Structure–property relationships of irradiation crosslinked flexible PVC: 1. Structural investigations

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An investigation has been carried out into the effect of irradiation dose and the amount of the unsaturated monomer trimethylolpropane trimethacrylate (TMPTMA) on the irradiation of a di-iso-octyl phthalate (DIOP) plasticized PVC compound. The type of network structure produced and the extent of deterioration of the PVC after crosslinking have been studied. Within the dose range studied, the degradation caused by the electron beam was found to be minimal, but the residual unsaturation in the crosslinked PVC was significant, implying inefficient use of crosslinking agent. Gel yield increased with increased irradiation dose and TMPTMA content, but crosslink density decreased at higher irradiation levels, suggesting the formation of a looser network. The phthalate plasticizer was not involved in gel formation.

(Keywords: poly(vinyl chloride); plasticized; irradiation; crosslinking)

INTRODUCTION

It is possible to use irradiation to convert plasticized poly(vinyl chloride) (PVC) from a thermoplastic to a thermoset, thus producing a material with improved high temperature properties. The process has been known for several years, the *locus classicus* being the work published by Miller in 1959[1], where he introduced the concept of crosslinking PVC with low irradiation doses in the presence of polyfunctional unsaturated monomers. The low irradiation dose minimized degradation of the PVC, while the monomer enhanced the crosslinking efficiency of the process. Before this, attempts to crosslink PVC[2,3] had resulted in severe dehydrochlorination, and even chain scission, in the presence of air, due to the high energies of the irradiation (> 20 Mrad) that were used in attempts to achieve crosslinking.

In the presence of a crosslinking monomer, irradiation produces homopolymerization of the monomer, graft copolymerization of the monomer onto PVC, and graft crosslinks between PVC chains[1,4–13]. During the early stages of irradiation, homopolymerization of the monomer is the preferred reaction, forming a gel mainly composed of monomer, with some graft copolymerization between the latter and the PVC. As the process continues, the crosslinking agent becomes exhausted and PVC crosslinking via graft copolymerization with the gel becomes the dominant process[4,6,11,12].

The extent to which the crosslinking occurs is a function of irradiation dose[1], monomer type[1,2,6], monomer concentration[12], temperature of irradiation[12] and the presence of plasticizer[13].

In principle, any polyfunctional unsaturated monomer is capable of promoting irradiation crosslinking of PVC, and the action of various classes of crosslinking agents has been investigated[1,4–13]. The most effective compounds have been shown to be polyfunctional acrylates and methacrylates, especially trifunctional monomers such as trimethylolpropane trimethacrylate (TMPTMA) and trimethylolpropane triacrylate[5,6,9,10]. These monomers are particularly efficient because they produce high yields of radicals during irradiation. They are also effective plasticizers, giving good contact with the PVC chains, and hence facilitating the grafting reactions[7].

Bowmer *et al.*[12,13] have shown that to effect good crosslinking in unplasticized PVC, TMPTMA loadings of about 20–40% are required with irradiation doses of 3–4 Mrad. They also suggested that increased temperature of irradiation (up to 80°C) increases the rate of crosslinking, and that the crosslink density may be increased further by post-irradiation annealing. Phthalate plasticizer considerably enhances the crosslinking action, and in its presence effective crosslinking may be achieved at room temperature[13]. De Hollain[14] found that plasticizer type affects both the crosslinking efficiency and the network stability of TMPTMA crosslinked PVC.

In this paper, the first of a series, we describe investigations into the influence of monomer (TMPTMA) level and irradiation dose on the network structure produced and the extent of deterioration of the PVC after crosslinking. In a forthcoming paper, the network structure will be related to tensile properties at room temperature, and at elevated temperatures, and the softening behaviour of the irradiation crosslinked samples will be investigated by thermomechanical analysis.

EXPERIMENTAL

Materials

The PVC compound used was plasticized with di-iso-octyl phthalate (DIOP). TMPTMA at loadings of up to 20 phr, was used to promote crosslinking.

The polyvinyl chloride compounds based on a PVC suspension resin (ICI Corvic S71/102) were prepared according to the formulations given in *Table 1*.

