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Cross-linking of unplasticised poly(vinyl chloride) with peroxide

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The peroxide cross-linking of poly(vinyl chloride) (PVC) with trimethylolpropane trimethacrylate (TMPTMA) has been investigated. The degree of cross-linking was measured in terms of the gel content of the material, i.e. the insoluble residue remaining after soxhlet extraction in tetrahydrofuran. Cross-linking gave rise to significant improvements in high temperature tensile strength, but at higher levels of peroxide, dehydrochlorination of PVC was found to compete with grafting and cross-linking reactions. The results have been analysed to predict the optimum amount of TMPTMA and peroxide to maximise gel content and strength while maintaining thermal stability.

Keywords: Poly(vinyl chloride), Cross-linking, Peroxide, TMPTMA

Introduction

Chemical cross-linking of plasticised poly(vinyl chloride) (PVC) has been used as a means of improving mechanical properties at elevated temperatures.^{1,2} The two methods that have been studied are the use of silanes³⁻⁸ and, to a lesser extent, the use of peroxides.^{9,10} Both methods can successfully produce cross-linked morphologies. The key to success is to produce compounds with adequate cross-linked density while maintaining thermal stability and avoiding premature reaction during processing.

In unplasticised (rigid) PVC, it is more difficult to achieve an optimum combination of properties through chemical cross-linking. Kelnar and Schatz^{11,12} have studied the cross-linking of rigid PVC using mercaptosilane and reported a high cross-linked density when basic lead salts were used as thermal stabilisers. However, cross-linking of rigid PVC was found to be much slower than plasticised PVC. This is owing to the reduced diffusion rate of water in rigid PVC, therefore reducing the rate of the silane hydrolysis reaction. Gilbert and Garcia-Quesada¹³ have investigated amino-silane cross-linking of rigid PVC. Although a notable improvement in tensile strength above the glass transition temperature of the cross-linked polymer was found, there was also a significant deterioration in thermal stability, which is attributable to reactive amine groups that provide high grafting efficiency but also abstract HCl and therefore reduce thermal stability.

Peroxide cross-linking of rigid PVC has been studied by Gilbert and Garcia-Quesada.^{13,14} They added a trifunctional monomer, trimethylolpropane trimethacrylate (TMPTMA) to the PVC. TMPTMA has the formula $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O}-\text{CO}-\text{CCH}_3=\text{CH}_2)_3$ and is compatible with PVC. Cross-linking is activated at

elevated temperature in the presence of peroxide. The TMPTMA undergoes rapid polymerisation followed by grafting on to the PVC chains and subsequent cross-linking. In these studies significant property improvements were found with as little as 0.5 part of peroxide per hundred parts of PVC (phr). Premature cross-linking during processing was largely avoided but thermal stability was found to deteriorate.

The aim of the present work is to investigate further the use of TMPTMA for the peroxide cross-linking of PVC. Experimental design software was used to determine the formulations and processing temperatures for the study. The resulting polymers were characterised in terms of their gel content, thermal stability and tensile strength at elevated temperature. The results have been analysed to predict the optimum formulation and processing conditions to maximise gel content and strength, while maintaining thermal stability.

Experimental

Formulations and processing

Table 1 shows the basic formulation used in the present study. The PVC was suspension grade Evipol SH6030 supplied by Ineos Vinyls. This polymer has a *K* value of 60, which corresponds to a weight average molecular weight of $\sim 64\,000$ and is in the lower molecular weight range of commercially available grades. The heat stabiliser was tribasic lead sulphate (TBLS). The relatively high addition level of 7 phr was chosen because from previous studies¹⁴ it was anticipated that thermal stability might be a problem. 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, TMPTMA, was supplied by Degussa. Two different peroxides supplied by Chemtura Corporation were used. USP 495D is (1,1-di-(*t*-butylperoxy)-3,3,5-trimethyl cyclohexane), incorporating

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Table 1 Formulation ingredients

Ingredient	Concentration, phr
Evipol SH6030	100
Tribasic Lead Sulphate	7
Loxiol G53	1.2
Loxiol G52	0.4
Hoechst PE 190	0.2
Paraloid K120N	1.5
TMPTMA	According to experimental design
USP 495D	According to experimental design
USP 333M	According to experimental design

