Structure–property relationships of irradiation crosslinked flexible PVC:
2. Properties

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Tensile properties at room temperature and at 130°C have been measured for two series of irradiation crosslinked plasticized poly(vinyl chloride) (PVC) samples. The samples have also been examined by thermomechanical analysis. Experimental variables consisted of irradiation dose and the amount of the crosslinking agent (trimethylolpropane trimethacrylate (TMPTMA)).

Crosslinking caused only minor changes in room temperature properties but a significant change in tensile properties at 130°C and in softening temperature. For this to be observed, a gel content of at least 40% is required. Properties depend on both gel content, and network type, which are in turn controlled by irradiation dose and TMPTMA content.

(Keywords: poly(vinyl chloride); plasticized; irradiation; crosslinked; properties)

In Part 1 of this paper[1] the network structure produced and the extent of degradation of the poly(vinyl chloride) (PVC) were investigated for a series of electron beam crosslinked plasticized PVC samples. The influence of the concentration of the crosslinking monomer trimethylolpropane trimethacrylate (TMPTMA) and irradiation dose were examined. Within the dose range studied, the degradation caused by the electron beam was found to be minimal. 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.

Very few publications have been concerned with TMPTMA crosslinked highly plasticized PVC compositions. In particular, there is little information about the relationship between network structure and properties. De Hollain[2] reported that, in flexible crosslinked PVC, the nature of the plasticizer influenced crosslinking efficiency and network stability. Aromatic plasticizers were considered to impart better properties after irradiation than aliphatic plasticizers. Bowmer *et al.*[3] showed that the presence of plasticizer in PVC enhances crosslinking rates.

In this paper tensile properties at both room temperature and 130°C are reported for the series of samples investigated in Part 1. The effect of irradiation on glass transition temperature and 'softening temperature' is also investigated.

EXPERIMENTAL

Samples examined

Samples were prepared and irradiated as described earlier[1]. Formulations are listed in *Table 1*.

Thermomechanical analysis

TMA traces were obtained for samples before and after irradiation using a Du Pont 990 thermal analyser fitted with a TMA attachment. The penetration mode was used, with a 10 g load on the probe. The temperature range was −60°C to 280°C, and the heating rate was 10°C/min. These traces were used to measure the glass transition of the samples. Also, in order to assess the increased resistance to flow caused by irradiation, a TMA 'softening temperature' was obtained. These temperatures were obtained from the experimental traces as shown in *Figure 1* for the non-irradiated sample without TMPTMA (sample A0).

Tensile testing

Tensile properties for the PVC samples before and after irradiation were measured at room temperature and at 130°C, using a JJ Lloyd tensometer. Dumbell specimens were cut using a BS003 A-2 die cutter. The stretching rate was 40 mm/min. Tensile strength (UTS) and elongation at break were recorded; 100% modulus was also measured at room temperature.

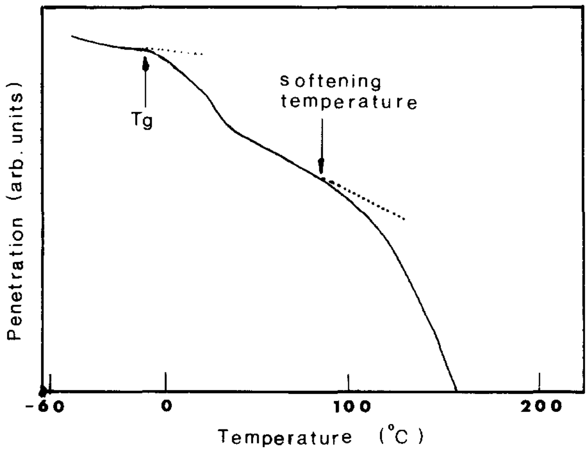

Figure 1 Evaluation of TMA trace for sample A0

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Table 1 Formulations

PVC[a] (phr)	DIOP[b] (phr)	TBLS[c] (phr)	Stearic acid (phr)	TMPTMA[d] (phr)	Radiation dose (Mrads)	Irradiation code before	Irradiation code after
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 = diiso-octylphthalate
[c] TBLS = tribasic lead sulphate
[d] TMPTMA = trimethylolpropane trimethacrylate (Ancomer ATM 11)

