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RADIATION CROSSLINKING OF PVC COMPOUNDS WITH SURFACE-TREATED CALCIUM CARBONATE

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Key Words: Polyvinyl chloride; Gamma-ray irradiation; Crosslinking; $CaCO_3$ fillers; Acid-base interactions; Inverse gas chromatography; Adhesion; Postirradiation heating

ABSTRACT

PVC compounds with surface-treated $CaCO_3$ were prepared and irradiated by ^{60}Co γ-rays under nitrogen atmosphere and in the presence or absence of trimethylol propane trimethacrylate (TMPTMA). Samples without TMPTMA did not respond to irradiation. The mechanical properties of other samples, such as tensile strength, yield strength, and % elongation, were affected and one was found to be most sensitive to irradiation. Lower values of Young's modulus were observed for samples irradiated in air compared with samples irradiated in nitrogen at lower doses, indicating the effect of atmosphere in the range of irradiation studied. Mechanical properties and the T_g were not affected by the presence of filler because of weak adhesion at the polymer–filler interface. Inverse gas chromatography showed both the $CaCO_3$ and the PVC to be acids, accounting for these observations. The weak interaction also explains the lower values of Young's modulus for samples using surface-treated $CaCO_3$ as compared with uncoated $CaCO_3$.

INTRODUCTION

One of the important applications for PVC compounds is in the wire and cable industry. PVC compounds used for this purpose are generally crosslinked by radiation in the presence of suitable crosslinking agents [1, 2]. It was reported that among those, trimethylol propane trimethacrylate (TMPTMA), a trifunctional monomer, was one of the most effective chemicals [3]. Crosslinkers are also useful for the prevention of diffusion and/or the migration of plasticizers. In preceding communications we have reported on the properties of radiation crosslinked PVC compounds [4, 5]. It is also known from relevant literature [6–9] that surface characteristics of fillers and polymeric matrixes and their interactions at interfaces may affect crosslinking processes. It is this interaction that determines good or poor adhesion at interfaces and, finally, the strength of composites. Interfacial interactions were initially classified as dispersion force interactions and polar interactions. Later it was found convenient to classify nondispersion interactions as due to the Lewis acid–base effect, dipole–dipole interactions usually being too small to be taken into account. Drago [10, 11] suggested that dipole–dipole interactions be neglected. He classified interactions into two categories: London–London dispersion and acid–base interactions. Later still, acid–base interactions were redefined by Gutmann as electron acceptor–donor interactions [12]. Gutmann has assigned numerical indices to designate the acceptor and donor tendencies of organic materials. These numbers are defined as AN and DN for acceptor and donor tendencies, respectively. Thus, it is possible to describe a substance as a base if it has a greater DN value than AN value, or an acid if AN > DN. By combining Gutmann's classification with the acid/base concepts introduced by Fowkes [13–15], it has been possible to correlate aspects of composite performance with acid/base interactions. In a preceding study on crosslinking of filled PVC [16], conventional $CaCO_3$ was used. IGC measurements showed the filler surface to be basic, with DN = 8.7 and AN = 1.3 [17]. During that study, samples were irradiated under atmospheric conditions.

The present study complements the earlier one by setting the following objectives:

1. To compare the effect of γ-irradiation carried out in a controlled N_2 atmosphere in place of air.
2. To clarify the role of polymer–filler interactions in crosslinking processes; this is done by replacing the original $CaCO_3$ with a surface-treated version shown to be acidic.
3. Finally, to seek the possible effects due to a thermally initiated reaction dependent on a preceding irradiation treatment.

EXPERIMENTAL SECTION

Materials and Methods

The products used in the various formulations are given in Table 1. The ingredients were fused and blended in a 30-mL Brabender mixing head at 170°C for 5 minutes and then compression molded at 190°C for 1 minute at 2 tons and for 2 minutes at 4 tons.

TABLE 1. Chemicals Used in the Compounds

	Function	Supplier
PVC	Polymer host	BFGoodrich
Tri(2-ethyl hexyl trimellitate) – TOTM	Plasticizer	Monsanto
Trimethylol propanetrimethacrylate – TMPTMA	Crosslinker	Sartomer
Lead sulfate – tribase	Stabilizer	Enelchem
Irganox 1010	Antioxidant	Ciba Geigy
Calcium carbonate Omyalite 90 T	Filler	Omya

The composition of the various compounds is given in Table 2. As seen in the table, Samples 1, 2, and 3 do not contain any crosslinker while Samples 3, 4, and 5 contain 10 phr of TMPTMA. Filler concentrations in both groups are 0, 5, and 15 phr.