Table 1 Formulations

PVC[a] (phr)	DIOP[b] (phr)	TBLS[c] (phr)	Stearic acid (phr)	TMPTMA[d] (phr)	Irradiation dose (Mrad)	Code before irradiation	Code after irradiation
100	46.5	7	0.5	0	4	A0	A0r
100	46.5	7	0.5	2	4	A2	A2r
100	46.5	7	0.5	5	4	A5	A5r
100	46.5	7	0.5	10	4	A10	A10r
100	46.5	7	0.5	20	4	A20	A20r
100	46.5	7	0.5	10	2	B2	B2r
100	46.5	7	0.5	10	6	B6	B6r
100	46.5	7	0.5	10	8	B8	B8r

[a] PVC grade: ICI Corvic S71/102
[b] DIOP, di-iso-octyl phthalate
[c] TBLS, tribasic lead sulphate
[d] TMPTMA, trimethylolpropane trimethacrylate (Ancomer ATM 11)

Sample preparation

The formulations were dry blended using a laboratory scale Fielder mixer at a mixing speed of 3000 rev min^{-1}. The jacket temperature was 70°C, and the powder was blended to 120°C, then dumped to a water-cooled chamber where it was agitated at 500 rev min^{-1} for 5 min.

The cooled powder was further homogenized and made into a sheet approximately 0.4 mm thick by milling at 140°C for 5 min on a two-roll laboratory mill. The friction ratio was 1:1.

The milled sheet was then compression moulded to a thickness of 0.3 mm by pressing at 170°C for 5 min (after 2 min pre-heat), at a pressure of 60 MPa. The mould was then immediately transferred to a water-cooled press and cooling was effected under the same pressure.

All samples were cut from these compression sheets.

Irradiation

Crosslinking was effected by exposing the specimens to electron beam (EB) irradiation. Irradiation doses ranged from 0–8 Mrad (0–80 kGy).

The irradiation was carried out in a nitrogen atmosphere at room temperature using a 170 keV electron beam curtain. All specimens were irradiated on both sides with irradiation doses of 2, 4, 6 or 8 Mrad, as appropriate. Double-sided irradiation was necessary because of the limited penetrating power of the electron beam (approximately 180 μm at unit density).

Characterization of samples

Samples were always tested approximately 10 days after irradiation. This avoided variations due to long lived radicals present immediately after the irradiation process.

Extractable plasticizer content and gel yield. The irradiated samples were examined for 'trapped' plasticizer by extracting the specimens with diethyl ether in a Soxhlet apparatus for 16 h. The extracted samples were vacuum dried at 40°C to constant weight and the percentage extracted plasticizer was determined from the weight loss of the specimen.

After ether extraction, the remaining material was Soxhlet extracted for 24 h with tetrahydrofuran (THF), and the final residue was dried and weighed. The amount of gel (i.e. insoluble material) was expressed as a percentage of the theoretical maximum, the latter being the total amount of material which could form a gel, i.e. the weight of all components which could be involved in gel formation, the plasticizer being excluded.

Unreacted monomer. The ether extracts of selected irradiated specimens (B2r, B6r, A20r) were evaporated to dryness and examined by infrared spectrophotometry (i.r.) to see whether the very strong absorption band at 1640 cm^{-1} due to TMPTMA monomer could be detected.

Residual unsaturation. Residual unsaturation was assessed by i.r. directly on the PVC films. A control sample (A0 or A0r) was placed in the reference beam to compensate for the strong absorption due to the thickness of the PVC. The percentage residual unsaturation was calculated by comparing the absorbance at 1640 cm^{-1} before and after irradiation.

