer, trimethylolpropane trimethacrylate (TMPTMA), was supplied by Degussa. The peroxide used was Trigonox 29-C75 from Akzo Nobel, which is (1,1-di(*t*-butylperoxy)-3,3,5-trimethyl cyclohexane), containing 75% peroxide.

The amount of peroxide and trifunctional monomer added to each formulation was varied according to the experimental plan shown in Table II. There were 10 different formulations. Also shown in Table II is the pressing temperature of the compression molding process of either 170 or 190°C. Hence there were 20 different trials altogether.

The dry blends were prepared in a laboratory-scale Fielder mixer. All components (except peroxide and TMPTMA) were added to the mixer at a temperature of 50°C and mixed at 2000 rpm. The peroxide and TMPTMA were added when the temperature reached 80°C, and blending continued until the temperature reached 120°C. At this point, the mixture was discharged into the cooling chamber.

The dry blends were processed on a twin roll mill for 5 min, with the roll temperatures set at 140°C. The sheets produced were compression-molded under a hydraulic pressure of 20 tons for 5 min at the appropriate pressing temperature, according to the experimental plan (Table II).

PHYSICAL AND MECHANICAL PROPERTY MEASUREMENTS

Gel content

The amount of crosslinked PVC (or gel content) was determined by Soxhlet extraction for 24 h using tetrahydrofuran (THF) as a solvent. THF was removed from the residue by drying the cellulose extraction thimble for 8 h at 100°C. The gel content was calculated as the percentage of dried sample remaining after extraction.

Color

The color of the crosslinked PVC samples was measured using a microcolorimeter. Reflected light is split into three components via an optical wave-guide and routed to three standard measurement filters. In this case, the color measurement of interest was the *b** value, which describes the yellow to blue scale (+ to −).

Glass transition temperature

The glass transition temperature (T_g) of each formulation was measured using dynamic mechanical ther-

TABLE II
Experimental Plan

Trial	TMPTMA concentration (phr)	Peroxide concentration (phr)	Pressing temperature (°C)
1	0	0	170
2	5	0	170
3	10	0	170
4	15	0	170
5	5	0.3	170
6	10	0.3	170
7	15	0.3	170
8	5	0.6	170
9	10	0.6	170
10	15	0.6	170
11	0	0	190
12	5	0	190
13	10	0	190
14	15	0	190
15	5	0.3	190
16	10	0.3	190
17	15	0.3	190
18	5	0.6	190
19	10	0.6	190
20	15	0.6	190

TABLE III
Experimental Results

Trial	% Gel content	Color (b*) ± 0.2	T_g (°C) ± 1°C	Tensile strength (MPa) at 130°C	% Elongation to break at 130°C
1	0	+13.2	90.5	1.06 ± 0.06	98.7 ± 1.1
2	1.5 ± 0.2	+9.0	81	1.01 ± 0.07	102.7 ± 4.1
3	2.3 ± 0.2	+5.6	71.5	0.66 ± 0.05	103.2 ± 2.5
4	8.6 ± 0.9	+3.7	65	0.60 ± 0.04	112.1 ± 6.7
5	21.3 ± 2	+11.9	91	1.32 ± 0.14	99.1 ± 7.8
6	32.6 ± 3	+15.4	92.5	1.90 ± 0.10	80.3 ± 8.3
7	57.8 ± 6	+15.9	95	2.59 ± 0.18	72.3 ± 7.1
8	37.5 ± 4	+16.1	90	1.42 ± 0.04	87.7 ± 3.1
9	40.8 ± 4	+16.6	91	1.96 ± 0.09	77.6 ± 3.2
10	47.9 ± 4	+20.3	92	2.24 ± 0.04	66.1 ± 4.6
11	0	+19.2	89.5	1.14 ± 0.07	120.3 ± 1.74
12	7.6 ± 0.8	+11.3	82	0.91 ± 0.05	116.2 ± 4.3
13	8.9 ± 0.9	+7.5	73	0.78 ± 0.05	118.5 ± 2.4
14	10.7 ± 1.0	+4.1	66.5	0.63 ± 0.03	115.1 ± 7.6
15	25.7 ± 2	+18.4	91.5	1.29 ± 0.04	117.1 ± 11.0
16	42.0 ± 4	+19.1	92.5	1.69 ± 0.06	93.6 ± 6.6
17	65.6 ± 6	+19.8	91.5	2.70 ± 0.20	73.0 ± 5.5
18	37.9 ± 4	+20.1	90.5	1.39 ± 0.03	104.8 ± 8.5
19	47.2 ± 4	+21.9	91.5	1.84 ± 0.03	101.6 ± 8.1
20	53.9 ± 5	+25.0	93	2.52 ± 0.06	75.4 ± 7.3

mal analysis (DMTA). An oscillating strain of frequency 1 Hz was applied and samples were heated from 30 to 140°C at a rate of 4°C/min. The glass transition temperature was taken as the maximum in the plot of tan δ as a function of temperature.

