

Radiation Crosslinking of Poly(vinyl Chloride) with Trimethylolpropanetrimethacrylate. IV. Effect of Diundecyl Phthalate: Dependence of Physical Properties on Composition

T. N. BOWMER and W. I. VROOM, *Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

Blends of poly(vinyl chloride) (PVC) with polyfunctional monomers may be crosslinked by ionizing radiation. The physical properties of PVC blended with trimethylolpropanetrimethacrylate (TMPTMA) and diundecyl phthalate (DUP) were studied. The TMPTMA monomer crosslinked the blend by homopolymerization and/or grafting to PVC. The plasticizer, DUP, was chemically inert under irradiation but, by plasticizing the macromolecules and diluting the monomer, changed the kinetics extensively. Characteristics of the glass transitions and the tensile mechanical properties have been correlated with blend composition and radiation dose. Before irradiation, poly(vinyl chloride) was plasticized by both DUP and TMPTMA monomer. The increase in glass transition temperature and mechanical strength following irradiation to 5 Mrad was correlated with the TMPTMA content of the blend. Both the molecular structure of the network and the DUP content of the blend were factors in determining the physical properties of the final crosslinked blend. The molecular structure was determined by the kinetics of the crosslinking reactions, which in turn were determined by the blend composition. A molecular interpretation consistent with the physical properties, chemical kinetics, and mechanism of the crosslinking system has been presented.

INTRODUCTION

Radiation curing by ultraviolet and electron beam irradiation has become more popular in recent years for a number of applications.¹⁻⁶ The radiation curing processes are energy-efficient, use solvent-free formulations, and produce little or no heat. These are advantages over the traditional thermal curing methods. For example, radiation-induced crosslinking of poly(vinyl chloride) (PVC), in the presence of polyfunctional monomers, produces a coating which has both heat and abrasion resistance,^{4,7} advantages over ordinary plasticized PVC. Among the unsaturated monomers studied, the methacrylates and acrylates were found to have the highest radiation sensitivity.⁷⁻¹¹ They are easily crosslinked by irradiation, incorporating the PVC into the network via grafting reactions.^{7,12-14} In this paper, the radiation crosslinking of a three-component system consisting of PVC blended with trimethylolpropanetrimethacrylate (TMPTMA) and diundecyl phthalate (DUP) has been considered. Such a blend is representative of many radiation-cured coatings since it contains a base resin (PVC), a crosslinking sensitizer (TMPTMA), and a physical modifier (DUP).

In previous papers,¹⁵⁻¹⁷ the effects of irradiation temperature, irradiation dose, and thermal treatment on PVC/TMPTMA blends were discussed. It was shown that there was an initial preference for TMPTMA homopolymerization, after

which PVC molecules were bound into the network. Postirradiation thermal treatment was shown to markedly alter the physical properties of the irradiated blends. This was caused by the reactions of residual monomer molecules and unreacted double bonds in the crosslinked network.

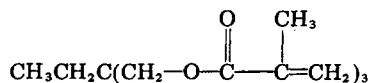
Over a wide range of blend compositions the crosslinking rate was found to be proportional to the TMPTMA concentration.^{16,18} As the TMPTMA concentration decreased, soluble graft copolymers were produced in addition to insoluble networks. A GPC-LC technique provided compositional information on the gel and sol fractions. Infrared spectroscopy was used to follow the reaction of the TMPTMA double bonds. The kinetics were then discussed in terms of a competition between homopolymerization, grafting, and degradation reactions.

In Paper III of this series of papers, the kinetics and mechanism of the three-component system, PVC/TMPTMA/DUP, were studied.¹⁸ The polyfunctional TMPTMA underwent polymerization incorporating the PVC into a network. DUP remained chemically inert during the irradiation, but changed the kinetics extensively as a result of plasticizing the macromolecules and diluting the monomer. These changes were observed as enhanced rates of TMPTMA homopolymerization, TMPTMA grafting, and PVC crosslinking. Different reactions were enhanced to different degrees depending on radiation dose and blend composition. The effect of DUP on the competition between polymerization, grafting, and degradation reactions was explained in terms of the enhanced mobility of the reacting species.

In this study, the tensile mechanical properties and the glass transition characteristics of the PVC/TMPTMA/DUP system will be examined. The correlations between the individual blend components and the macroscopic physical properties will be discussed in terms of molecular structure and chemical kinetics.

EXPERIMENTAL

Poly(vinyl chloride) with $\overline{M}_n = 60,000$ was obtained from the Goodrich Co. Trimethylolpropanetrimethacrylate (TMPTMA) having the structure



was procured from the Ware Chemical Corp. The plasticizer diundecyl phthalate (DUP) was obtained from the Monsanto Co.

The TMPTMA monomer (with thermal stabilizers) plus DUP was added gradually to the PVC in a high speed blender at 60–70°C. These powders were roll-milled to ensure adequate mixing and then compression-molded in a steam press at 150–160°C for 2.5 min to produce sheets 100–400 μm thick. The compositions of the blends were checked by gel permeation chromatography and chlorine elemental analysis and are listed in Table I.

Irradiations were carried out with a Dynamitron electron beam accelerator using 1.5 MeV electrons at currents of 0.4–1.0 mA, to doses up to 5.0 Mrad. The irradiations were carried out under a nitrogen atmosphere at room temperature (20–23°C) as previously described.¹⁵

The glass transition characteristics of the blends were determined by differ-

TABLE I
Blend Compositions^a

| Blend | Composition | | | |
|-------|---------------|--------|------------------|---------------|
| | % PVC from | | % TMPTMA from | % DUP from |
| | GPC | % Cl | GPC | GPC |
| A | 100 | 100 | 0 | 0 |
| B | 91 ± 1 | 91 ± 1 | 9 ± 1 | 0 |
| C | 77 ± 2 | 74 | 18 ± 2 | 0 |
| D | 62 ± 2 | 63.5 | 32 ± 2 | 0 |
| E | 91 ± 1 | — | 0 | 9 ± 1 |
| F | 78 ± 2 | — | 0 | 20 ± 1 |
| G | 81 ± 1 | 78 | 8.5 ± 1 | 8 ± 1 |
| H | 73 ± 2 | 75 | 18 ± 1 | 7 ± 1 |
| I | 61 ± 1 | — | 29 ± 2 | 6 ± 1 |
| J | 64 ± 2 | 62 | 17 ± 1 | 16 ± 1 |

^a All blends contain 2–4% dibasic lead phthalate as a thermal stabilizer.

ential scanning calorimetry (DSC). A Perkin-Elmer DSC-2 instrument was used with a 10–15-mg sample, and a heating rate of 10°C/min. Either the temperature at which the transition began (T_g') or at the midpoint of the transition (T_g) may be used as parameters without effecting the conclusions in this paper. The midpoint value (T_g) was used for the figures in this paper.

The mechanical characteristics were followed by measuring the tensile properties of strength, modulus, percent elongation, and energy-to-rupture. ASTM Test Method D638 was used, employing type V specimens¹⁹ with a universal testing machine from Instron Corp. The tests were done at 23 ± 2°C with a strain rate of 0.004–0.01 s⁻¹. Tensile testing performed at 120 ± 2°C was conducted in a similar manner, but within a preheated environmental chamber (Instron Corp. testing machine accessory). A 30-s dwell period (for specimen acclimation) was allowed between chamber closure and test initiation, with the temperature being monitored from a thermocouple positioned within 1 cm of each specimen's test region. Strain rates were 0.004, 0.01, and 0.02 s⁻¹.