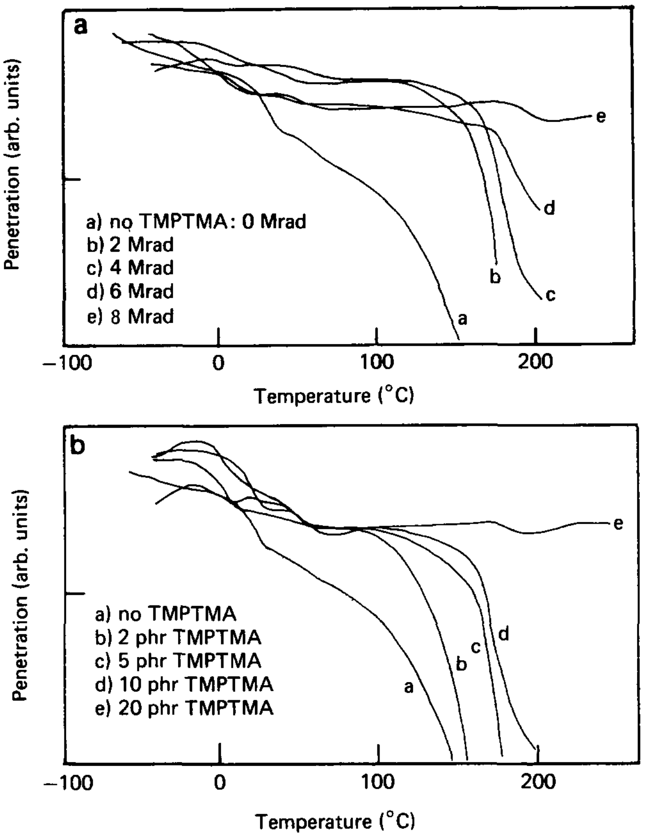

Figure 2 TMA traces. (a), effect of irradiation dose; (b) effect of TMPTMA level

RESULTS AND DISCUSSION

Thermomechanical analysis

TMA traces showing the effect of increased irradiation dose and increased TMPTMA concentration are shown in *Figure 2*. With the load used, most of the samples initially showed some expansion before the glass transition temperature was reached. Although the samples used were only 0.3 mm in thickness to allow the electron beam to penetrate through the sample when double sided irradiation was used, both transitions of interest could readily be detected n all cases. Most measurements were carried out in duplicate. The measured transitions were found to be reproducible.

The glass transition and TMA softening temperatures of the polymers, together with their gel contents (i.e. amount of material insoluble in tetrahydrofuran expressed as a percentage of residue left after removal of plasticizer) measured previously[1] are shown in *Table 2*. For the non-irradiated samples, the glass transition temperatures would decrease through the 'A' series due to the addition of TMPTMA, which acts as a plasticizer[4]. It appears that this effect is at least partly counterbalanced by irradiation, although for the thin samples used, the results used are not accurate enough to see the effect of changes in gel content. These results are consistent with the results of Dobo[4], who showed that for irradiation crosslinked UPVC no change in T_g is observed.

Uncrosslinked PVC softens at approximately 95°C and thermoplastic flow occurs above this temperature. Crosslinking causes the development of a plateau in the TMA trace, which reflects the modulus of the sample, and increases the softening temperature of the PVC. The actual softening temperature is determined by the degree of crosslinking. *Figure 3* shows the effect of iradiation dose and TMPTMA loading on softening temperature.