Samples were irradiated with a ^{60}Co γ-ray source at room temperature. The sample holder was designed in such a way that the factor related to the radiation profile in the cavity was always constant near 1. The dose rate for samples irradiated in air was 8.99 kGy/h. For samples irradiated in nitrogen, the dosage rate was 8.64 kGy/h. A nitrogen atmosphere was established by placing the samples into glass tubes which were purged with nitrogen, degassed, and sealed prior to irradiation.

Mechanical properties of the samples were measured by using a table top Instron-4201 traction machine. All tests were in conformity with ASTM D-638M; that is, they were performed at 25°C and an elongation speed of 5 mm/min.

A DuPont thermal gravimetric analyzer (TGA) was used to investigate postirradiation heating effects. For this purpose the samples were first conditioned at 80°C for 5 minutes and then heated at a rate of 20°C/min up to 400°C. This procedure was repeated with additional 5 minute isothermal periods at 120 and 155°C, followed by the same heating ramp to degradation at 400°C. All TGA measurements were done under an inert atmosphere.

TABLE 2. Composition of Test Compounds[a]

	Sample					
	1	2	3	4	5	6
PVC	100	100	100	100	100	100
TOTM	20	20	20	20	20	20
TMPTMA	0	0	0	10	10	10
Tribase	7	7	7	7	7	7
Irganox	0.2	0.2	0.2	0.2	0.2	0.2
$CaCO_3$	0	5	15	0	5	15

[a] Composition in parts per hundred resin.

RESULTS AND DISCUSSION

Plasticization Effect of Crosslinker

An initial study, similar to one carried out in our earlier work [16], was intended to show the effect of TMPTMA on the mechanical properties of the PVC network. This is documented by the results shown in Fig. 1. The stress-strain curve of Sample 1, which contains neither $CaCO_3$ nor a crosslinker, shows a yield point. When 10 phr TMPTMA is added to this sample (Sample 4), the yield point vanishes and the modulus decreases. The decrease in modulus clearly signals softening of the PVC. The disappearance of the yield point is also related to softening, usually ascribed to the plasticization of polymers. Thus, TMPTMA acts as a plasticizer before irradiation. Irradiating the plasticized PVC with high energy ^{60}Co γ-rays then forms a three-dimensional structure, as reported in Ref. 2. In this structure TMPTMA is homopolymerized and with the PVC forms a matrix in which load is initially carried elastically, producing a yield point, similar to the control specimen 1 of Fig. 1.

Effect of Irradiation Atmosphere

The effect of atmospheric control in γ-irradiation is illustrated by the results in Figs 2, 3, and 4. Figure 2 compares the behavior of Young's moduli. These are greater for samples irradiated under N_2 and at low dosages. The presence of 15 phr