75% peroxide and the other peroxide is USP 333M (ethyl 3,3-di-(*t*-butylperoxy) butyrate), also incorporating 75% peroxide. These peroxides were chosen because similar peroxides had been used successfully in previous studies.^{1,13,14}

The experimental plan for the present study was produced using the ECHIP software package¹⁵ and is shown in Table 2. A standard quadratic design was chosen with four design variables: pressing temperature (170–200°C), TMPTMA concentration (5–15 phr), peroxide concentration (0.12–0.6 phr) and peroxide type (either USP 495D or USP 333M). This gave 16 unique trials, with a number of repeats to check the statistical significance of the results. An additional midpoint trial at a pressing temperature of 185°C and TMPTMA concentration of 10 phr but without any peroxide was included for comparison.

The ingredients were weighed and the dry blends were prepared in a laboratory scale Fielder mixer. All components (except liquid peroxides and TMPTMA) were added to the mixer at a temperature of 50°C and mixed at 2000 rev min⁻¹. When the temperature reached 80°C the peroxide and TMPTMA were added and blending continued until a temperature of 120°C was reached. At this point the blend was discharged into the cooling chamber.

Processing of the dry blends was carried out for 5 min on a twin roll mill, with the roll temperatures set at 140°C. The sheets produced were compression moulded under a hydraulic pressure of 20 t for 5 min at the appropriate pressing temperature according to the experimental plan.

Table 2 Experimental design

Trial	Pressing temperature, °C	TMPTMA concentration, phr	Peroxide concentration, phr	Peroxide type
1	170	15	0.12	USP 495D
2	200	5	0.6	USP 495D
3	170	10	0.6	USP 495D
4	185	10	0.36	USP 495D
5	200	15	0.6	USP 495D
6	200	5	0.12	USP 495D
7	170	5	0.12	USP 495D
8	185	15	0.12	USP 495D
9	170	5	0.36	USP 495D
10	185	5	0.12	USP 333M
11	170	10	0.12	USP 333M
12	170	5	0.6	USP 333M
13	200	10	0.6	USP 333M
14	200	15	0.12	USP 333M
15	200	5	0.36	USP 333M
16	170	15	0.6	USP 333M

Characterisation and property measurements

Gel content

The amount of cross-linked PVC (or gel content) was determined by Soxhlet extraction for 24 h using tetrahydrofuran (THF) as a solvent. The 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.

Thermal stability

The thermal stability of the PVC samples was determined using an oven at 190°C, according to ASTM D2115-67. Small strips of sample were cut and placed in an aluminium foil holder, which was put on an oven tray. Strips were removed from the oven every 10 min and any changes in colour were observed.

Tensile properties

Ultimate tensile strength (UTS) was determined at 130°C using a Hounsfield tensometer at a strain rate of 50 mm min⁻¹. 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 before testing.

Results and discussion

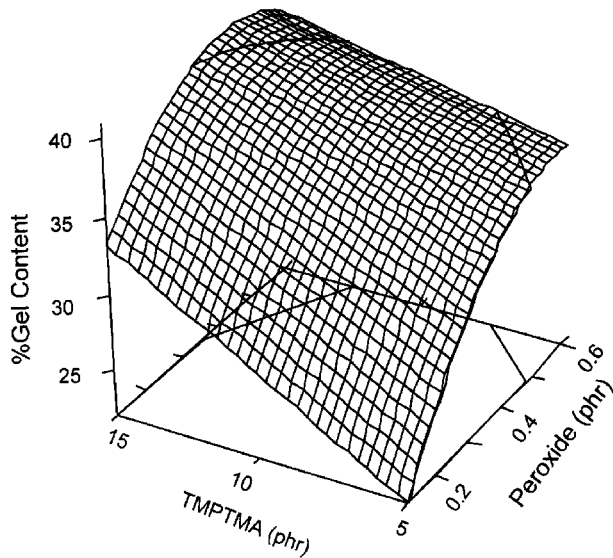
Gel content

Results of gel content measurements from the 16 different trials and three repeat formulations are given in Table 3. The gel content of the control sample pressed at 185°C and containing 10 phr of TMPTMA but no peroxide was 8.5%. This result shows that there is some cross-linking of the TMPTMA under the action of heat even in the absence of peroxide.

