# STABILITY OF GAMMA IRRADIATED PVC FORMULATIONS WITH CROSSLINKING DENSITY ENHANCEMENT BY USING TRANSFER AGENTS


R. Benavides[a], C. García-Castañeda[a], G. Neira[a], M.E. Martínez-Pardo[b], C. Kotzian[c], (robertob@ciqa.mx)

[a]*Centro de Investigaciòn en Química Aplicada, Blvd. Enrique Reyna, Saltillo, Coahuila, México.*

[b]*Instituto Nacional de Investigaciones Nucleares, Ocoyoacac, Edo. De México, México*

[c]*Hospital Universitario, U.A.de C., Fco. I. Madero 1291, Saltillo, Coahuila, México*



## Abstract

Gamma irradiated PVC has a very low reaction yield, so the use of a crosslinking agent is needed. TMPTMA is a trifunctional additive commonly used for such purpose. During irradiation TMPTMA suffers homopolymerization before any crosslinking reaction occurs. In this work we have added 3 transfer agents to PVC formulations (mercaptoethanol-ME, dodecylmercaptane-DDM, bencyltriphenyl phosphonium chloride-CBF) in order to reduce TMPTMA homopolymerization reaction, enhancing crosslinking density of the PVC network. Gel percentage and crosslinkg densities are reported for PVC formulations, as well as Mechanical (DMA) and spectroscopic (FTIR) evaluations. Stability has been evaluated by HCl evolution and Activation energies (Ea) for dehyrdrochlorination measured by a TGA-Arrhenius method.


## Introduction

Irradiated PVC has been widely studied due its cost and versatility as in electrical wire and cable coating. On the other hand, high energy radiation has an important role in several chemical processes, like polymerization and graft reactions; however, the main reaction observed during polymer irradiation is crosslinking. For PVC, addition of a crosslinking agent as trimethylolpropane trimethacrylate (TMPTMA) is needed to improve networking PVC chains. Moreover, during first stages of irradiation TMPTMA suffers homopolymerization, affecting crosslinking density[1-3].

The use of transfer agents is widely known to have control in growing chains in order to get a polymer with specific molecular weight. Any kind of chemicals, including the own solvent could behave as a transfer agent, especially if they include sulphur in their structures[4]. Mercaptides, are transfer agents widely used; the ones involving n-dodecyl and the mercaptoethanol has been studied by several authors as agents for high temperatures, they have enough sensibility to react with double bonds, and been intensively used in reactions with acrylics[5,6]. In this work, we used three different transfer agents and TMPTMA to study their effect in the crosslinked density of PVC formulations.

## Methods

An industrial PVC K=72 was used to prepare typical plasticized formulations. The polyfunctional TMPTMA, obtained from Sartomer, and a synergistic mixture of Ca/Zn stereates (2/1 % w) stabilizers were added, both industrial grade. Three transfer agents were also added: mercaptoethanol (ME), dodecylmercaptide (DDM) and bencyltriphenylphosphonium chloride (CBF). Other components (filler, plasticizer and co-stabilizer) were also industrial grade.
Samples were initially mixed in a roller mill at 150ºC, with an initial roller separation of 0.5 mm and steadily increased until 1.5 mm in a time period of 3 minutes. After milling, the final samples were prepared in a hot press PHI mod. Q230, to make plates with a 2 mm thickness following two steps: 1 minute hot press at 180ºC and 15 Tons and 5 minutes in cold press at 20 Tons. Plates were cut into final probes of 1/2 x 1/8 x 5 in.
The gamma treatment was carried out in an industrial irradiator with a $^{60}Co$ source under oxidative conditions and a dose rate of 12.4 kGy/h. Final dose was around 75 kGy. Characterization of irradiated samples consisted in gel percentage, spectroscopic studies with FTIR, mechanical using DMA, HCl evolution and Activation energy (Ea) to degradation by TGA. Flory-Rehner equation was used to calculate crosslinking density when sample was kept under THF during 48 h and then dried during 24 h at 50ºC for obtaining soak and dried weights of samples.

## Results

FTIR spectra (Figure 1) show a growing band in the 3400 $cm^{-1}$ region corresponding to peroxide formation and carbonyls in 1720 $cm^{-1}$ as a consequence of irradiation and presence of oxidation in the material. PVC added with transfer agents have less oxidation comparing with the blank.