Tensile properties

The effects of irradiation dose and TMPTMA level on room temperature tensile properties are shown in *Figures 4* and *5*. The effects on properties measured at 130°C are shown in *Figures 6* and *7*.

Figure 4 shows that dose level has no dramatic effect on tensile properties at room temperature, relative to a sample containing no TMPTMA. (The unirradiated sample containing TMPTMA has low UTS and modulus and high elongation because the monomer behaves as additional plasticizer.) *Figure 5* shows that increased TMPTMA loading does cause an increase in 100% modulus and a decrease in elongation at break, although the effect on UTS is insignificant.

Figures 6 and *7* show that crosslinking causes a large increase in UTS at elevated temperatures. Elongation at break increases with irradiation dose, while a maximum is observed with increase in TMPTMA level.

Effect of crosslinked network on properties

Gel content and high temperature tensile strength increase continuously with increased irradiation dose and increased TMPTMA level. However, other measured parameters, particularly crosslink density, behave differently as a function of the two experimental variables due to the different types of network produced[1].

This differing behaviour is reflected in the high

Table 2 TMA transition temperatures of irradiated and control samples

Sample code	A0	A0r	A2r	A5r	A10r	A20r	B2r	B6r	B8r
Gel content %	0	0	5	38	45	67	28	49	55
Tg (°C)	−10	−10	−10	−12	−10	0	−15	−12	−10
Softening temperature (°C)	+90	+95	+100	+120	+145	+175	+110	+170	+175

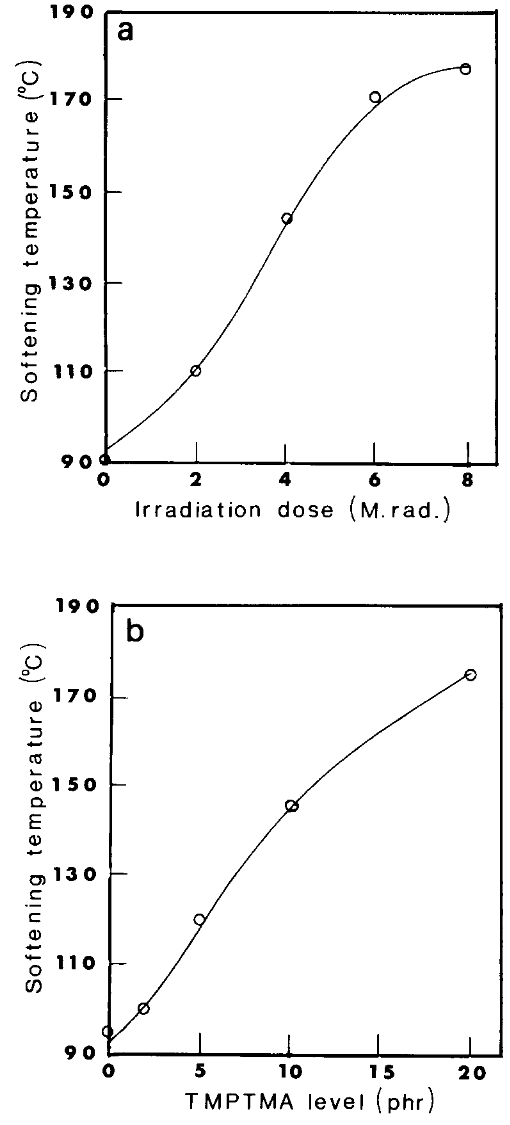

Figure 3 (a) Effect of irradiation dose and (b) TMPTMA level on TMA softening temperature