Gel content results were fed back into the ECHIP programme to model the effect of the input variables (pressing temperature, TMPTMA concentration, peroxide concentration and peroxide type) on the gel content. Regression analysis was carried out to obtain

Table 3 Experimental results

Trial	Gel content, %	Time to degradation, min	Tensile strength, MPa
1	25.0	30	2.17
2	35.0	30	1.67
3	30.0	30	1.90
4	40.0	30	1.97
5	25.0	30	1.60
6	13.6	30	1.43
7	13.0	30	1.48
8	30.0	30	2.22
9	18.0	30	1.43
10	26.0	20	1.46
11	25.0	30	1.78
12	26.0	20	1.40
13	33.0	10	2.24
14	28.0	20	2.51
15	31.0	30	2.36
16	39.4	10	2.10
1R	29.4	30	2.35
9R	18.6	30	1.33
12R	23.4	20	1.52



1 3D contour plot of effect of TMPTMA and peroxide concentration on gel content: temperature=185°C and peroxide=USP 495D

the best fit quadratic equation from the data. The equation derived is given below. In this and subsequent equations the terms 'TMPTMA' and 'peroxide' refer to the addition levels of these materials

$$\begin{aligned} \% \text{ Gel content} = & 38.546 + 0.0158(\text{Temperature} - 185) \\ & + 0.7719(\text{TMPTMA} - 10) + 20.631(\text{Peroxide} - 0.36) \\ & - 0.0521(\text{Temperature} - 185)(\text{TMPTMA} - 10) \\ & - 1.442(\text{TMPTMA} - 10)(\text{Peroxide} - 0.36) \\ & - 0.03936(\text{Temperature} - 185)^2 - 65.884(\text{Peroxide} - \\ & 0.36)^2 - 2.146(\text{if USP495D}) + 2.146(\text{if USP333M}) \end{aligned}$$

As expected, it was found that increasing the concentration of both TMPTMA and peroxide in the formulation gave a significant increase in the gel content. Peroxide USP 333M gave a slightly higher gel content than USP 495D. Pressing temperature was not found to have a significant effect overall.

The relationship is displayed graphically in the contour plot of Fig. 1. This three-dimensional graph shows gel content on the vertical axis plotted against both TMPTMA and peroxide concentration. Gel content can be seen to increase with increasing concentration of both TMPTMA and peroxide but reaches a plateau at a peroxide concentration of ~0.5 phr.

These observations can be explained by considering the cross-linking process. It is known¹⁶ that polymerisation of TMPTMA occurs more readily than grafting on to PVC, therefore, this will be the initial reaction. In their work on irradiation cross-linking of PVC, Bowmer *et al.*¹⁶ showed that 30% of the double bonds in TMPTMA are used during this initial polymerisation. Subsequently the TMPTMA homopolymer grafts on to the PVC to produce a gel, with further double bonds reacting. Increasing TMPTMA concentration would clearly be expected to increase gel content, as reported in previous work by Garcia-Quesada and Gilbert.¹⁴ In the previous study a plateau in gel content was obtained with 0.5 phr peroxide, but lower concentrations of peroxide were not investigated. In the present study, it

is confirmed that gel content is lower with lower peroxide concentrations, and the plateau is still seen at a peroxide concentration of ~0.5 phr. This level is therefore necessary; further peroxide is not beneficial, irrespective of TMPTMA concentration. The TMPTMA homopolymer will have pairs of double bonds closely spaced along the polymer chain, and it will be impossible for all of these to react to produce gel because of steric hindrance.¹⁷ If reaction was possible, it would be expected that the plateau for peroxide concentration would move to higher concentrations as the TMPTMA concentration increased. As this is not observed, it is more likely that excess peroxide causes chain scission as well as gel formation. It is known that chain scission (associated with thermal degradation) can occur during PVC processing, and it is reasonable that this could be enhanced in the presence of excess free radicals and also at higher pressing temperatures.