RESULTS

Figures 1 and 2 show the DSC profiles from our blends. The main transition observed is due to the motion of PVC chain segments. Pure PVC has a glass transition temperature (T_g) at 82 ± 2°C. Addition of TMPTMA or DUP decreased the T_g and broadened the width of the transition. At high temperatures (greater than 120°C), an exothermic transition began which was previously shown to arise from thermally induced TMPTMA homopolymerization.¹⁵

Endothermic peaks were generated at 50–60°C if the samples were annealed at 25°C for periods greater than 1 h (Figs. 1 and 2). The temperature and magnitude of these peaks were a function of the annealing conditions (i.e., annealing temperature and time). The peaks may be partially due to the excess enthalpy effect. This effect results from a free volume decrease as the sample ages below the glass transition.^{20,21} However, this relaxation effect would be observed during the transition, and not well above T_g as occurred for a number of our blends (blends D, I, and J). In PVC lightly plasticized with diisodecyl phthalate, it has been suggested that the syndiotactic segments of the PVC chains

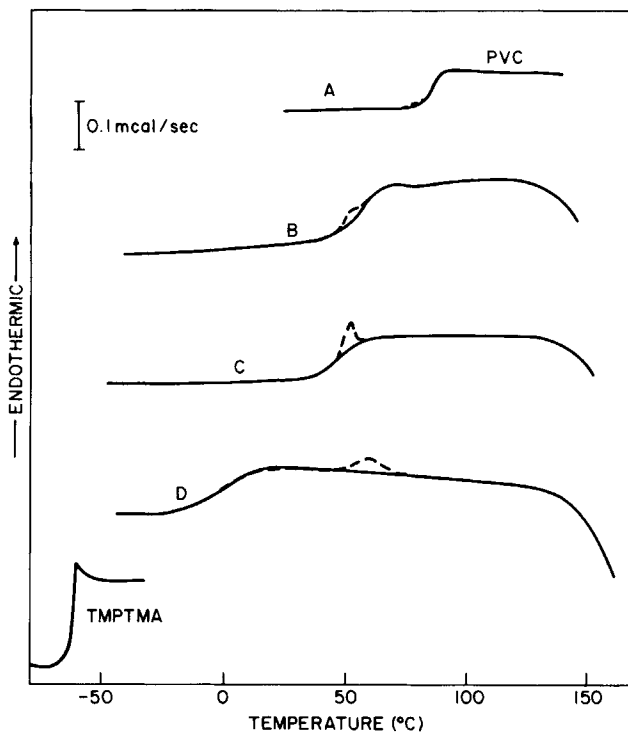


Fig. 1. DSC profiles for unirradiated blends; (—) cooled at $10^{\circ}\text{C}/\text{min}$ from 100°C ; (---) after annealing at 25°C for 24 h. PVC/TMPTMA blends, no DUP. Blend designation as shown in Table II.

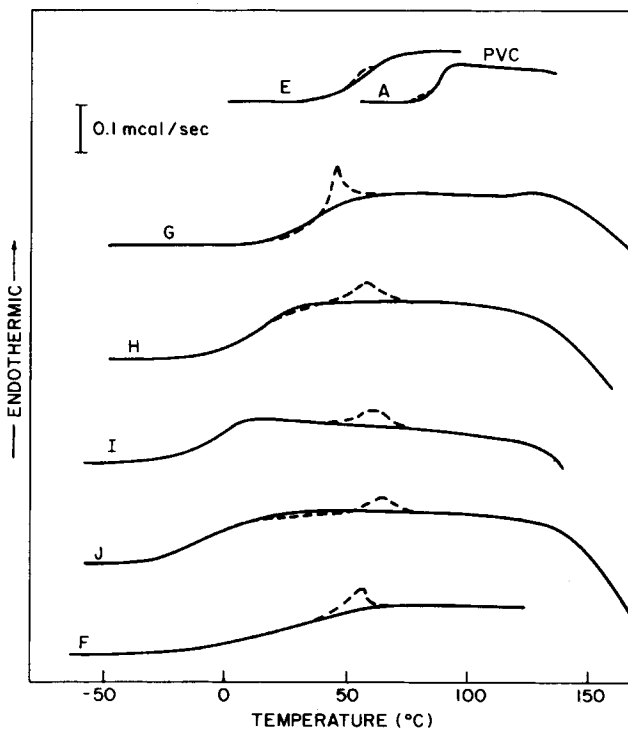


Fig. 2. DSC profiles for unirradiated blends; (—) cooled at $10^{\circ}\text{C}/\text{min}$ from 100°C ; (---) after annealing at 25°C for 24 h. Blends with DUP present. Blend designation as shown in Table II.

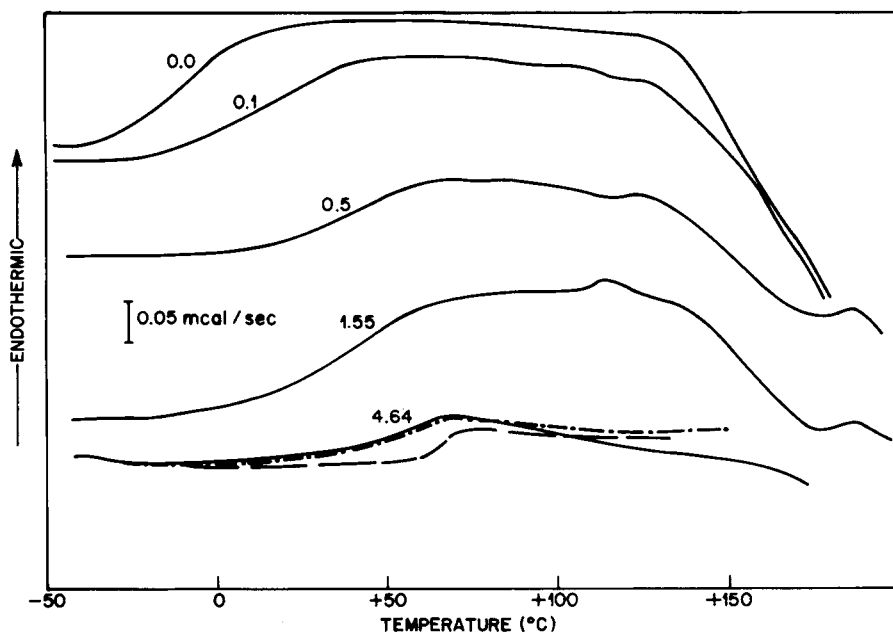


Fig. 3. DSC profiles after doses of 0, 0.1, 0.5, 1.55, and 4.64 Mrad for blend J. (—) No thermal treatment; (- - -) after 3 h at 120°C; (- · -) after 40 h at 150°C.

were not easily plasticized and produced phase separation.²² The chemical structure associated with our endothermic peaks is at present unknown, but may derive from similar configurational interactions. In previous studies this transition was found to remain until the final stages of crosslinking, suggesting that these PVC segments were not readily accessible to monomer.

Figure 3 shows the DSC profiles from a representative three-component blend (blend J) obtained after various radiation doses. Initially PVC was plasticized by both TMPTMA and DUP, which lowered the T_g by $\sim 100^\circ\text{C}$. As the radiation dose increased and crosslinking occurred, the T_g increased and the magnitude of the transition (ΔC_p) diminished. The exothermic peak at high temperatures ($>120^\circ\text{C}$) decreased in magnitude as the monomer reacted to form the network.