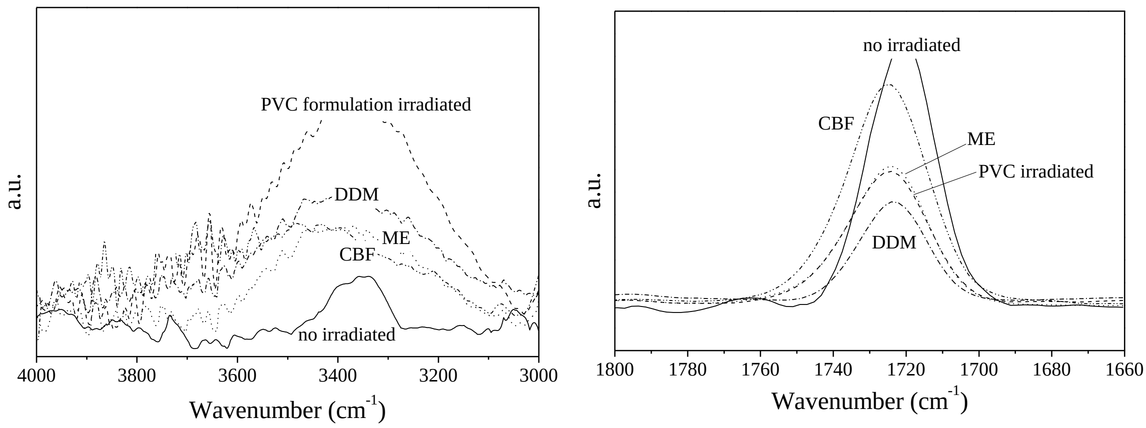


**Figure 1.** Peroxides and carbonyls in FTIR for different gamma irradiated PVC formulations.

Table 1 show the results obtained for gel percentage, crosslinking density and mechanical behaviour from DMA tests; although there are no significant changes in crosslinking density, the effect in storage modulus is important.

**Table 1.** % Gel and density crosslinking for PVC formulations irradiated with gamma.

| *Formulations* | *% Gel* | *Crosslinking Density (mol/m$^3$)* | *Storage modulus at 35°C (MPa)* |
|---|---|---|---|
| Ca/Zn | 20 | 44.34 | 152.6 |
| Ca/Zn-ME | 30 | 46.66 | 158.8 |
| Ca/Zn-DDM | 33 | 46.71 | 189.6 |
| Ca/Zn-CBF | 8 | 37.77 | 131.2 |

Finally, thermal sensitization was measured with HCl evolution and activation energy (Ea) by TGA and Arrhenius equation (Figure 2).

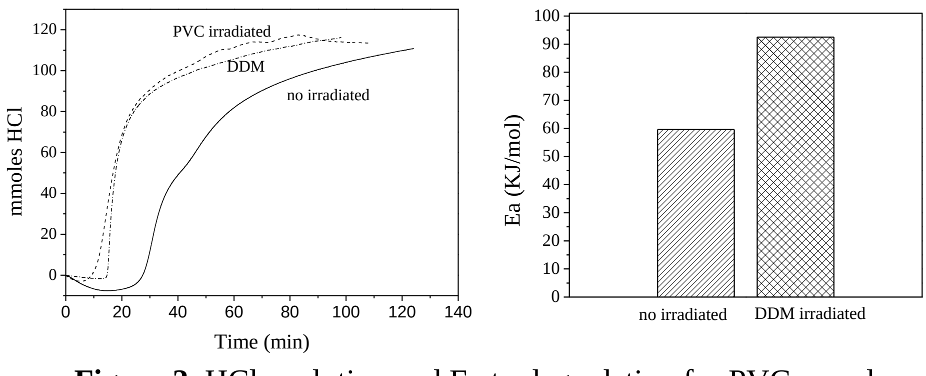


**Figure 2.** HCl evolution and Ea to degradation for PVC samples.

## Discussion

Growing bands at peroxide and carbonyl regions is consequence of irradiation under oxidative conditions, although the initial values could be an effect of the preparation (processing) step. However, PVC formulated with transfer agents shows noticeable lower levels of oxidation, comparing with blank PVC formulations. The latter suggests that crosslinking is occurring through oxi and peroxi radicals.

Gel formation in the polymer is an evidence of crosslinking reactions among the chains of PVC, however crosslinking density values give direct information about the effect of transfer agents on such reactions. CBF is apparently less efficient and it is believed to be the consequence of an inhibition effect from stabilizers and pentaerythritol (co-stabilizer). Even though the changes in density values are not very significative, they are having an important impact over mechanical properties.

Finally, addition of transfer agents and irradiation affect behaviour in sensitization to thermal degradation; differences between both dynamic (TGA) and static (HCl evolution) temperature measurements are clearly seen. PVC+DDM degrades easily as measured statically but in contradiction needs high energy to activate degradation when measured by TGA. The latter indicates that stability measurements have to be taken with care and decided according to final use of materials.

## Conclusion

Transfer agents are having control on the homopolimerization of TMPTMA and induce crosslinking reactions through oxidation functionality. Mechanical properties and thermal stability have changes for the plasticized PVC formulations and DDM shows to be better enhancement over the rest of transfer agents evaluated.

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