Tensile properties

Ultimate tensile strength (UTS) and elongation to break were determined at 130°C using a Hounsfield tensometer at a strain rate of 50 mm/min. The samples were prepared according to ASTM D638-84. Eight test pieces were used for each test. Testing was carried out at 130°C, because from previous work this was found to be a suitable temperature for assessing improvements in elevated temperature properties.[13] Samples were conditioned at this temperature for 20 min prior to testing.

RESULTS AND DISCUSSION

Gel content

Results of gel content measurements are given in Table III and, for the pressing temperature of 190°C, are plotted in Figure 1.

The first thing to point out about these results is that there is some crosslinking of the TMPTMA under the action of heat even in the absence of peroxide. This result is not unexpected because Bowmer et al.[1] in their work on irradiation crosslinking of PVC using TMPTMA reported that 30% of the double bonds in TMPTMA are used in initial polymerization of the trifunctional monomer, which subsequently grafts onto the PVC to produce a gel. Hence polymerization of TMPTMA occurs more readily than grafting on to PVC, and this will be the initial reaction.

Figure 1 clearly shows that, as expected, increasing the content of TMPTMA from 5 to 15 phr gives an increase in gel content and hence crosslinking of the PVC. A similar result has been reported in previous work by Garcia-Quesada and Gilbert.[10] It is also seen from Figure 1 that increasing the peroxide concentration increases the gel content. However, at high levels of TMPTMA (15 phr), there is a maximum gel content at a peroxide level of 0.3 phr and thereafter the gel content decreases. It seems that further peroxide is not beneficial. This can be explained by assuming that excess peroxide does not promote further crosslinking of TMPTMA, probably due to steric hindrance along

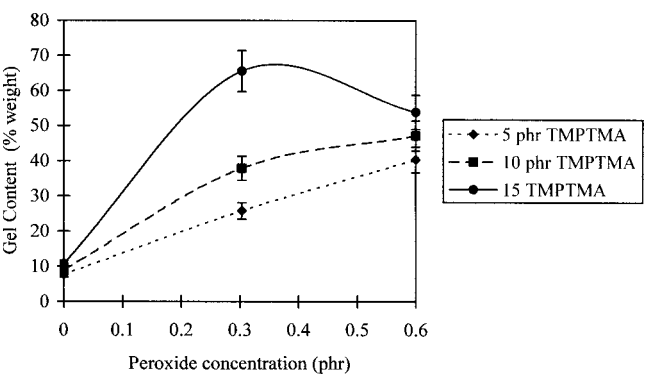

Figure 1 Gel content as a function of peroxide and TMPTMA concentration for samples pressed at 190°C.

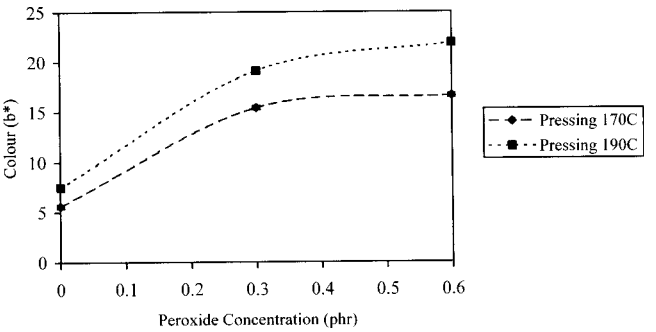

Figure 2 Color (b^*) as a function of peroxide concentration and pressing temperature for samples containing 10 phr of TMPTMA.

the TMPTMA homopolymer chain preventing further reaction.[14] Instead it seems that excess peroxide causes chain scission associated with thermal degradation and so prevents further gel formation.

In a previous study, Thomas et al.[13] predicted that the optimum formulation for maximizing gel content with a concentration of 15 phr of TMPTMA was a concentration of 0.3 phr of peroxide and this has been born out by the current work.

In addition, it is seen from the gel content results in Table III that increasing the pressing temperature from 170 to 190°C gives a slightly higher gel content. This is particularly noticeable in the absence of peroxide, indicating that homopolymerization of TMPTMA occurs more readily at the higher temperature.

Color (b^*)

Results of color measurements are shown in Table III. It should be noted that b^* values are high compared with what would be expected in commercial PVC formulations because these samples are unpigmented.