The dependence of T_g on irradiation dose is shown in Figure 4 for the blends.

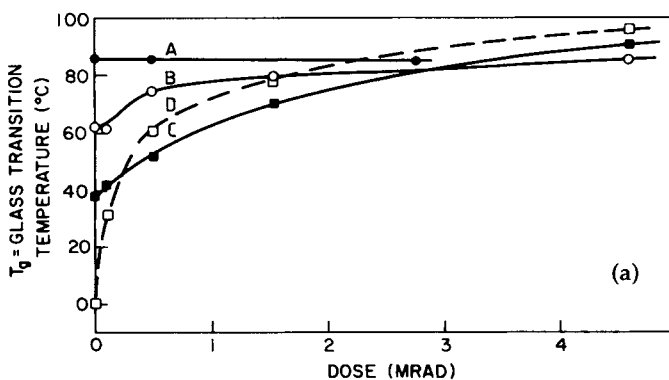


Fig. 4. Glass transition temperature (T_g) vs. radiation dose for blends. Blend designation as in Table II: (a) blends A, B, C, and D; (b) blends G, H, I, and J.

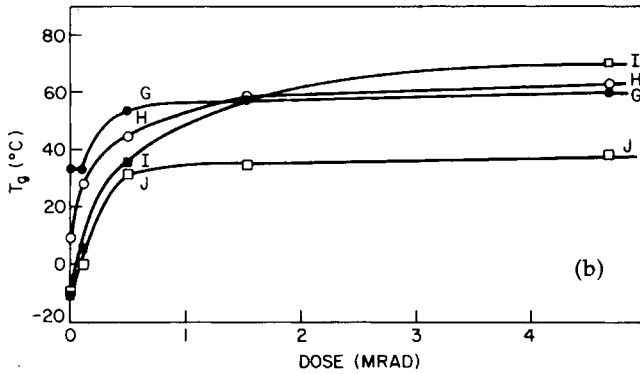


Fig. 4 (Continued from the previous page.)

Initially, T_g rapidly increased as TMPTMA polymerized, and the PVC was incorporated into the network. At high doses (>2 Mrad), a limiting value for T_g was approached which was dependent on blend composition. There are three parameters of interest derived from this plot: (1) the initial T_g value, (2) the final value after crosslinking, and (3) the increase in glass transition temperature upon irradiation.

The initial T_g determines the processing conditions prior to irradiation of the blend. A correlation was found between initial T_g and plasticizer content. The plasticizing ability of an additive is directly related to its volume fraction not its weight fraction.²³ Figure 5 shows the initial T_g as a function of volume fraction of PVC (Φ_{PVC}). The T_g values are independent of the relative amounts of DUP and TMPTMA in the blend, depending only on the volume fraction of PVC.

The increase in T_g (ΔT_g) upon irradiation is a measure of the extent of the crosslinking reaction. After irradiation to 5 Mrad, the ΔT_g was found to be proportional to the TMPTMA content of the blend as shown in Figure 6. This

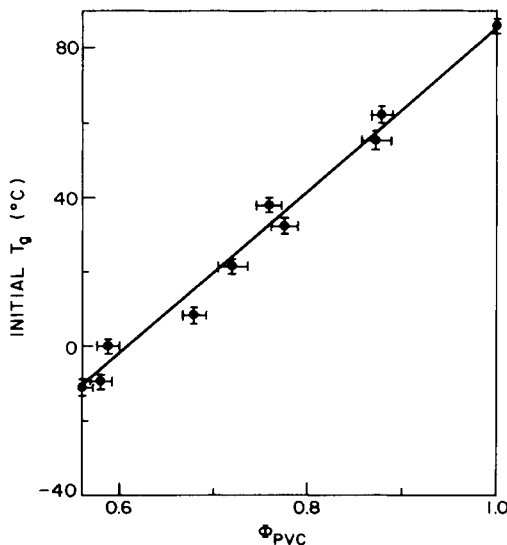


Fig. 5. Initial T_g vs. volume fraction of PVC (Φ_{PVC}).

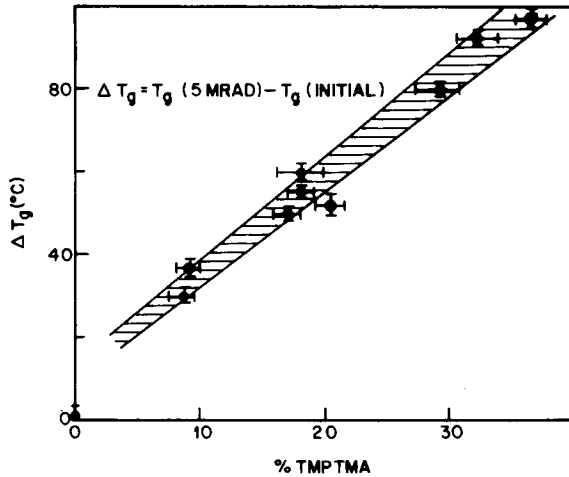


Fig. 6. $\Delta T_g = T_g (5 \text{ Mrad}) - T_g (0 \text{ Mrad})$ vs. wt % TMPTMA.

implies that TMPTMA is the primary crosslinking species. Not only does the monomer homopolymerize to form a 3-dimensional network, but also it initiates PVC incorporation into the network by grafting to the PVC chain. The final T_g of the crosslinked blends (after 5 Mrad) correlated with the DUP content, as seen in Figure 7. After the TMPTMA has reacted, the DUP is the major plasticizing agent and determines the mobility of the PVC chain segments.

The fabrication, molding, and extrusion characteristics for the blends are related directly to their mechanical properties. The ultimate applications for the crosslinked resin and the processing conditions in the preirradiation stage are

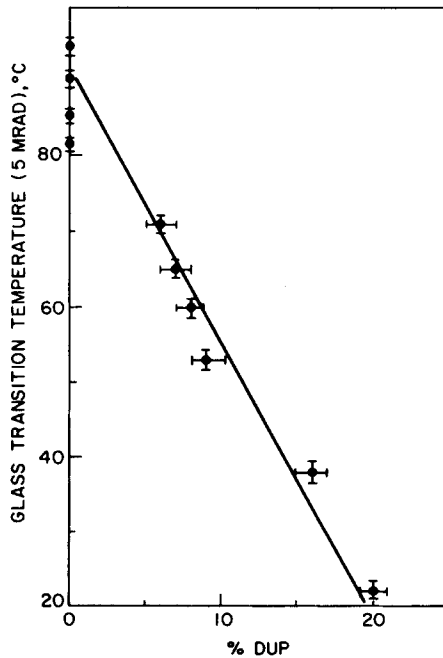


Fig. 7. T_g after 5 Mrad vs. wt % DUP.