Thermal stability

Thermal stability was measured as time to degradation as specified in ASTM D2115-67 based on the change of colour of the PVC samples at 190°C. The results are shown in Table 3. It is seen that all samples containing peroxide USP 495D had a thermal stability of 30 min, whereas those containing USP 333M had reduced thermal stability. The control sample (with pressing temperature 185°C, TMPTMA concentration 10 phr and no peroxide) also had a time to degradation of 30 min.

Regression analysis was carried out on these data using the ECHIP software and the best fit equation was determined to model the effect of the input variables on thermal stability as shown below

$$\begin{aligned} \text{Degradation time (min)} = & 23.62 - 0.0252(\text{Temperature} - \\ & 185) - 0.5897(\text{TMPTMA} - 10) - 13.618(\text{Peroxide} - \\ & 0.36) - 1.937(\text{TMPTMA} - 10)(\text{Peroxide} - 0.36) \\ & + 4.290(\text{if USP495D}) - 4.290(\text{if USP333M}) \end{aligned}$$

It is found that pressing temperature has no significant effect on thermal stability, whereas increasing the concentration of both TMPTMA and peroxide causes a reduction in thermal stability for reasons discussed earlier. However, the overriding effect is the type of peroxide used: USP 333M clearly has a deleterious effect on thermal stability compared with USP 495D. USP 333M has higher active oxygen content (8.2%) than USP 495D (7.9%). This could account for both the higher gel content and lower thermal stability of compounds in which USP 333M is used.

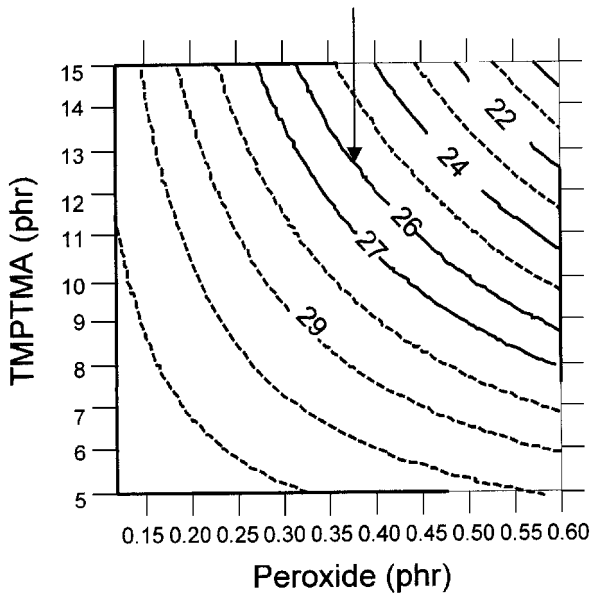
These results are illustrated in the two-dimensional contour plots of Figs. 2 and 3. These graphs show peroxide concentration on the abscissa and TMPTMA concentration on the ordinate. Time to degradation is plotted as a series of contour lines. Peroxide USP 333M (Fig. 3) is shown to give a shorter time to degradation than peroxide USP 495D (Fig. 2).

Tensile strength

Data obtained for UTS of the samples at 130°C are shown in Table 3. The control sample had a UTS of 0.8 MPa.

Multiple regression analysis was used to derive the best fit quadratic equation describing the effect of the

Time to Degradation (minutes)

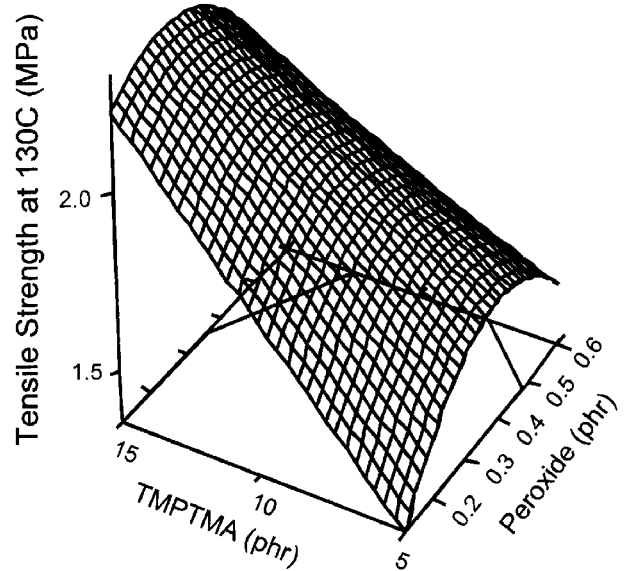


2 2D contour plot of thermal stability: temperature=185°C and peroxide=USP 495D

input variables on UTS at 130°C as shown below:

$$\begin{aligned}
 \text{UTS at } 130^{\circ}\text{C}(\text{MPa}) = & 2.11 + 0.006(\text{Temperature} - 185) \\
 & + 0.059(\text{TMPTMA} - 10) - 0.197(\text{Peroxide} - 0.36) \\
 & - 0.0019(\text{Temperature} - 185)(\text{TMPTMA} - 10) \\
 & - 0.112(\text{TMPTMA} - 10)(\text{Peroxide} - 0.36) \\
 & - 4.34(\text{Peroxide} - 0.36)^2 - 0.12(\text{if USP495D}) \\
 & + 0.12(\text{if USP333M})
 \end{aligned}$$

From this analysis it is found that the concentration of TMPTMA is the most important variable governing tensile strength at 130°C. The higher the concentration of

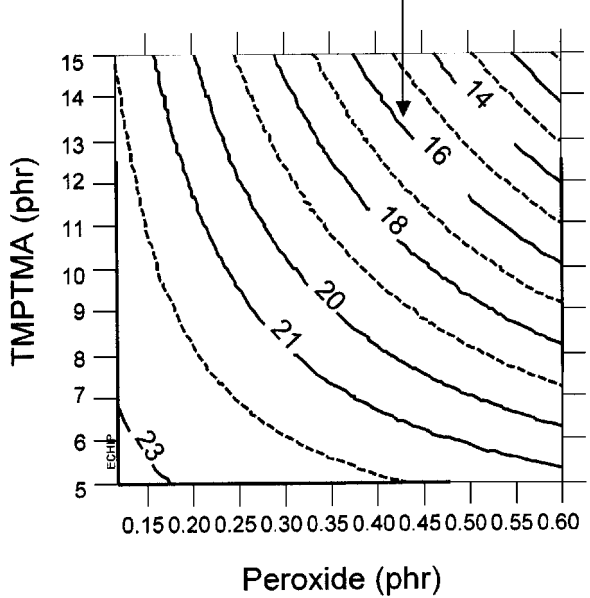


4 3D contour plot of effect of TMPTMA and peroxide concentration on tensile strength at 130°C: temperature=185°C and peroxide=USP 495D

TMPTMA, the higher the UTS. Increasing peroxide concentration causes an increase in UTS up to a maximum value. As shown in the 3D contour plot of Fig. 4, UTS reaches a maximum at intermediate levels of peroxide and then decreases. Peroxide type USP 333M gives higher values of UTS than peroxide type USP 495D.

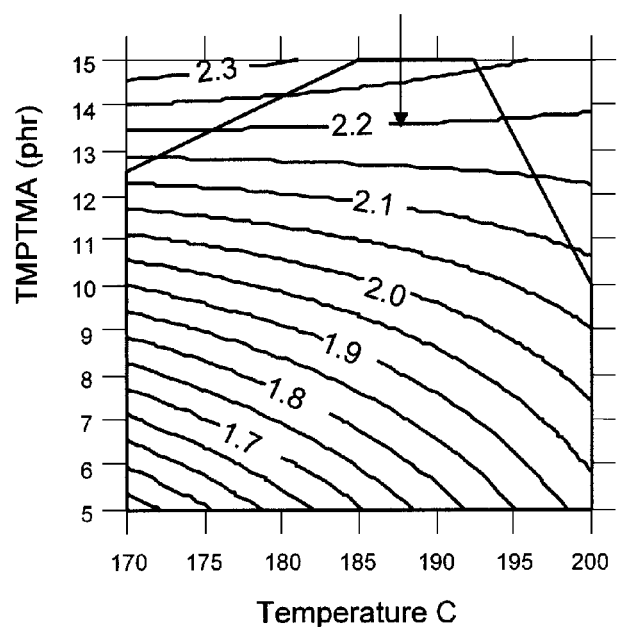
The effect of pressing temperature on UTS at 130°C is rather complex. Although pressing temperature is found to have no overall effect, there is significant interaction between pressing temperature and the TMPTMA concentration. As shown in the 2D contour plot of Fig. 5, at high concentrations of TMPTMA there is no effect of pressing temperature on UTS, whereas at low