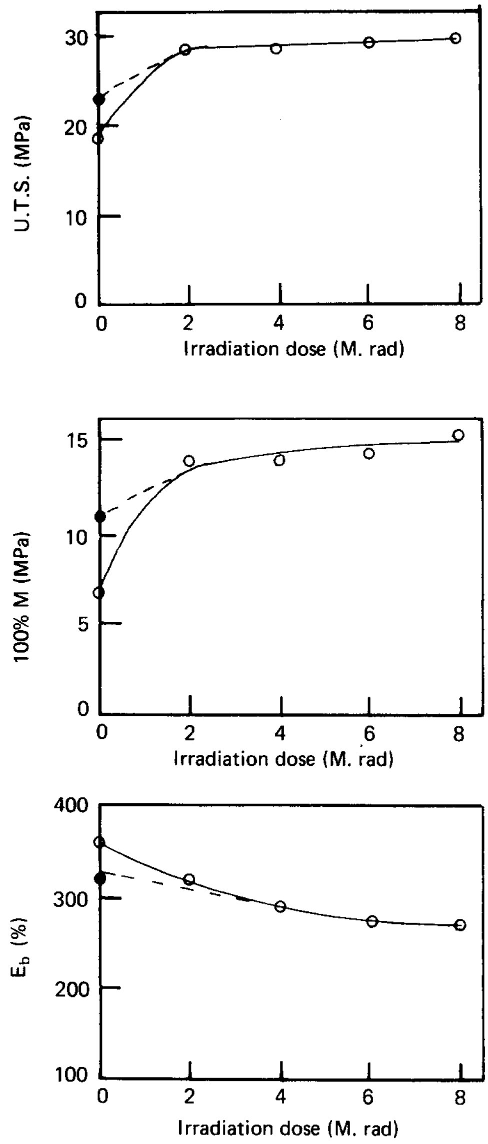

Figure 4 Influence of irradiation dose on room temperature tensile properties. (●, no TMPTMA; ○, 10 phr TMPTMA)

temperature tensile properties. At constant TMPTMA loading (*Figure 6*) both the UTS and elongation at break increase with increased irradiation dose. However *Figure 7* shows that at constant irradiation dose the UTS increases with increased TMPTMA loading, but the elongation at break increases to a maximum at 5 phr TMPTMA and then decreases rapidly. The difference in elongation behaviour as a function of the two variables must be attributed to the different types of network structure present. It has been shown[1] that crosslink density increases continuously with increased TMPTMA level. This will, of course, lead to increased UTS, while elongation at break is initially increased due to this increased strength. However, as crosslink density continues to increase chain mobility is reduced and elongation is decreased.

When irradiation dose is increased at constant TMPTMA level, crosslink density increases until the dose is 4 Mrad, after which it decreases. This has been explained in terms of the formation of a looser network. Again UTS will increase as the gel content increases but a decrease in elongation is not observed because chain mobility is maintained.

The significant increase in load bearing capacity of crosslinked samples at 130°C is not observed at room temperature when tensile properties do not vary very