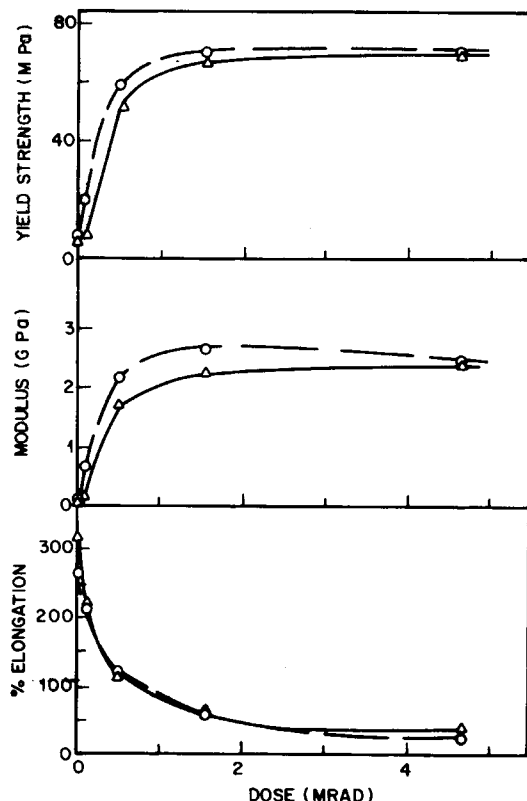


Fig. 8. Tensile properties vs. radiation dose for blends I (O) and D (Δ) (% TMPTMA = 30 ± 2).

determined by these mechanical properties. The tensile properties for the blends are shown in Figures 8–11 as a function of radiation dose.

The modulus and strength of PVC were reduced by addition of TMPTMA and/or DUP and the % elongation was increased. Irradiation of blends containing TMPTMA monomer resulted in a rapid increase in the strength and modulus as a network formed. Concomitantly, the % elongation decreased exponentially to a plateau value as seen in Figures 8–10. The plateaus were reached after 2–3 Mrad. For blends with no TMPTMA, the mechanical properties remained essentially constant across the dose range studied (Fig. 11).

An investigation of the property–composition correlations for the tensile data was performed similar to the glass transition analysis. The % elongation, modulus, and strength of the unirradiated blends were found to be correlated to the PVC content of the blend (see Figs. 12–14). Both TMPTMA and DUP act as plasticizers, prior to irradiation. Their contributions were observed to be additive. Plasticization increased % elongation, but reduced modulus and strength. At low levels of diluent (less than 10%), an antiplasticization phenomenon was seen in the modulus and strength curves shown in Figures 13 and 14. Similar antiplasticization has been observed in numerous polymer diluent systems^{24–28} and has been attributed to induced crystallization, reduction in free volume, and phase separation. The shape of the modulus vs. % PVC curve in

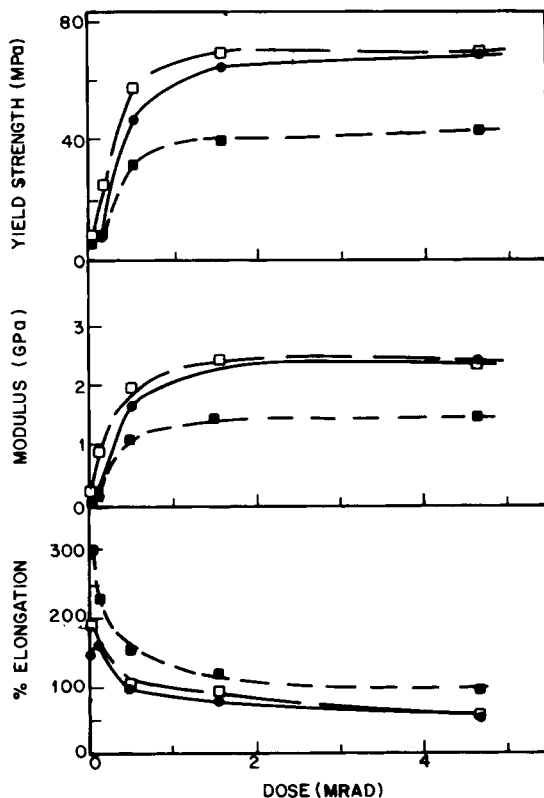


Fig. 9. Tensile properties vs. radiation dose for blends C (●), H (□), and J (■) (wt % TMPTMA = 17 ± 1).

Figure 13 was influenced by the physical state of the blends at the test temperature (23°C). The S-shaped curve had a transition at $\sim 75\%$ PVC. Such a blend has a glass transition at approximately room temperature, i.e., the test temperature. The S-shaped curve therefore reflects the rubber-to-glass transition as the blend composition was changed. Figures 15 and 16 show the modulus and % elongation measured at 120°C as a function of PVC content. Under these conditions all the blends are in the rubbery state. The modulus at 120°C showed no discontinuity with % PVC, but rather a smooth decrease in modulus as the PVC was diluted, as shown in Figure 15. The % elongation at break showed similar behavior at both test temperatures (Figs. 12 and 16), that is, a monotonic increase in % elongation as the PVC was diluted.

Upon irradiation, modulus and strength increased and % elongation decreased as shown in Figures 8–10. The dose of 5 Mrad was selected as the point at which the crosslinking reaction has effectively ceased. Figures 17–19 show the correlations found between blend composition and the changes in tensile properties upon irradiation to 5 Mrad. As expected from the glass transition study (Fig. 6), the TMPTMA content correlated with the tensile property changes as seen in Figures 17 and 18. However, $\Delta\%$ elongation was also found to correlate equally well with % PVC (see Fig. 19). The TMPTMA changed from being a plastizer to become the most rigid component of the irradiated blend [i.e., poly(TMPT-

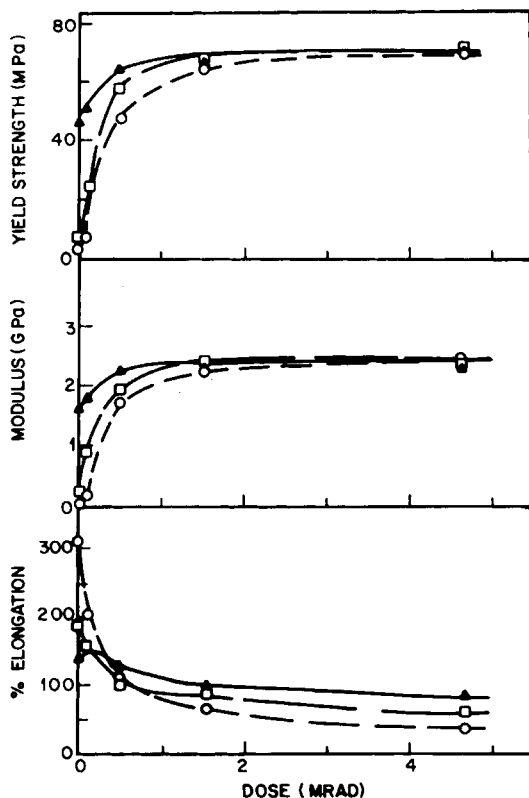


Fig. 10. Tensile properties vs. radiation dose for blends G (▲), H (□), and I (○) (blends with wt % DUP = 7 ± 1).

MA)]. The extent of the reduction in flexibility, and hence the reduction in % elongation produced by radiation crosslinking, is proportional to the amount of TMPTMA initially present. The other components also change their contributions to the mechanical behavior but not to the same extent as TMPTMA. Initially, PVC is the most rigid component in the blend. With irradiation and formation of the rigid poly(TMPTMA) network, it appears that the PVC chains "plasticize" the network. The PVC chains act as flexible segments between the highly rigid poly(TMPTMA) segments. Therefore, we obtain the correlation shown in Figure 19.