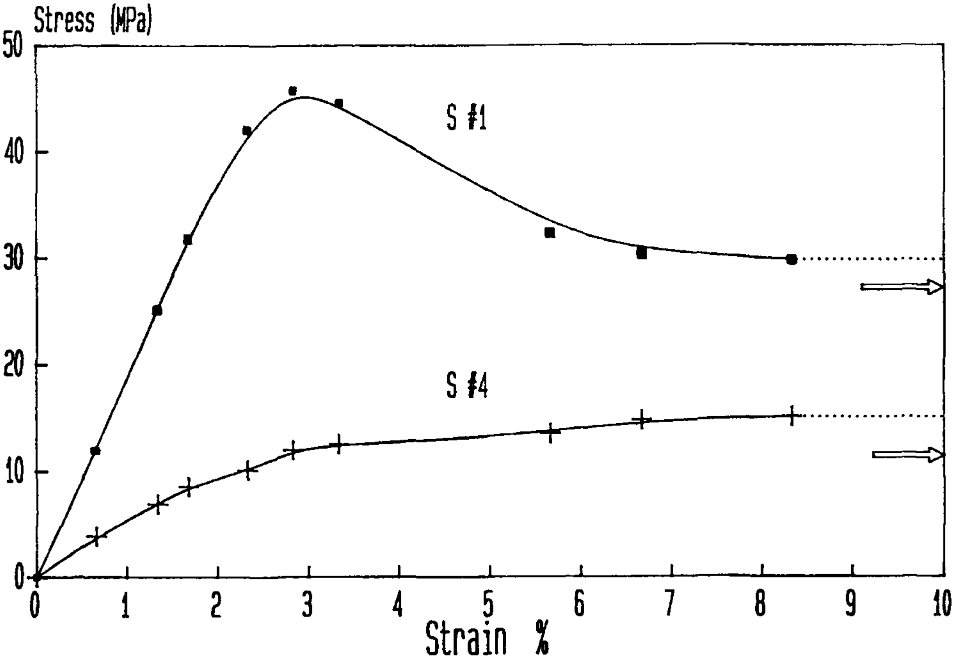

FIG. 1. Plasticizer effect of TMPTMA on unirradiated samples: (■) Sample 1 without TMPTMA, (+) Sample 4 with TMPTMA.

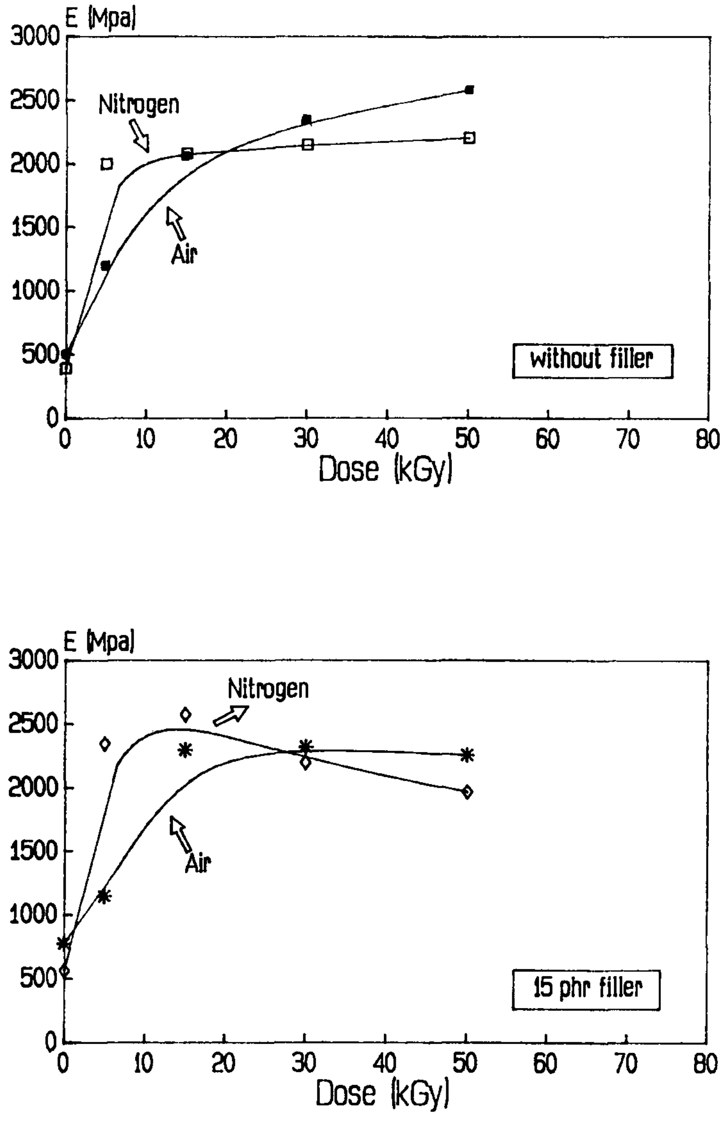

FIG. 2. Effect of irradiation atmosphere on Young's modulus.

filler has little effect on the coordinate placement of these curves. Yield stresses are compared in Fig. 3. Again, irradiation in nitrogen and at dosages below about 20 kGy produces higher yield stresses than irradiation in air, and once more the presence of filler has relatively little effect on the absolute values of the yield stress. The enhanced modulus and yield stress suggest that irradiation in nitrogen is more effective in generating cross-links, presumably because of the absence of inhibiting effects due to oxygen. The effects of different irradiation atmospheres and dosage can also be noted in the elongation at rupture, as shown in Fig. 4. There is a sharp decrease in ultimate elongation for early stages of irradiation under nitrogen. The