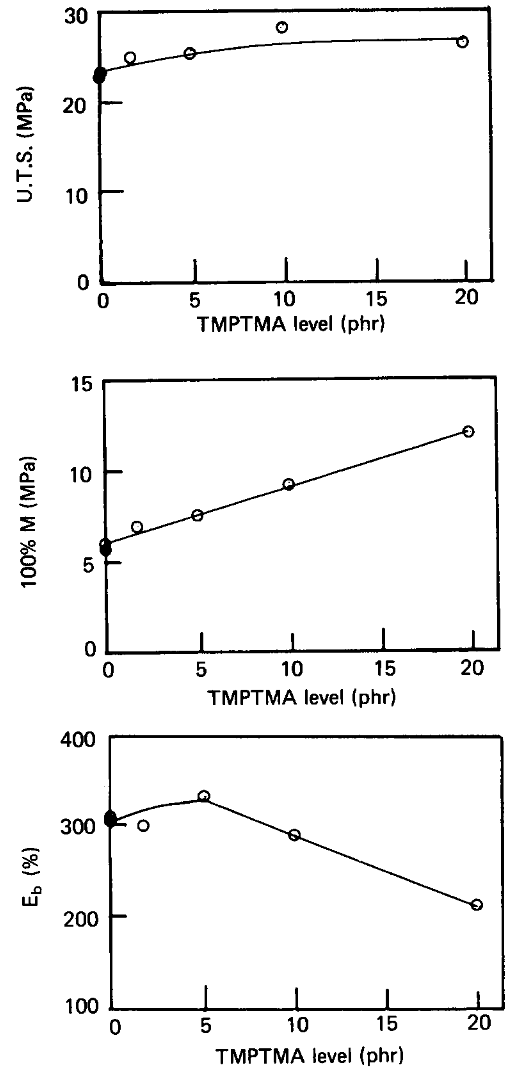

Figure 5 Influence of TMPTMA level on room temperature tensile properties. (●, 0 Mrad; ○, 4 Mrad)

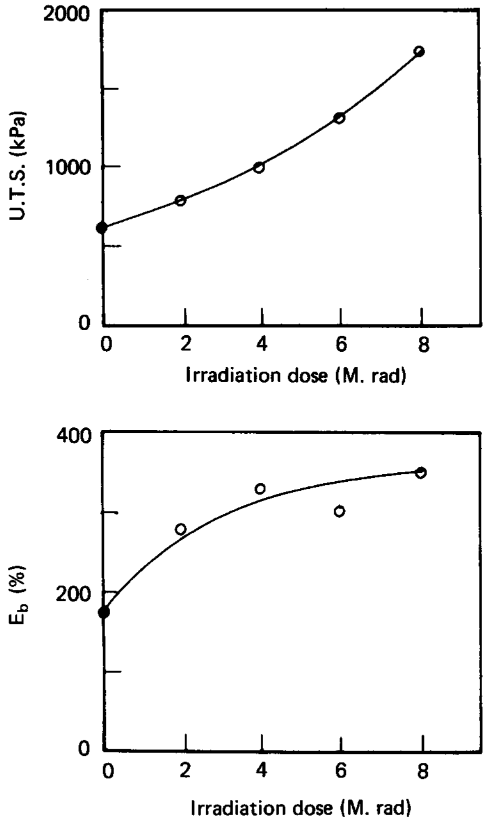

Figure 6 Influence of irradiation dose on tensile properties at 130°C (●, no TMPTMA; ○, 10 phr TMPTMA)

much, except for samples with a high TMPTMA content, where features such as decreased elongation at break as observed at high temperatures, are detectable (*Figures 4* and *5*). The difference in behaviour at the two temperatures is a consequence of chain mobility which is greater at higher temperatures, well above the glass transition temperature of the compounds. Hence the restriction in mobility caused by the crosslinks has a much more significant effect at higher temperatures. At 130°C flow in the unirradiated specimen is only prevented by the presence of small crystallites in the network, which act as physical crosslinks[5].

The high temperature load bearing capacity of the crosslinked PVC relates very well to the increase in softening temperature as measured by TMA. This is demonstrated in *Figures 8* and *9*, in which points for all compounds are plotted. The curves show that for an appreciable increase in softening temperature and consequently good high temperature tensile strength, the PVC must be crosslinked to achieve a gel yield of 40% or over. Optimum properties may be achieved by crosslinking to a gel yield of 50–55%. Properties are not improved by further increasing gel yield but the highest gel yield is achieved by using 20 phr TMPTMA, which is possibly having a significant plasticizing effect, hence limiting UTS