The complex nature of the final crosslinked product is reflected in the composition-property plots shown in Figures 20–22. The % elongation after 5 Mrad depended on both TMPTMA and DUP content of the blend (Fig. 20). Since the number of crosslinks increases with TMPTMA content, the rigidity of the final network also increases, resulting in a lowering of the % elongation. Superimposed on this effect is the plasticization by DUP which increases % elongation, as shown in Figure 20. The large arrow in Figure 20 illustrates that, as one moves across the shaded region, the % TMPTMA in the blend is monotonically increasing. The amount of TMPTMA present determines not only the extent of network formation, but also the nature of the network (i.e., the amount of PVC incorporated). The DSC results showed a correlation between the final

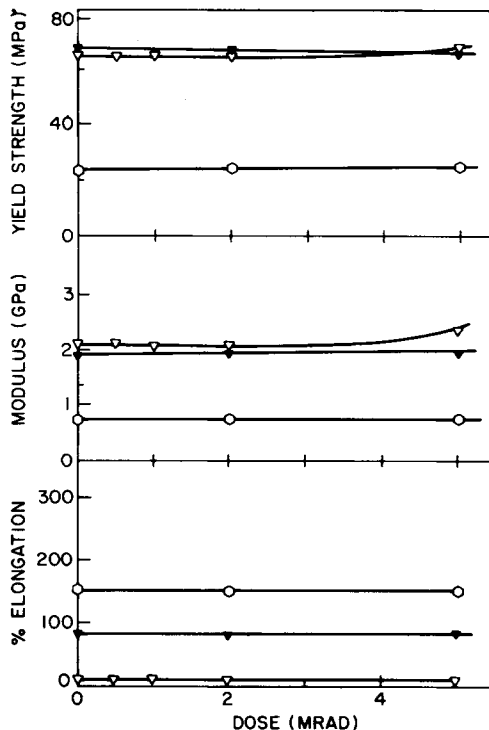


Fig. 11. Tensile properties vs. radiation dose for blends A (∇), E (\blacktriangledown), and F (\circ) (no TMPTMA present).

property and % DUP (see Fig. 7). This reflects the mobility of the PVC segments not bound to the network after 5 Mrad. In contrast to the DSC results, the tensile properties were determined by the nature and extent of the network and therefore were correlated more closely to % TMPTMA (Figs. 20 and 21). Although the DUP content plays a part in determining mechanical properties, the primary role is played by the poly(TMPTMA) network.

Figure 22 shows the tensile modulus for the irradiated blends measured at 23°C. At this test temperature some blends were below T_g and others were above T_g . This difference between the rubber state and the glassy state masks the effects due to molecular structure of the crosslinked blend. Tensile properties at 120°C are shown in Figure 23 for blends irradiated to 5 Mrad. At 120°C all blends were in a similar rubbery state. Since the % TMPTMA determines the crosslink density in the irradiated blend, the tensile modulus increases with increasing amounts of TMPTMA. However, the effects of the plasticizer (DUP) in diluting the effective crosslink density was significant as can be seen in Figure 23. At 120°C, the PVC segments that are not bound into the network will also "plasticize" the network and hence reduce the modulus.

Not all these property variations were due to the physical dilution of the crosslink density. For example, the extent of PVC incorporation in the network and the ratio of TMPTMA homopolymerization to TMPTMA-PVC grafting reactions determine the nature of the network formed. The scheme by which the chemical kinetics and mechanism of the crosslinking reaction depend on

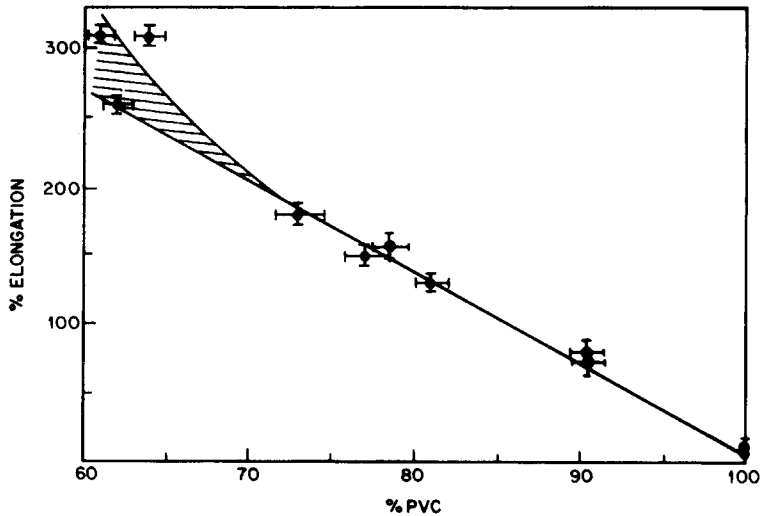


Fig. 12. % Elongation at break vs. wt % PVC for unirradiated blends.

blend composition was reported previously.¹⁸ We will now discuss how the physical properties and molecular structure fit into this scheme.

DISCUSSION

Single glass transitions were observed for our three-component blends, showing compatibility across the composition range studied. However, as seen in Figures 1 and 2, the width of the transition is increased markedly by the addition of either DUP or TMPTMA, suggesting a distribution of PVC chains among different environments. Distinct phase separation has been observed for a related system of PVC/tetraethyleneglycoldimethacrylate blends.¹² We suggest that the widths

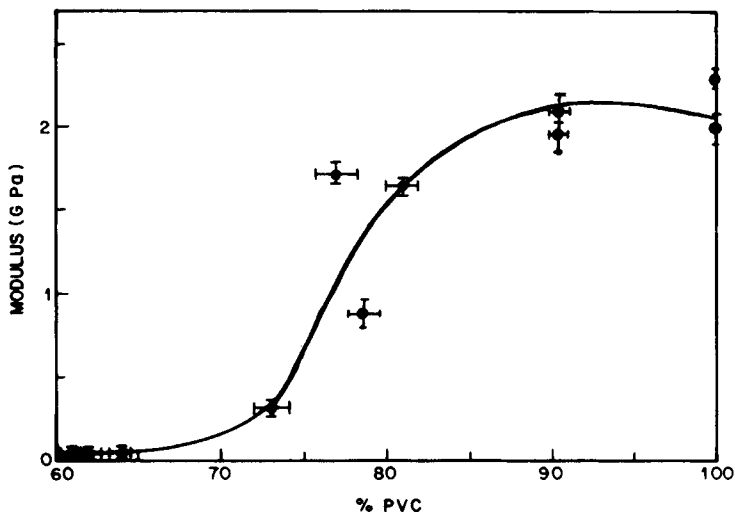


Fig. 13. Tensile modulus vs. wt % PVC for unirradiated blends.

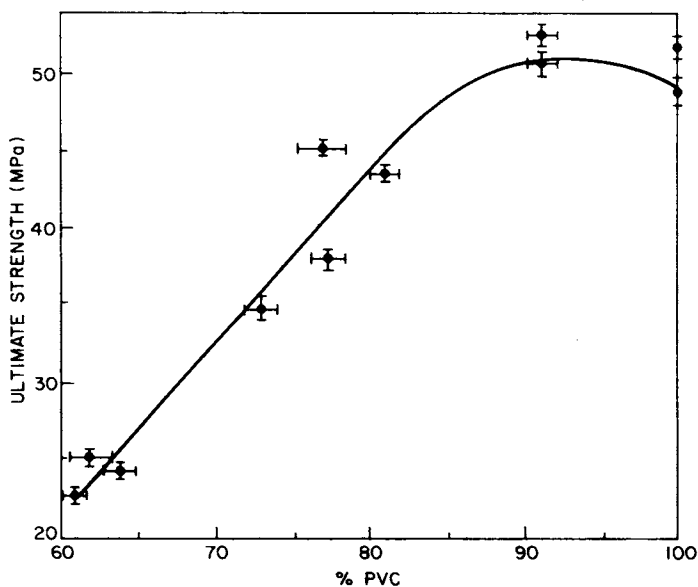


Fig. 14. Ultimate strength vs. wt % PVC for unirradiated blends.

of 40–80°C found for our blends arise from structural heterogeneity of the plasticized polymer; i.e., the PVC segments are plasticized to differing degrees which are not sufficiently distinct so as to obtain phase separation on the scale of a DSC experiment. The addition of DUP broadens the transition to a larger extent than TMPTMA (compare blends F and C in Figs. 1 and 2).