PVC content in the gel fraction. The PVC content in the gel fractions was estimated by chloride analysis. THF extracted specimens were pyrolysed in an oxygen combustion flask, the gases absorbed into distilled water and the chloride content of the solutions determined using a flow injection analysis technique, with a spectrophotometer detector[15,16]. This measurement is based on the formation of a red colour by the reaction of $Hg(SCN)_2$ with Fe^{3+} ions in the presence of Cl^- ions. The dissociation of the $Hg(SCN)_2$ is activated by the Cl^- ion to give $Fe(SCN)^{2+}$. After appropriate calibration the concentration of Cl^- can then be obtained by measuring absorbance at 480 nm, and the chloride content of the gels calculated. Hence the amount of PVC used in the crosslinking process can also be obtained. The accuracy of the chloride analysis was checked against virgin PVC, and the results were found to be in good agreement with the theoretical value (Cl^- content expected 56.8%; experimental values 56.8, 55.9%).

Crosslink density measurements. The molar mass between crosslinks, $\bar{M}_c$, and the crosslink density in the gels, $1/2\bar{M}_c$, were obtained from swelling measurements. Samples were allowed to swell in methyl ethyl ketone (MEK) for 4 d at 25°C. They were weighed swollen, dried to constant weight and reweighed, and crosslink density was calculated from the Flory–Rehner equation[17,18]. (χ for PVC in MEK was taken to be 0.41[19].)
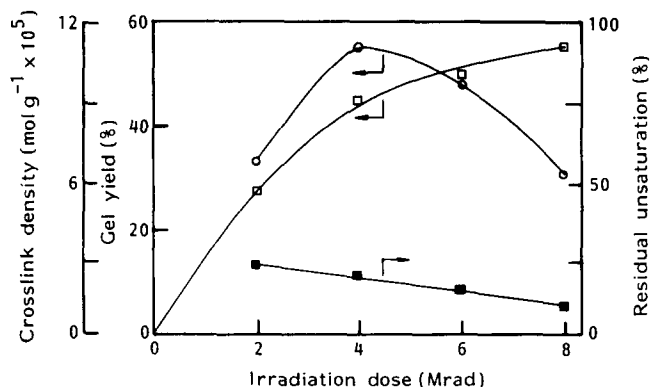
Figure 1 Influence of irradiation dose on gel yield (□), residual unsaturation (■) and crosslink density in gels (○)

Examination of the THF soluble PVC. Ether extracted PVC samples (before and after irradiation) were extracted with THF, and the sol fraction was precipitated with methanol and dried.

Molecular weight distribution curves were obtained for the precipitated PVC in THF solution using a 0.5 μm Styragel column and a refractive index detector. I.r. traces were obtained for films cast from THF.

RESULTS AND DISCUSSION

Results are generally plotted as a function of irradiation dose at a constant TMPTMA level of 10 phr, and as a function of TMPTMA level at a constant irradiation dose of 4 Mrad.

Appearance of samples

All specimens were initially white; none were discoloured by irradiation within the dose range used (0–8 Mrad).

Gel yields

Figure 1 shows that increased irradiation dose at constant TMPTMA level markedly increases the crosslinking efficiency (gel yield) in plasticized PVC. However, further increases in dose above 4 Mrad have less effect. This dose was therefore selected for the investigation of the effects of monomer level.

Figure 2 shows that at an irradiation dose of 4 Mrad increased TMPTMA concentration also increases the efficiency of crosslinking, the rate of increase being relatively high at first, and then decreasing. At a loading of 20 phr TMPTMA almost 70% gel yield can be obtained.

Plasticizer extraction

In all cases, over 98% of the plasticizer was ether extractable, irrespective of the gel yield. This implies that none of the plasticizer is chemically bound to the polymer after irradiation.

Unreacted monomer

Samples examined by infra-red spectrophotometry included crosslinked specimens containing 10 phr TMPTMA irradiated with a dose of 2 Mrad (B2r), 10 phr TMPTMA irradiated with a dose of 4 Mrad (A10r), and 20 phr TMPTMA irradiated with a dose of 4 Mrad

(A20r). No ether extractable monomer was detected in any of the samples, suggesting that all the monomer is linked into the crosslinked network. It was therefore not considered necessary to examine other samples, since those examined covered the extremes of low irradiation dose, and high monomer level. These results suggest that all the TMPTMA is incorporated into the gel during early stages of irradiation.

Residual unsaturation

Despite all the monomer being consumed in the early stages of irradiation, *Figures 1* and *2* show that the residual unsaturation in some of the PVC films was very high, increasing with increased monomer content, and decreased irradiation dose.