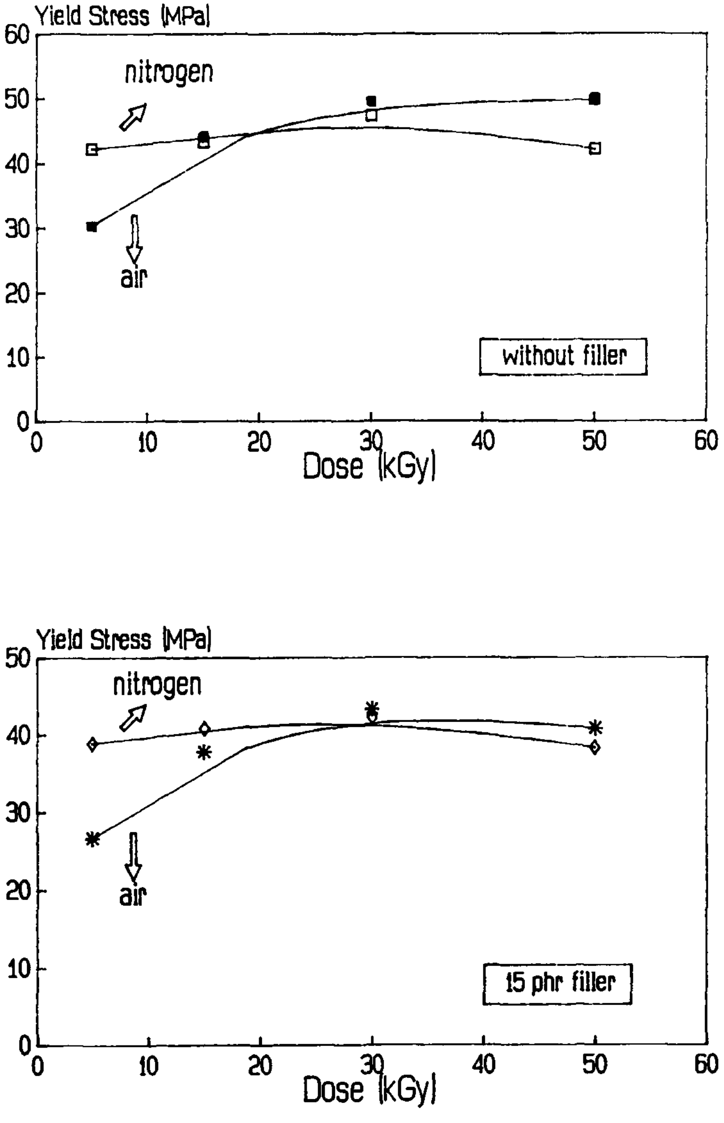

FIG. 3. Effect of irradiation atmosphere on the yield stress.

critical point in Figs 2-4 is irradiation at 5 kGy. The sharp decrease in elongation at rupture (Fig. 4), already alluded to, is accompanied by an increase in the modulus of these samples, as shown in Fig. 2. Batch to batch variations result in different ordinate points (zero irradiation) in these data representations, but the systematic trends followed by the results justify arguments on the effect of irradiation atmosphere. We suggest that under nitrogen, irradiation leads to the immediate development of a crosslink network structure, a logical consequence of removing the inhibiting effect of oxygen.