Upon irradiation of the three-component blends, free radicals are produced in the TMPTMA and PVC molecules. DUP has a relatively high stability

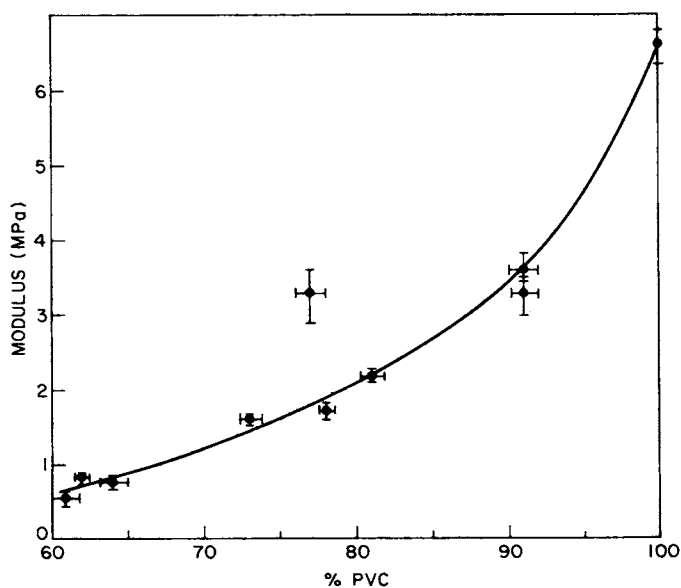


Fig. 15. Tensile modulus at 120°C vs. wt % PVC for unirradiated blends.

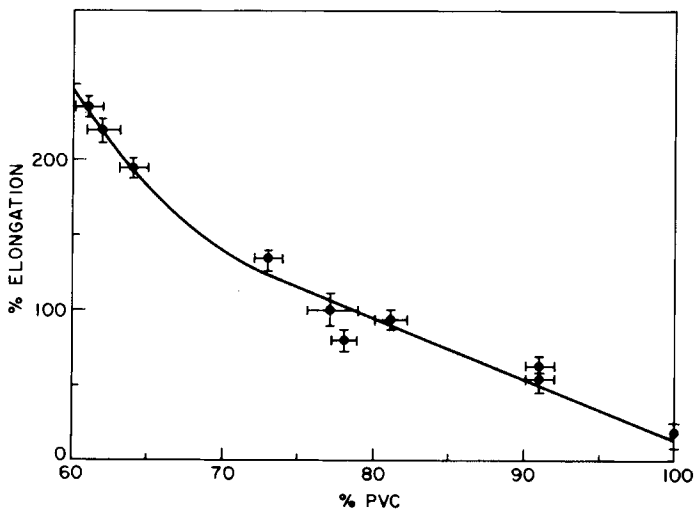


Fig. 16. % Elongation at break measured at 120°C vs. wt % PVC for unirradiated blends.

towards irradiation and can be considered to be essentially inert. Similar stability has been observed in other aromatic compounds and has been attributed to energy transfer to the aromatic ring with subsequent nondegradative dissipation of the energy.²⁹ Radicals produced during irradiation will primarily initiate homopolymerization of the TMPTMA or grafting onto the PVC backbone. In PVC, carbon-chlorine and carbon-hydrogen bonds are the most susceptible to cleavage by ionizing radiation, producing free radical sites on the

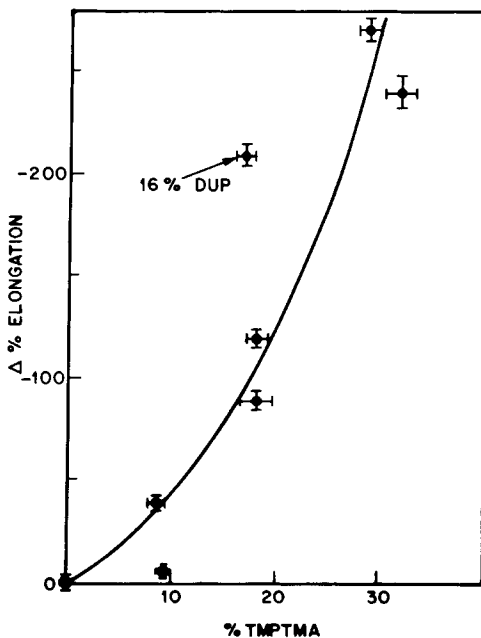


Fig. 17. Δ % Elongation [= % elongation (5 Mrad) - % elongation (0 Mrad)] vs. wt % TMPTMA.

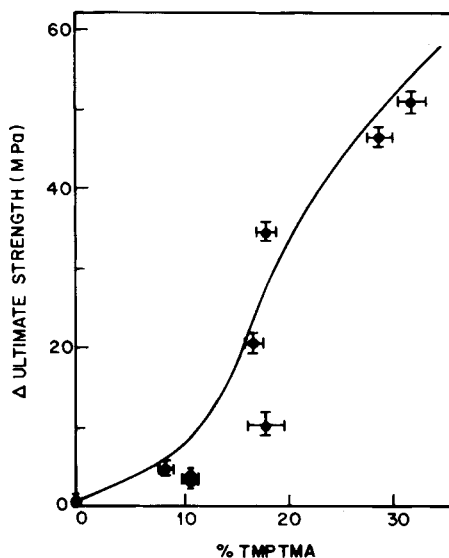


Fig. 18. Δ Ultimate strength vs. wt % TMPTMA after 5 Mrad.

polymer backbone.^{30,31} During irradiation of pure PVC, these radicals mainly initiate dehydrochlorination in addition to small amounts of main chain scission and crosslinking. The radiation chemical yields for PVC are $G(\text{HCl}) = 13$, $G(\text{crosslinking}) = 0.3$, $G(\text{scission}) = 0.2$ at 25°C.³⁰⁻³² This dehydrochlorination proceeds via a chain reaction to produce conjugated double bonds. These unsaturated structures absorb in the visible region, thereby producing discoloration in the PVC.