The irradiated control sample (A0r) did not show any development of unsaturation after irradiation. Therefore, all the residual unsaturation observed in the crosslinked material must almost certainly be due to unreacted double bonds from the trifunctional monomer. Due to the bulky structure of the TMPTMA molecule, shown below, it is likely that these become sterically hindered due to restriction in mobility in the three dimensional TMPTMA network.

$$CH_3-CH_2-CH_2-(CH_2-O-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}-\overset{\displaystyle CH_3}{\underset{\displaystyle |}{C}}=CH_2)_3$$
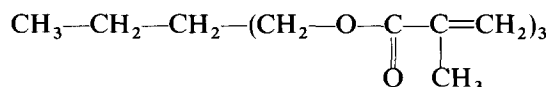
As the TMPTMA concentration is increased, the amount of residual unsaturation also increases as consequence of the faster rate of formation of the three-dimensional network, causing restricted mobility at an early stage. Bowmer et al.[13] have shown that the crosslinking rate, especially during the early stages of irradiation, is proportional to the TMPTMA concentration.

The lack of unsaturation in the irradiated control sample (A0r) is discussed below.

PVC content of the gel

Chlorine contents for extracted gels shown in *Table 2* were used to calculate PVC contents for the gels, and
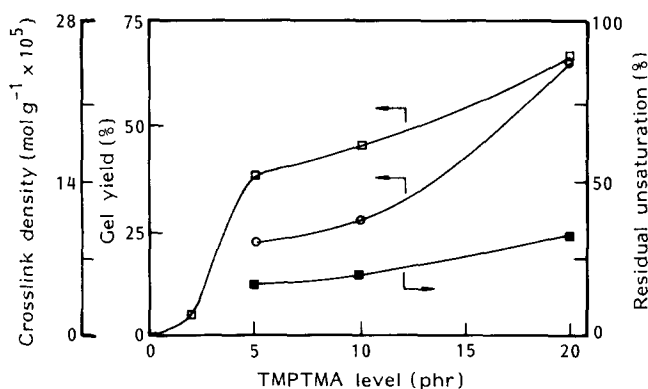

Figure 2 Influence of TMPTMA level on gel yield (□), residual unsaturation (■) and crosslink density in gels (○)

Table 2 Chlorine content of gel fraction

Sample code	A2r	A5r	A10r	A20r	B2r	B6r	B8r
Chlorine (%)	a	42.5	42.6	39.4	32.3	47.2	38.2

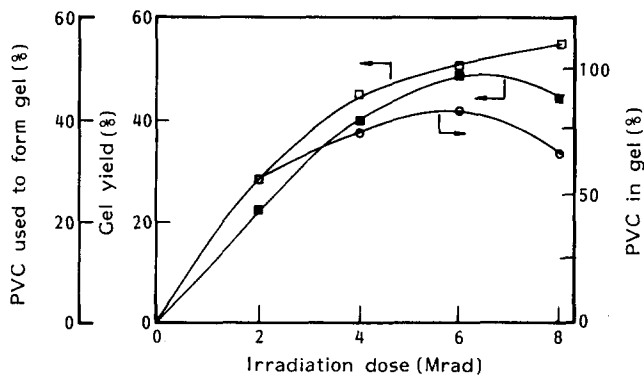a Gel yield insufficient for analysis

Figure 3 Influence of irradiation dose on gel yield (□), PVC content in gel (○) and PVC utilized in gel formation (■)
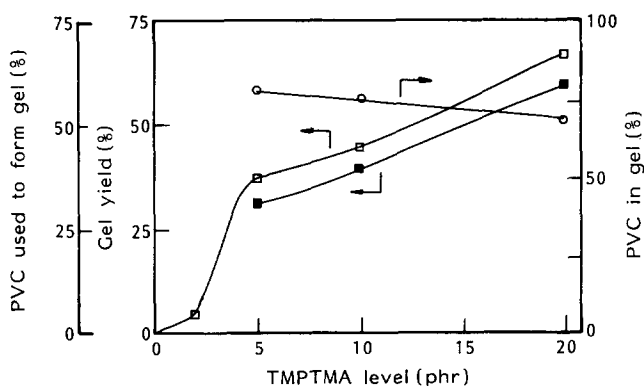

Figure 4 Influence of TMPTMA level on gel yield (□), PVC content in gel (○) and PVC utilized in gel formation (■)

hence assess the amount of PVC actually used in gel formation. These results are shown in *Figures 3* and *4*, as a function of irradiation dose and TMPTMA content, respectively. Samples containing 2 phr TMPTMA did not yield sufficient gel for analysis.