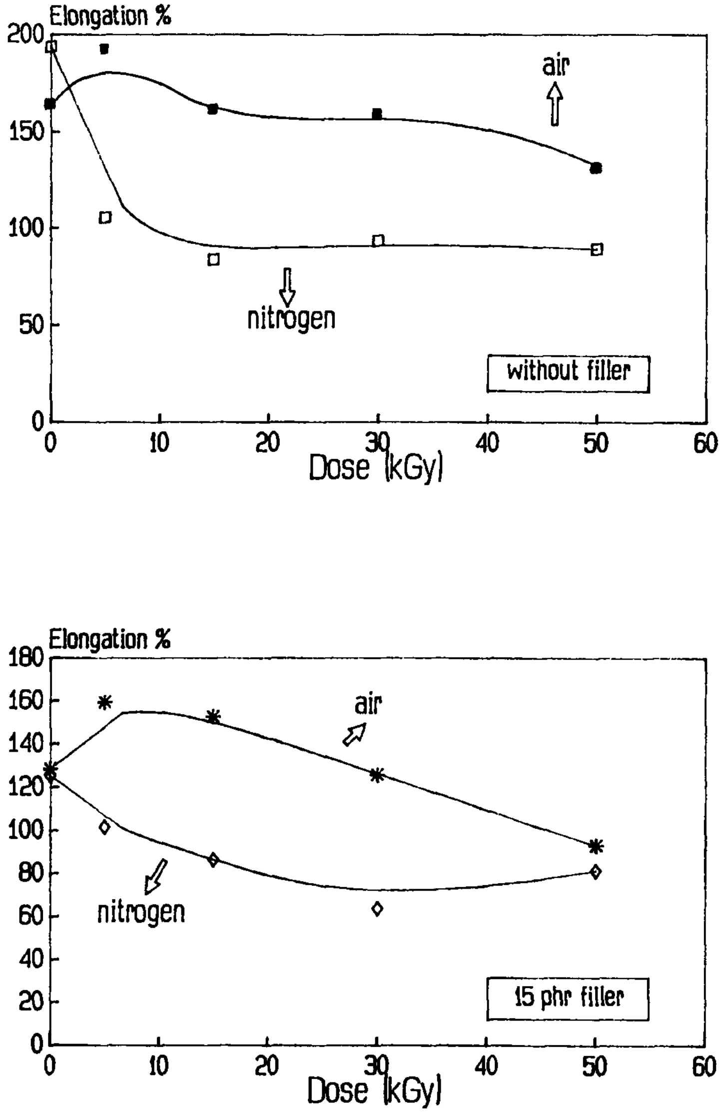

FIG. 4. Effect of irradiation atmosphere on % elongation.

Effect of Filler-Polymer Interaction

As discussed previously, IGC analysis of the $CaCO_3$ used in earlier work [16, 17] showed the filler to be a strong base, with donor and acceptor indices of DN = 8.7 and AN = 1.3. It has also been shown that the surface of PVC is acidic due to its acidic hydrogens. The corresponding indices for the polymer are DN = 2.7 and AN = 8.4 [4, 5]. Naturally, when PVC is contacted with $CaCO_3$, strong acid/base interaction is to be expected, and this was confirmed in previous work [16]. In this study we have used a surface-treated $CaCO_3$ instead of a conventional one. It

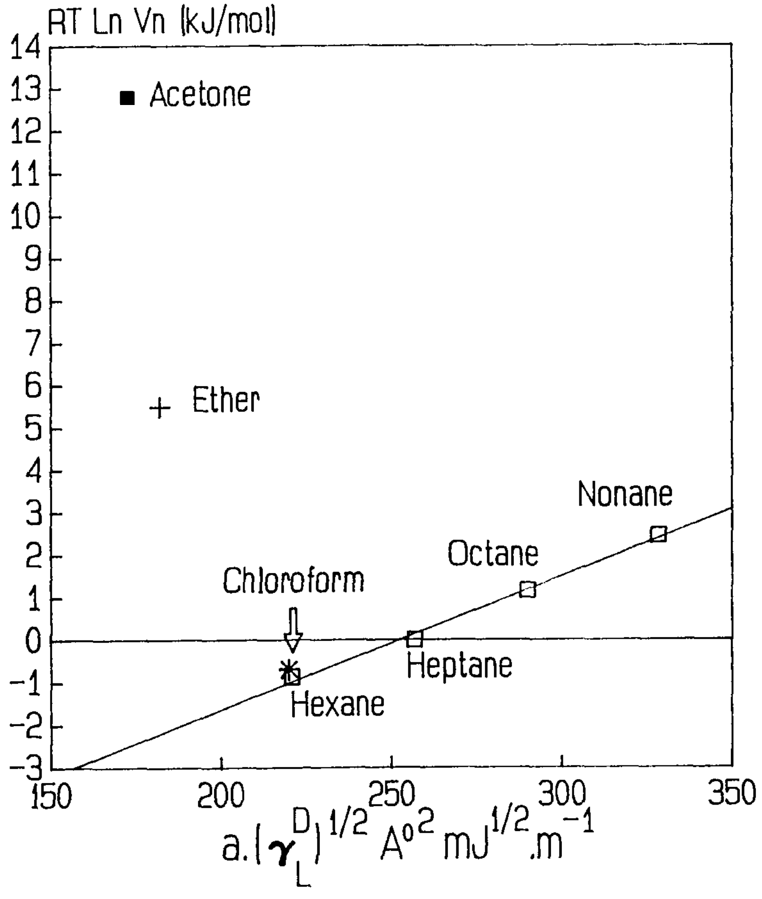

FIG. 5. IGC results on surface treated calcium carbonate at 120°C probe codes: (□) alkanes, (■) acetone, (+) ether, (*) chloroform.