It has been shown for this present system that the free radical sites created on PVC are scavenged by TMPTMA, which grafts to the polymer chain thereby

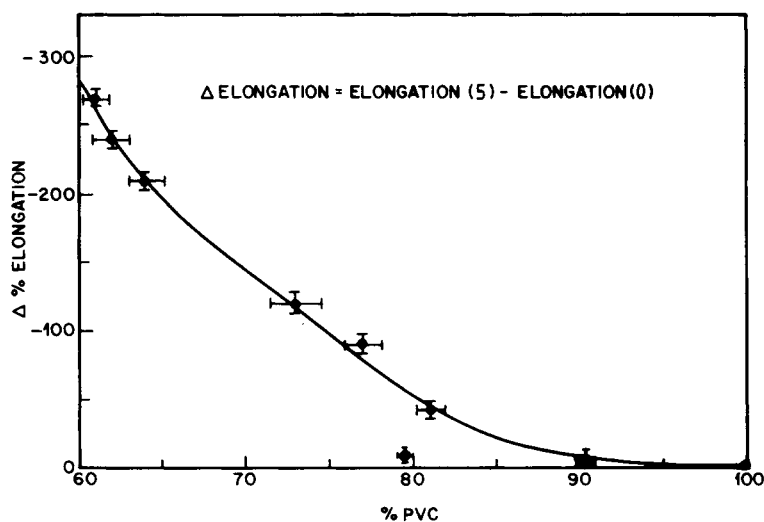


Fig. 19. Δ % Elongation vs. wt % PVC.

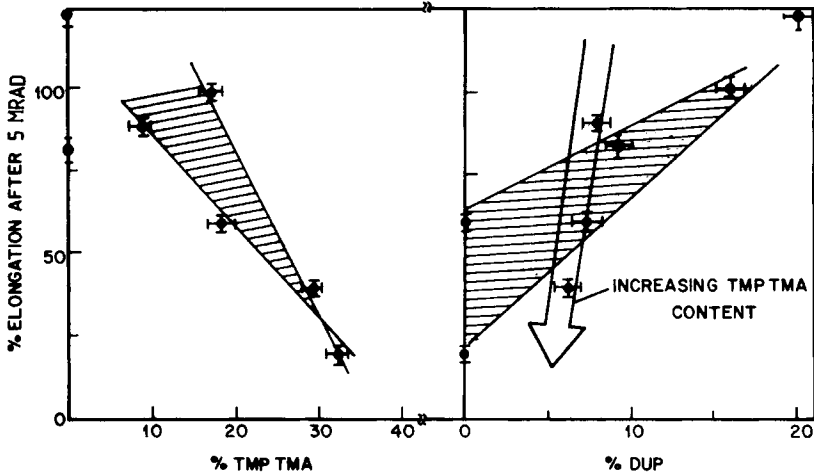


Fig. 20. % Elongation after 5 Mrad vs. wt % TMPTMA and wt % DUP.

incorporating PVC into the network via structures like $\text{PVC}-(\text{TMPTMA})_x$, $\text{PVC}-(\text{TMPTMA})_x\text{PVC}$, etc.^{16,18} This competition between (1) homopolymerization of TMPTMA and (2) grafting onto the PVC has been previously examined by following molecular weight changes in the soluble PVC fractions. It was found that the lower the % TMPTMA in the initial blend, the higher was the probability of a TMPTMA molecule being grafted to PVC instead of homopolymerizing to another TMPTMA molecule. This was true during the initial stages of irradiation. Continued reaction of the graft copolymers results in their incorporation into the network and an increase in crosslink density. The plas-

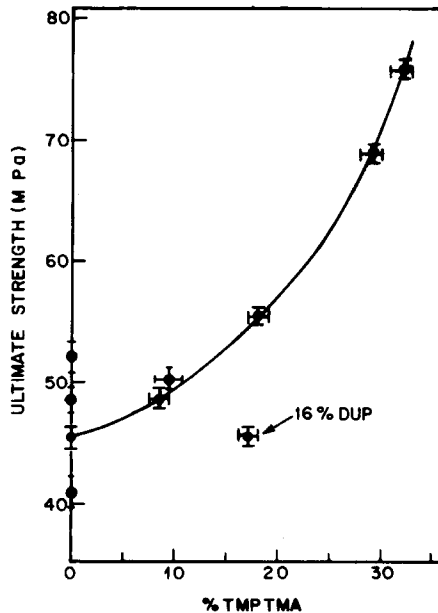


Fig. 21. Ultimate strength after 5 Mrad vs. wt % TMPTMA.

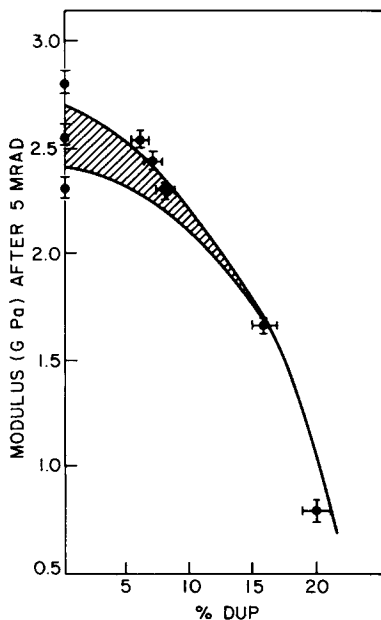


Fig. 22. Modulus after 5 Mrad vs. wt % DUP.

ticizer, DUP, alters the kinetics by increasing the mobility of the reacting species, leading, for example, to an increased rate at which $\text{PVC}-(\text{TMPTMA})_x\text{PVC}$ structures are bound onto the network.

Therefore, the chemical nature of the network will depend on the composition of the blend. As shown previously, for PVC/TMPTMA blends (no DUP), the onset of gelation occurred with minimal consumption of double bonds, e.g., 80%

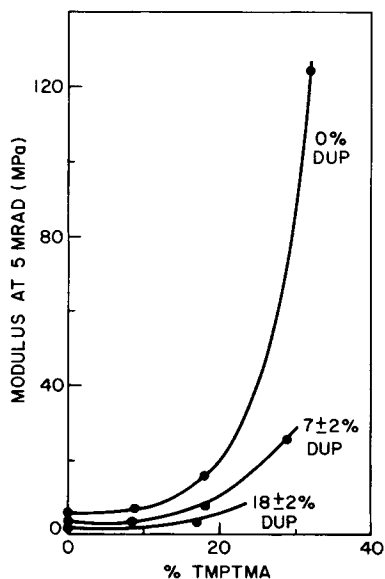


Fig. 23. Tensile modulus after 5 Mrad (measured at 120°C) vs. wt % TMPTMA.

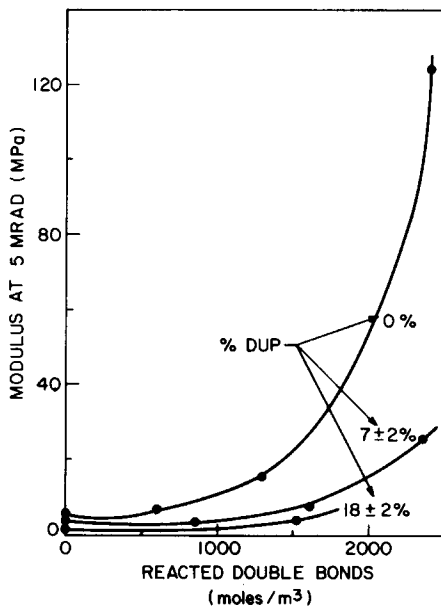


Fig. 24. Tensile modulus after 5 Mrad (measured at 120°C) vs. concentration of reacted double bonds.

gelation was reported using only ~30% of the available double bonds.^{16,18} Only one of the three double bonds per TMPTMA molecule was used in the initial network formation. The residual double bonds were restricted but were not inert. Even after 100% gelation, the residual double bonds and methacrylate free radicals continue to slowly diffuse together, continuing polymerization and increasing crosslink density. The introduction of DUP into the blends resulted in a higher proportion of double bonds reacting to form both the poly(TMPTMA) based network and PVC-(TMPTMA)_xPVC graft structures.¹⁸ The distribution of these double bonds between poly(TMPTMA) and the graft structures depends on the initial blend composition.