Figure 4 shows that at constant irradiation dose (4 Mrad), the percentage PVC used in the crosslinking increases rapidly with TMPTMA content. This implies that the greater the TMPTMA loading, the greater the amount of PVC linked into the crosslinked network, and therefore the greater the efficiency of PVC crosslinking. The actual PVC content of the gel does not vary significantly with TMPTMA level.

The amount of PVC incorporated into the gel, and used in the crosslinking process are both increased by increasing irradiation dose (see *Figure 3*). However, the irradiation dose is critical, as exposure to a dose higher than 6 Mrad gives a slight decrease in the percentage of PVC utilized during crosslinking, even though the actual gel yield increases. The validity of these results has been confirmed, but the reason for this apparent anomaly is not at present understood.

Crosslink density measurements

Crosslink densities and $\bar{M}_c$ values were calculated from swelling measurements on the extracted gel fractions, and the results are shown in *Table 3*. For comparison with other parameters, crosslink densities are also plotted in *Figures 1* and *2*. *Figure 1* shows that at constant TMPTMA level crosslink density increases to a maximum at an irradiation dose of 4 Mrad, then decreases as the

irradiation dose is increased further. This implies that the initial network formed by the crosslinked TMPTMA breaks down, or radiolyses, at irradiation doses greater than 4 Mrad, and the resulting radicals formed react with more PVC molecules to give a more open structure. The gel yield increases as more PVC is incorporated.

As expected, at constant irradiation dose (*Figure 2*), increased TMPTMA loadings increase the crosslink density of the gel.

Examination of THF soluble PVC

Sample A10r was extracted with ether to remove plasticizer, then with THF. The THF soluble material was compared with the unirradiated control sample (A0), the processed and irradiated PVC without crosslinking agent (A0r), and virgin PVC, as described above. Gel permeation chromatography results are shown in *Table 4*. These show that the THF soluble fraction of the crosslinked PVC consists of low molar mass material, suggesting that the longer PVC molecules are preferentially bound to the crosslinked network.

Figure 5 shows the infrared spectra of the above samples. The spectra show that, upon irradiation, there is a build up of carbonyl groups (peak at $1720\ \text{cm}^{-1}$), hydroxyl groups ($3500\ \text{cm}^{-1}$) and peroxides ($3620\ \text{cm}^{-1}$), which are not present to any significant extent in the unirradiated polymer. However, no conjugated unsaturation, which would result in a band at $1640\ \text{cm}^{-1}$, could be detected in the irradiated product. These results imply that although there is no unsaturation developed during the irradiation, the precursors to PVC degradation have been formed. This suggests that degradation is initiated, although the formation of polyenes at this stage is insignificant. The results also imply that all the unsaturation present is crosslinked into the gel.

The absence of polyene sequences is consistent with the lack of discolouration of the irradiated samples.

CONCLUSIONS

The di-iso-octyl phthalate was not involved in gel formation for any of the systems studied.