An increase in the value of b^* (i.e., yellowing) implies that degradation of the PVC has started to take place. It is well known that PVC degrades on heating to lose HCl (dehydrochlorination), which gives rise to long sequences of polyenes and yellowing of the material. This process can be exacerbated in the presence of peroxide.

Results of this analysis show that pressing temperature and peroxide concentration are the two variables that have a significant effect on initial color. This is illustrated in Figure 2. Degradation occurs as the peroxide level is increased and also as the pressing temperature is increased.

The effect of TMPTMA concentration on color is more complex. In the absence of peroxide, it is found that increasing the concentration of TMPTMA causes a reduction in yellowing. This is because TMPTMA acts as a plasticizer for PVC and so reduces the shear during processing and hence the propensity for degradation. However, in the presence of peroxide when free radicals are produced, there is a slight increase in yellowing with increasing TMPTMA concentration.

Glass transition temperature

The value of the glass transition temperature for the base PVC formulation, as measured by DMTA, is found to be 90°C. The effects of formulation ingredients and pressing temperature on the value of T_g are shown in Table III.

In the absence of peroxide, it is found that the value of T_g shows a substantial decrease with increasing level of TMPTMA. It has long been recognized that TMPTMA monomer acts as a plasticizer for PVC[9] and so increasing the TMPTMA content increases the free volume in the PVC matrix and hence decreases T_g.

In the presence of peroxide, it is found that there is a small (< 5°C) but significant increase in T_g with increasing level of TMPTMA. This result is consistent with the crosslinking process and results of the gel content measurements. The effect of TMPTMA and peroxide level on the glass transition temperature for samples pressed at 170°C is plotted in Figure 3. Note that pressing temperature is not found to have a significant influence on the value of T_g.

Tensile properties

Data obtained for the ultimate tensile strength (UTS) and % elongation to break of the samples at 130°C are tabulated in Table III and, for the pressing temperature of 170°C, results of UTS and % elongation to break are plotted in Figures 4 and 5, respectively.

It is seen that in the absence of both TMPTMA and peroxide, the UTS at 130°C of the control samples is 1.1 MPa. Addition of TMPTMA alone causes a reduction in UTS because of the plasticizing effect of TMPTMA on PVC. When peroxide is present, there is

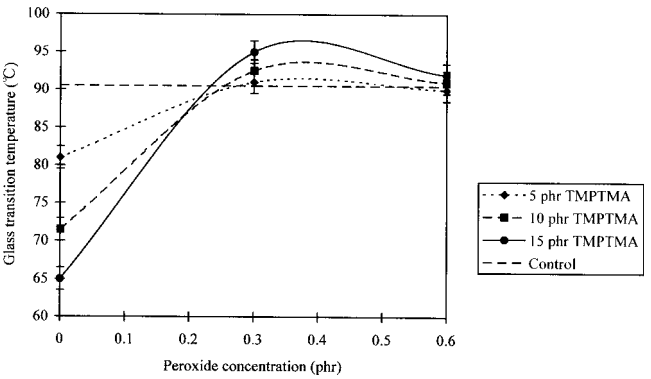

Figure 3 Glass transition temperature as a function of peroxide and TMPTMA concentration for samples pressed at 170°C.

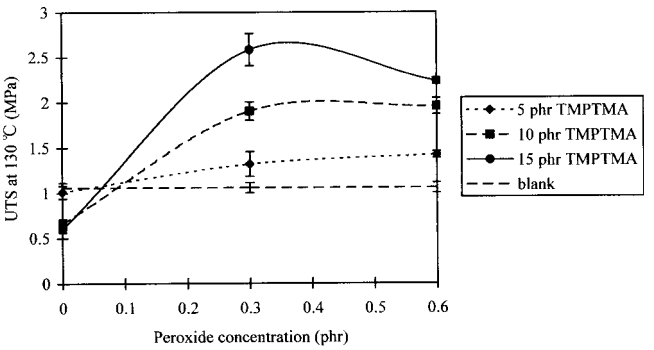

Figure 4 Tensile strength at 130°C as a function of peroxide and TMPTMA concentration for samples pressed at 170°C.

a marked increase in UTS due to the crosslinking reaction and the formation of a chemical network.

It is interesting to compare the relative effects of TMPTMA and peroxide on the values of UTS measured. From Figure 4, it is clear that the concentration of TMPTMA is the most important variable governing tensile strength at 130°C: the higher the concentration of TMPTMA, the higher the UTS. At a TMPTMA concentration of 15 phr, it is possible to get an increase in UTS by a factor of almost 2.5. Increasing peroxide concentration causes an increase in UTS up to a maximum value. It is seen that the optimum value of the peroxide addition level is 0.3 phr. As the addition level of peroxide is increased above this value, the tensile strength measurements reach a plateau or (as in the case of 15 phr TMPTMA) may even reduce.