It is therefore apparent that the blend composition determines the structural nature of the crosslinked network and therefore determines the physical properties of the blend. Pure poly(TMPTMA) is a high-modulus, low-elongation glass with T_g greater than 300°C.¹⁵ PVC is a rigid plastic with a T_g at 82°C. The physical properties of the irradiated blend will be dependent on the distribution of the components between (1) poly(TMPTMA) networks, (2) PVC-(TMPTMA)_xPVC segments of the network, where x is small (e.g., <10), (3) PVC molecules, (4) PVC chains plasticized by DUP and/or residual TMPTMA monomer, and (5) low molecular weight components, DUP, and residual TMPTMA.^{16,18} This list could be further subdivided into various viscoelastic groups spanning the range between the glassy poly(TMPTMA) to the plasticizer, DUP. Clearly a complex composite is being formed upon irradiation.

The observed glass transition derives from motion of the PVC chain segments. As the irradiation proceeds, the environment of the chain segments changes as the PVC becomes attached to the network. The magnitude of the transition,

ΔC_p , decreases as dose increases (see Fig. 3). Therefore, the heat capacity for bound and unbound PVC chains became similar as dose increased. The PVC chain segments, not covalently bound to the network, have become entangled and thereby restricted by the network. In addition, the PVC chain segments become less mobile since the plasticizing effect of TMPTMA monomer is lost with increasing radiation dose. This causes the T_g to increase towards that for unplasticized PVC. However the segments are bound onto the poly(TMPTMA) network, in PVC(TMPTMA)_x type macromolecules and physically entangled by the network. These segments are more restricted than segments in pure PVC, and hence the final T_g is higher than T_g for pure PVC (compare blends A, B, C, and D in Table II). For the three-component blends, the plasticizing effect of DUP is to reduce T_g while maintaining the above relationship between bound and free PVC chains. For example, compare blends G, H, and I with blend E in Table II. All these blends have a PVC/DUP ratio of 10/1. It was not possible to distinguish between (A) PVC-(TMPTMA)_x-PVC, where x is small, and (B) PVC chains bound to the insoluble network, from the DSC experiments. The DSC behavior of the restricted PVC chain segments does not distinguish between being bound to short grafts or to 3-dimensional networks.

The structural elements (1)–(5), listed above, all contribute to the mechanical properties of the final product. To select a blend composition for a specific application, one is required to compromise between desirable properties. In cable insulation for example, both flexibility and strength are required. Sufficient DUP must be present for flexibility while strength and high temperature stability are attained through increasing the TMPTMA content. But the relationships are complex with the TMPTMA content increasing rigidity as well as strength of the product. The complex relationships between mechanical properties and blend composition arise from the heterogeneity of the structural elements present. They all contribute, but the proportion to which they contribute is determined by the initial blend composition. This composition determines the formation kinetics of the various structural elements and thereby the chemical structure of the network.¹⁸

One may observe these elements in Figure 24 where the modulus after 5 Mrad (measured at 120°C) is plotted vs. the concentration of reacted double bonds.

TABLE II
Transition Temperatures after 5 Mrad

| Blend | Composition | | | T_g (°C) after 5 Mrad |
|-------|-------------|----------|-------|-------------------------------|
| | % PVC | % TMPTMA | % DUP | |
| A | 100 | 0 | 0 | 81 |
| B | 91 | 9 | 0 | 86 |
| C | 77 | 18 | 0 | 91 |
| D | 62 | 32 | 0 | 95.5 |
| E | 91 | 0 | 9 | 53 |
| F | 78 | 0 | 20 | 22 |
| G | 81 | 8.5 | 8 | 60 |
| H | 73 | 18 | 7 | 65 |
| I | 61 | 29 | 6 | 71 |
| J | 64 | 17 | 16 | 38 |

At 120°C one should be high enough above T_g for the blends to be in the rubbery regime of the resin, where structural differences alone will determine the modulus. That is, there will be no phase differences between blends (glass vs. rubber) similar to those observed in Figure 13. The double bond data was determined from the infrared spectroscopy experiments reported in our previous paper.¹⁸ One would expect that the number of reacted double bonds would be proportional to the number of crosslinks. Figure 24 shows a series of distinct curves corresponding to different DUP contents. At 120°C, DUP acts as the major plasticizer of the network. PVC also acts as a "plasticizer" but to a much lesser extent than DUP. Therefore, the modulus of the blend decreases with increasing DUP content, as is observed in Figure 24. The modulus curved exponentially upwards as the crosslink density increased. If all the reacted double bonds formed equally effective crosslinks, then one would expect to obtain a linear relationship in Figure 24.^{33,34} The curvature observed in our system implies that the double bonds in high % TMPTMA blends react to form more effective crosslinks than those in blends with low % TMPTMA. This is a macroscopic result of the kinetic competition between TMPTMA homopolymerization and grafting reactions. In low % TMPTMA blends, grafting reactions account for a significant proportion of the double bonds reacted. Therefore, these reactions do not produce crosslinks directly. Only after further reactions will the grafted structures form crosslinks and join the growing network. Therefore, the double bonds that react to form the poly(TMPTMA) structure are seen as more effective crosslinks in terms of the tensile properties. The contributions from entanglements may also be significant. The intercepts on the modulus axis decrease with increasing DUP content, reflecting the dilution of entanglements. The formation of a poly(TMPTMA) 3-dimensional network would favor the production of trapped entanglements. Preference for homopolymerization over grafting will favor the production of trapped entanglements and glassy segments in the network. Both of these structures will increase the modulus. Distinguishing between the individual contributions is difficult due to the heterogeneous nature of our composites.

Measurements of the dynamic mechanical properties [e.g., storage and loss moduli, $G'(\omega)$ and $G''(\omega)$] as a function of temperature, frequency, and blend composition may elucidate the individual contributions of the blend components. Such measurements are currently being analyzed, and a detailed discussion will be given in a subsequent paper. The preliminary results support the conclusions in this paper. The behavior of the glass-to-rubber transition observed in the rheological experiments supports the calorimetry results shown in Figures 5-7 and Table II. That is, the unirradiated blend properties have a linear dependence on PVC content while the postirradiation properties correlate with the DUP content. Values found for the rubbery plateau moduli (G_N^0) agree with the tensile moduli results shown in Figures 23 and 24.

CONCLUSIONS

The physical properties of PVC blended with TMPTMA and DUP have been studied. In this paper we have shown how the initial composition determined the physical properties of the blend and how individual components of the blend were related to the macroscopic properties of the system. Prior to irradiation,

poly(vinyl chloride) was plasticized by both DUP and TMPTMA. The physical properties of the unirradiated blends were correlated to the PVC content, and were found to be independent of the relative amounts of TMPTMA and DUP present. Increases in glass transition temperatures and mechanical strength upon irradiation were correlated with the TMPTMA content of the blend. TMPTMA was the major reactive species in all of the crosslinking reactions. The molecular structure of the network and the DUP content of the blend determined the physical properties of the crosslinked blend.

The molecular structure was determined by the kinetics of the crosslinking reactions, which in turn were determined by the blend composition. A molecular interpretation consistent with the physical properties, chemical kinetics, and mechanism of the crosslinking system has been presented.

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