Table 3 $\bar{M}_c$ and crosslink densities (c.l.d.) for irradiated samples

	A2r	A5r	A10r	A20r	B2r	B6r	B8r
Gel content (%)	5	38	45	67	28	49	55
$\bar{M}_c$ (g mol^{-1})	–	5520	4560	2110	7600	5300	8020
$10^5 \times$ c.l.d. (mol g^{-1})	–	9.1	11.0	24.0	6.6	9.5	6.2

Table 4 Molar mass data for THF soluble fraction

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Virgin PVC	73 000	124 300	1.70
A0	61 300	105 400	1.72
A0r	65 400	118 100	1.80
A10r	37 300	85 000	2.30

$\bar{M}_n$, number average molar mass; $\bar{M}_w$, weight average molar mass
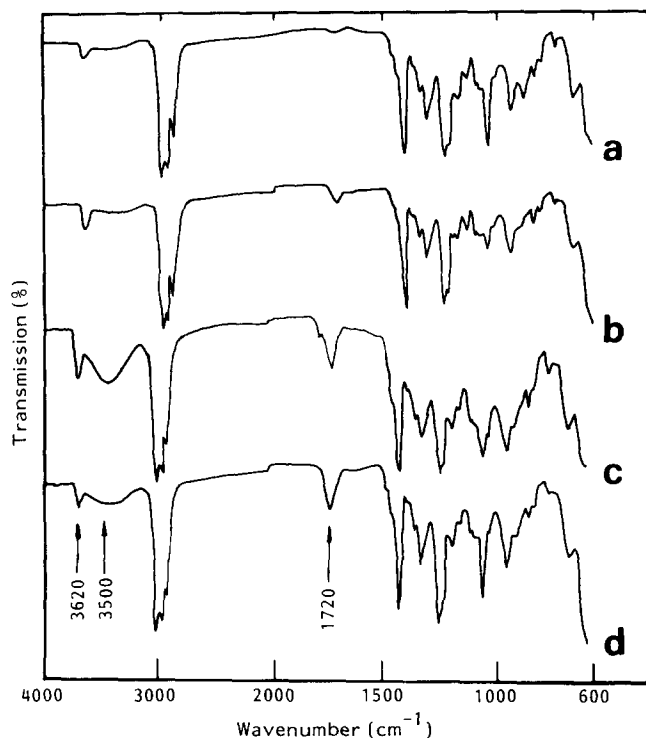
Figure 5 Infrared spectra of THF soluble PVC: (a) virgin PVC; (b) unirradiated processed PVC; (c) sample A0r; (d) sample A10r

It was shown that an irradiation dose of 4 Mrad was particularly suitable for these systems, since a significant gel yield could be obtained, while further increase in dose increased gel yield only slightly. Similarly, 10 phr was selected as an optimum concentration of TMPTMA. Increasing TMPTMA content increased crosslink density, but parallel studies showed that above 10 phr, a decrease in tensile properties was observed.

The crosslinking monomer is used up very early in the irradiation process. The type of network structure formed depends on irradiation dose. At doses above 4 Mrad the initial crosslinked network formed by the crosslinked TMPTMA/PVC breaks down, as shown by crosslink density measurements (*Figure 1*). Although the gel yield increases, a more open network structure is formed. When TMPTMA content is increased, crosslink density continues to increase over the range studied (*Figure 2*). The amount of PVC used in gel formation also increases.

The amount of dehydrochlorination during irradiation is minimal, probably in part due to the stabilizing action of TBLS, and in part due to retardation of radiation-induced degradation of the PVC by the plasticizer. Hegazy *et al.*[20] have shown that radiation-induced degradation, and evolution of HCl, is considerably less for plasticized PVC than for unplasticized PVC. The formation of carbonyl groups, hydroxyl groups and hydroperoxide groups without polyene sequences has also been reported elsewhere[21,22] for irradiated PVC.

Although the degradation of the PVC during irradiation

was minimal, and the monomer was fully reacted very early in the process, there was an unexpected amount of residual unsaturation in the crosslinked product arising from unreacted unsaturation from the trifunctional monomer (*Figures 1* and *2*). Its presence may be explained in terms of steric hindrance of the double bonds of the TMPTMA due to restriction in mobility of the growing three-dimensional TMPTMA network. However, it means that the maximum potential efficiency of the trifunctional crosslinking agent is not being fully utilized. Moreover, and perhaps more important, unsaturation is known to promote oxidative degradation in polymers. Hence its presence in the crosslinked PVC is undesirable since the service life of the crosslinked product will be reduced, particularly when exposed to ultraviolet light or elevated temperatures.

ACKNOWLEDGEMENTS

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