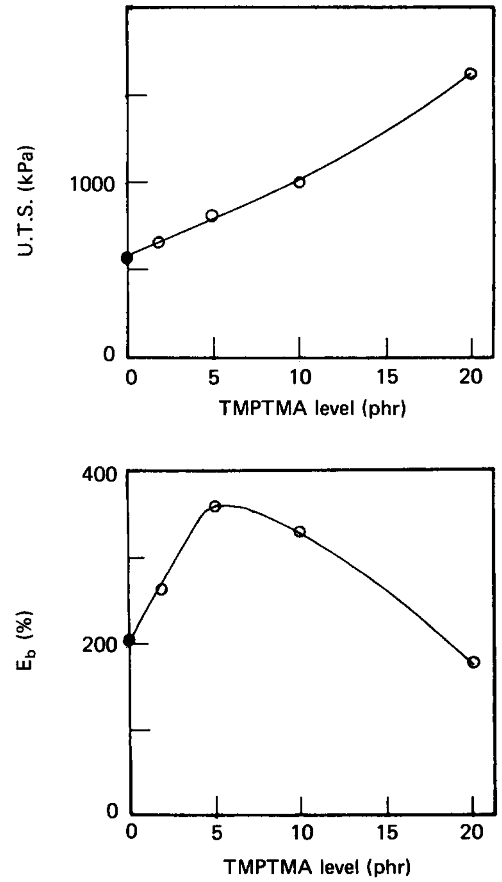

Figure 7 Influence of TMPTMA level on tensile properties at 130°C (●, 0 Mrad; ○, 4 Mrad)

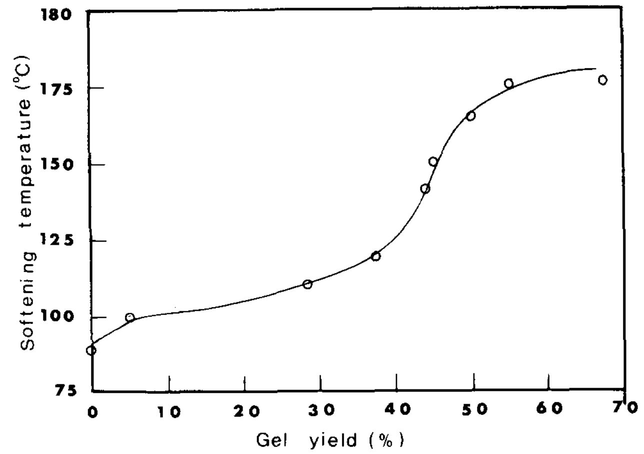

Figure 8 Dependence of TMA softening temperature on gel yield

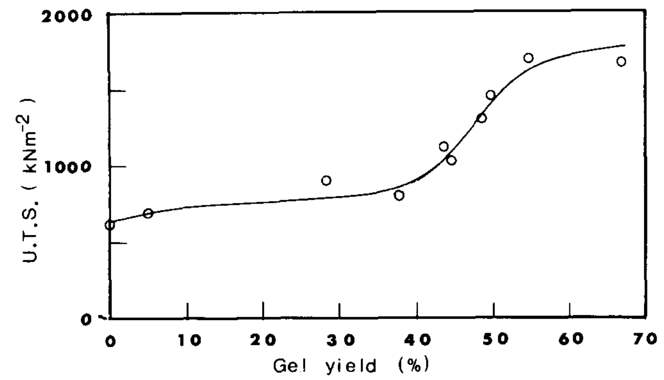

Figure 9 Dependence of high temperature UTS on gel yield

and softening temperature, although *Figure 2b* does suggest that the modulus of this compound would be relatively high.

Although it may be expected that softening temperature and UTS at 130°C should relate to crosslink density, a useful relationship is not observed because of the different types of network produced under different conditions, as discussed earlier.

CONCLUSIONS

(1) Crosslinking plasticized PVC increases its maximum service temperature. The extent of increase is determined by the irradiation dose and TMPTMA level, which control gel content.

(2) The differences in tensile properties between crosslinked and uncrosslinked PVC are more evident at 130°C than at room temperature.

(3) For an appreciable increase in the high temperature tensile properties and in the softening point of the PVC, the gel content must be at least 40% by mass of the PVC from which plasticizer has been extracted.

(4) The tensile properties at elevated temperatures and the softening temperature of a crosslinked compound depend on both the amount and the type of the network structure formed.

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