These results are entirely consistent with the results of gel content reported above. Increasing the concentration of TMPTMA increases both gel content and UTS. This is expected because more molecules are available for grafting onto the PVC and hence crosslinking. However, in the case of peroxide, it is found that the higher levels are not beneficial. In the presence of 15 phr of TMPTMA, there is an optimum value of peroxide of 0.3 phr at which gel content reaches a maximum. Also in the analysis of the UTS results, there is a distinct maximum at intermediate values of peroxide. Above this value there is found to be a decrease in high temperature tensile strength, as seen in Figure 4. These observations can be explained by the occurrence of chain scission, as discussed earlier.

The results reported here are in agreement with earlier work by Garcia-Quesada and Gilbert,[10] who reported a reduction in high temperature tensile strength with increasing peroxide concentration. Also a recent study by Thomas et al.[13] predicted that 15 phr of TMPTMA and 0.3 phr of peroxide were optimum concentrations for maximizing tensile strength at elevated temperature, and this is in agreement with the current results.

The results for % elongation to break (Fig. 5) have relatively large error bars compared with UTS. Nevertheless, the trend in the data is clear and in agreement with the discussion above. Addition of TMPTMA in the absence of peroxide has a plasticizing effect and therefore causes a slight increase in % elongation to break. However, crosslinking occurs in the presence of peroxide and so at higher levels of TMPTMA there is a significant reduction in % elongation to break. Again there is no benefit in increasing the level of peroxide above 0.3 phr.

CONCLUSIONS

This study confirms that PVC can be successfully crosslinked using trimethylolpropane trimethacrylate together with the peroxide Trigonox 29-C75, which is (1,1-di(*t*-butylperoxy)-3,3,5-trimethyl cyclohexane) containing 75% peroxide.

It is found that the gel content (i.e., amount of crosslinked PVC) increases with increasing concentration of TMPTMA from 5 to 15 phr. Increasing the peroxide concentration also increases the gel content, but at high levels of TMPTMA (15 phr), there is a maximum gel content at a peroxide level of 0.3 phr and thereafter the gel content decreases. It seems that additional peroxide does not promote further crosslinking of TMPTMA, probably due to steric hindrance along the TMPTMA homopolymer chain. Instead it is apparent that excess peroxide causes chain scission associated with thermal degradation and so causes a reduction in gel formation.

TMPTMA acts as a plasticizer of PVC. Hence, in the absence of peroxide, it is found that addition of TMPTMA causes a reduction in T_g compared with the control PVC sample. However, in the presence of peroxide, there is a small (< 5°C) but significant increase in T_g with increasing level of TMPTMA. This result is consistent with the crosslinking process and results of the gel content measurements.

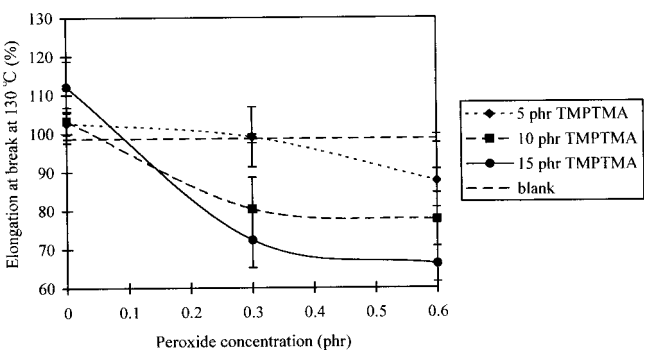

Figure 5 % Elongation-to-break at 130°C as a function of peroxide and TMPTMA concentration for samples pressed at 170°C.

Similarly, results of tensile strength measurements at 130°C confirm the crosslinking reaction. Addition of TMPTMA alone causes a reduction in tensile strength because of the plasticizing effect of TMPTMA on PVC. When peroxide is present, there is a marked increase in tensile strength due to the formation of a chemical network. The amount of TMPTMA is very important in determining the improvement seen in tensile properties; the higher the concentration of TMPTMA, the higher the UTS. This is expected because more molecules are available for grafting onto the PVC and hence crosslinking. At a TMPTMA concentration of 15 phr, it is possible to get an increase in UTS by a factor of almost 2.5. Increasing peroxide concentration causes an increase in UTS up to a maximum value. It is found that the optimum value of the peroxide addition level is 0.3 phr: above this value there is a decrease in high temperature tensile strength, which can be explained by the occurrence of chain scission.

It is concluded that the optimum concentrations of TMPTMA and peroxide to maximize gel content, T_g, and tensile strength are 15 and 0.3 phr, respectively. It is recommended that the lower pressing temperature of 170°C be used to minimize thermal degradation.

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