was therefore possible to investigate the effect of surface modification on the final properties. The surface characteristics of the filler used in this report were also determined by inverse gas chromatography (IGC). The protocols related to the determination of surface acidity and basicity have been successfully applied by many authors [18]. It is not our purpose to focus on the IGC technique, which has been described recently in considerable detail [18]. One of the significant uses of the technique is the evaluation of dispersion surface energy and of acid/base interaction parameters for the stationary phase in the IGC experiment. The principal statement relating to these uses is

$$RT\ln Vn = 2N(\gamma_L^D)^{1/2}a(\gamma_S^D)^{1/2} + C'$$

where Vn is the net retention volume, a is the surface area of an adsorbed vapor molecule, and (γ_L^D) (γ_S^D) are the dispersion surface energies of vapor and solid, respectively. C' is a constant for a given chromatographic column which depends

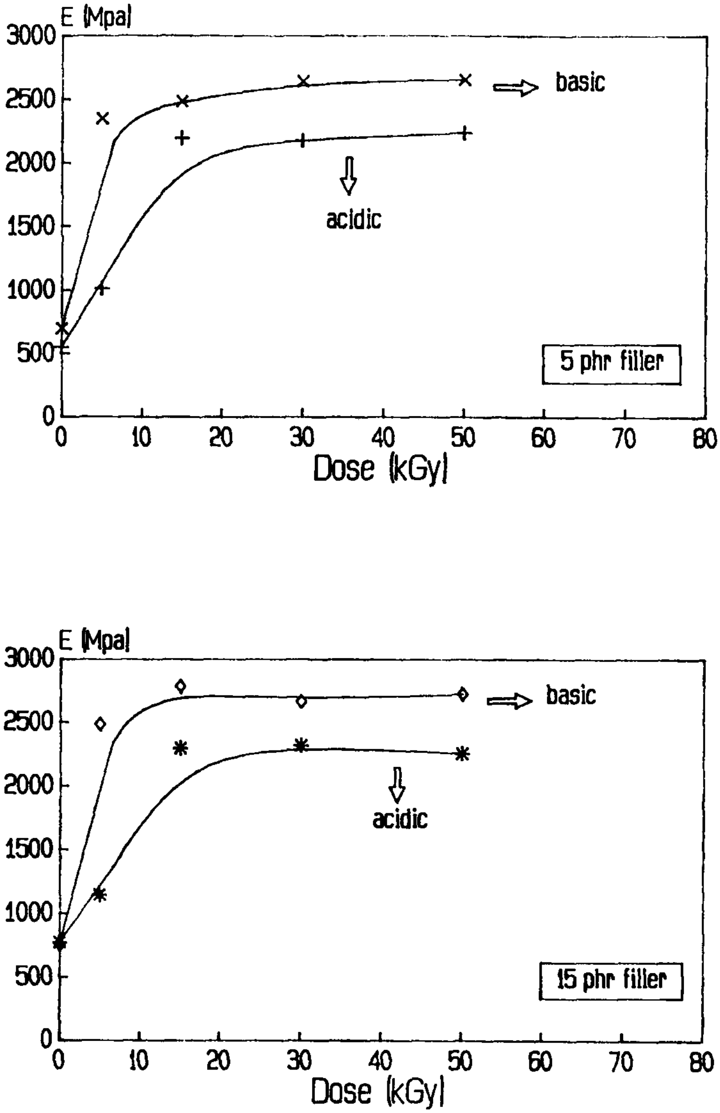

FIG. 6. Effects of acidic and basic fillers on Young's modulus.

on the chosen reference states. When the volatile phase is able to interact with only the dispersion forces (e.g., *n*-alkane vapors), then $RT \ln Vn$ vs $a(\gamma_L^D)^{1/2}$ should generate a straight line. As shown in Fig. 5, the expectation is fully met at 120°C. Similar excellent linearity was produced at 110 and 130°C.