Time to Degradation (minutes)



3 2D contour plot of thermal stability: temperature=185°C and peroxide=USP 333M

Tensile Strength at 130C



5 2D contour plot of effect of TMPTMA concentration and temperature on tensile strength at 130°C: peroxide level=0.36 phr and peroxide type=USP 495D

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Table 4 Optimum conditions

Pressing temperature, °C	TMPTMA concentration, phr	Peroxide concentration, phr	Peroxide type
175±2	15	0.27±0.03	USP 495D

concentrations of TMPTMA increasing pressing temperature does increase UTS. This possibly relates to melt viscosity before cross-linking occurs; initially TMPTMA will act as a plasticiser, therefore, it will be possible to fuse the PVC effectively at a lower temperature, enabling cross-linking reactions to occur.

A number of observations on these data require further discussion. It is found that increasing the concentration of TMPTMA increases both gel content and UTS. This is expected because more molecules are available for grafting on to the PVC and therefore cross-linking. However, in the case of peroxide, the analysis shows an optimum value of ~0.5 phr at which gel content reaches a plateau. Also in the analysis of the UTS results, there is a distinct maximum at intermediate values of peroxide. Above this value a decrease in high temperature tensile strength is found as shown in Fig. 4. This would be consistent with the occurrence of chain scission as discussed earlier. Another observation is that, as seen in Table 3, there is no significant correlation between gel content and UTS at 130°C. It is interesting to note that similar observations have been made in previous work by Garcia-Quesada and Gilbert.¹⁴ This could be explained by chain scission. Although gel content is not increased at higher peroxide levels, neither will it be reduced. However, chain scission in the uncross-linked polymer would cause a reduction in elevated temperature tensile strength.

Optimum conditions

Analyses of the results of gel content, thermal stability and tensile strength measurements have been combined to predict the set of conditions that will maximise gel content and strength while maintaining thermal stability. The optimum set of conditions is shown in Table 4. Pressing temperature should be kept to the bottom end of the range to avoid thermal degradation. The optimum value of peroxide is in the middle of the range investigated whereas the optimum value of TMPTMA is the maximum value investigated. Of the two peroxides investigated, type USP 495D is preferable because it gave less reduction in thermal stability.

Inserting these optimum values into the equations derived above, it is found that the predicted gel content is 37%, the time to degradation is 27 min and the tensile strength at 130°C is 2.4 MPa.

Conclusions

The present study has examined the peroxide cross-linking of PVC using TMPTMA as the polyfunctional monomer. Experimental design was used to investigate

the effects of pressing temperature, the concentration of TMPTMA and the concentration and type of peroxide on gel content, tensile strength and thermal stability of the blends. Using the experimental design approach, it was possible to model the results and therefore map out the effects of a wide range of formulations. Gel yield was found to increase with increasing concentration of TMPTMA but reached a plateau at a peroxide concentration of ~0.5 phr. High temperature tensile strength showed significant increase with increasing TMPTMA but reached a maximum value at a peroxide level of ~0.3 phr and then started to fall as peroxide level was increased. This was interpreted as chain scission associated with degradation of PVC. Of the two peroxides investigated, USP 333M (ethyl -3,3-di-(t-butylperoxy) butyrate) gave higher gel content but worse thermal stability than USP 495D (1,1-di-(t-butylperoxy)-3,3,5-trimethyl cyclohexane). USP 333M has a higher active oxygen content (8.2%) than USP 495D (7.9%) which may account for both the higher gel content and the lower thermal stability of compounds in which USP 333M was used.

Combining the various analyses it was possible to predict the set of conditions that will maximise gel content and strength while maintaining thermal stability. It is concluded that the optimum conditions are as follows: TMPTMA level of 15 phr, peroxide level of 0.3 phr, peroxide type USP 495D and pressing temperature of 175°C.

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