Figure 5 also shows the retention times for chloroform, ether, and acetone. These substances have been designated by Gutmann as acid, base, and amphoteric, respectively, and are used here as reference probes. The position of the *Vn* for these vapors shows Omyalite 90 T to be acidic, since the basic ether is much further removed from the alkane reference line than is the acid reference, chloroform. A

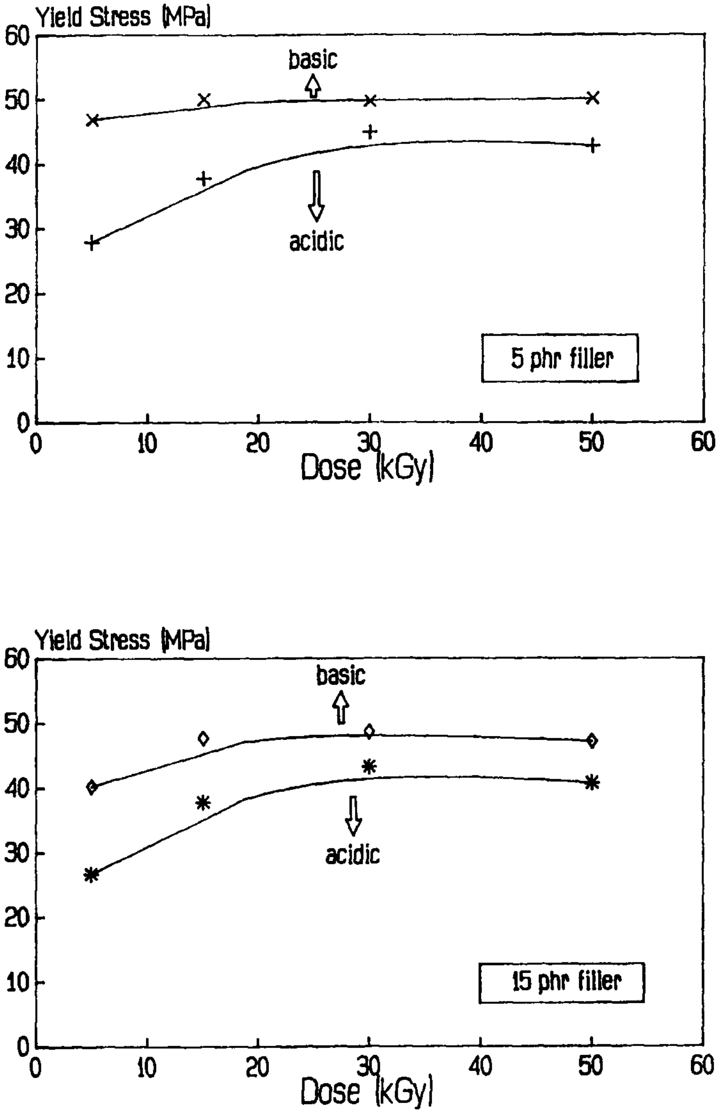

FIG. 7. Effects of acidic and basic fillers on the yield stress.

mixture of PVC with this $CaCO_3$ therefore would not involve significant acid/base interaction. Given the evidence [18, 19] that interfacial adhesion is dependent on acid/base interactions, it follows that PVC/$CaCO_3$ adhesion in the present case is much weaker than in the earlier reported work [16]. As a result, the filler is not likely to reinforce the polymer matrix. The consequences of this may be seen in Fig. 6 where Young's modulus is plotted versus dose at two levels of adding the acidic and basic fillers. Young's moduli of samples with acidic $CaCO_3$ are much smaller

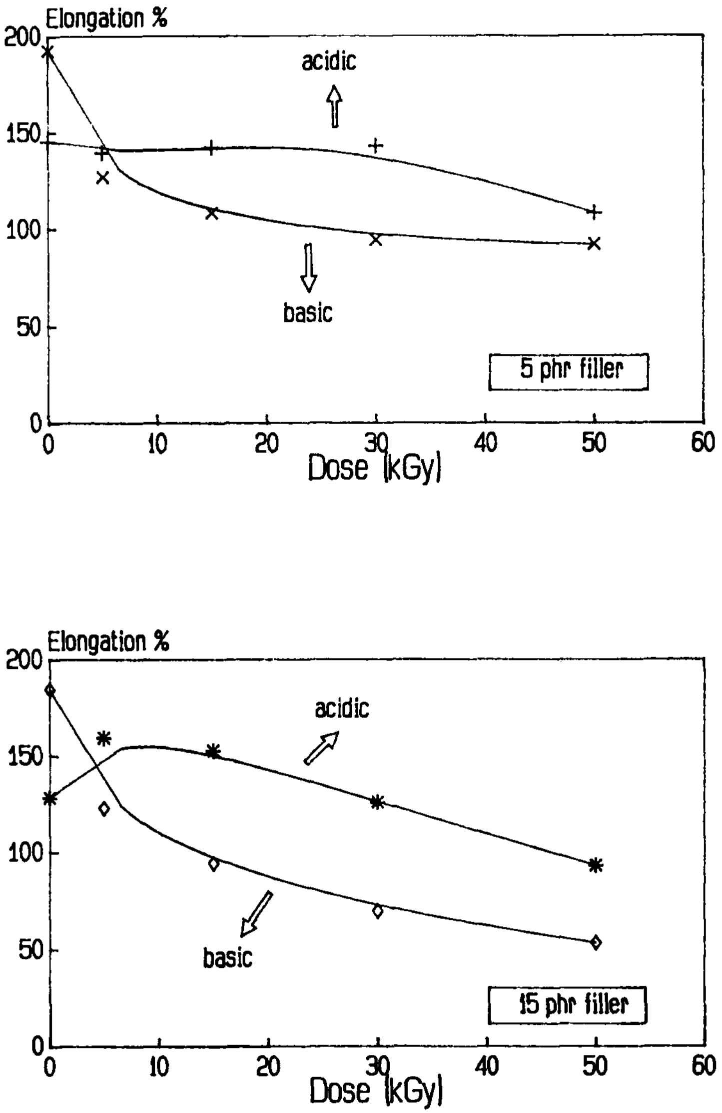

FIG. 8. Effects of acidic and basic fillers on % elongation.

than when basic $CaCO_3$ is used. The yield strengths and ductilities of samples with acidic $CaCO_3$, similarly, are lower than those where the basic filler is used, as shown in Figs. 7 and 8. The results in Fig. 8 are particularly interesting, showing the ductility of irradiated samples to be very sensitive to interfacial forces. Weak adhesion here actually benefits performance, presumably because strong network links in regions of $PVC/CaCO_3$ contact cannot be formed. Consequently, slippage may occur at these loci during the application of stress, with the result of enhanced elastic deformability to rupture.

TABLE 3. Weight Loss vs Temperature History

	Weight loss % between 310 and 370°C
Sample 4 conditioned at 80°C for 5 minutes and then degraded	33.5
Sample 4 conditioned at 80 and 120°C for 5 minutes and then degraded	30.8
Sample 4 conditioned at 80, 120, and 155°C for 5 minutes and then degraded	29.9

Effect of Postirradiation Heating

It has been noted in the literature [1] that postirradiation heating can increase the strength of PVC–TMPTMA samples due to thermally induced polymerization after irradiation. The detection of methacrylate radicals by electron spin resonance (ESR) was also reported [1]. Data relating to this question are to be found in Table 3. Reported are TGA results of weight losses in the 310–370°C range of irradiated specimens that had been heated successively at 80, 120, and 155°C. The change in weight loss is slight and within the limits of experimental uncertainty. Thus, the results do not show conclusively that additional crosslinking or TMPTMA homopolymerization did or did not occur during the heat treatments. They do show, however, that any such event has very slight effects on the thermal stability of irradiated, filled PVC compounds.

CONCLUSION

The results of this work have shown the following:

1. The use of $CaCO_3$ with acidic surfaces leads to PVC composites with lower Young's moduli and yield stresses as compared with composites prepared with conventional, basic $CaCO_3$.
2. Irradiation atmosphere has an effect on crosslinking and therefore on properties at the early stages of irradiation. Lower values for Young's modulus and yield stress, but enhanced ductility, are observed when the irradiation atmosphere is air. Relatively higher values of Young's modulus and yield stress are obtained when the irradiation atmosphere is nitrogen. Ductilities of the samples irradiated in nitrogen are lower than those irradiated in air.
3. Postirradiation heating has little effect on the weight loss of crosslinked samples. The possible further crosslinking of PVC and/or the homopolymerization of TMPTMA during heating has negligible effects on the thermal stability of the composites.

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