Novel Method for Polymer Cross Linking By Gamma Radiation

David Shechter
Sor-Van Radiation, Soreq Nuclear Research Center, Yavne, Israel

ABSTRACT

Novel method for accelerating polymer cross linking by Gamma radiation was developed.

In this method* cross linking rate and maximum attainable gel content is higher in comparison with radiation under vacuum or in nitrogen atmosphere.

Upon irradiation, the competition between crosslinking and chain scission reactions, determine crosslinking and crosslinking rate. G value which express this ratio is being reduced in this method from 0.25 (in vacuum) to 0.14 for certain polymers.

* Sor-Van method - Patent pending.

INTRODUCTION

Polyolefin polymers are known to crosslinked under influence of ionizing radiation (1). The significant chemical effects of ionizing radiation on those polymers in the absence of oxygen are - evolution of hydrogen and generation of free radicals.
Two main kinds of free radicals have been detected by ESR method (2) - Alkyl radical and Allylic type radical. Recombination between two Alkyl radicals is believed to be the main source of radiation induced crosslinking (3) . The Allylic type radical which is more stable tend to conserve or undergo further reactions resulting in chain scission (4) .

The effect of various atmospheres present during irradiation, has been investigated and compared with the radiation induced reactions in vacuum.
Some atmosphere like nitrogen or xenon show accelerating effect but only in the range of 5- 10 percent. A better accelerating atmosphere has been reported with acetylene, but with the disadvantage of using hazardous material (5).

In our method, in which we exposed the polymers to irradiation under a special condition, much higher yields of crosslinking is obtained, compared to the polymers irradiated in vacuum or nitrogen atmosphere. This method accelerates the recombination between the Alkyl radicals and reduce formation of the Allylic type radicals. The result is high crosslinked polymer with a minimal amount of free radicals conserved in the material.

EXPERIMENTAL

Three Types of polyolefin elastomers produced in metalocenic process were used:

1. POE 8150 engage from DuPont- Dow.
   Molecular weight 140,000 , M.F.I. 0.5 .

2. POE 8411 engage from DuPont- Dow.
   Molecular weight 80,000 , M.F.I. 18 .

3. POE 8401 engage from DuPont- Dow.
   Molecular weight 50,000 , M.F.I. 30 .

All samples in 3 mm thick.

All the samples were irradiated in our Cobalt 60 commercial facility under a dose rate of 3 KGy per hour, to nominal doses of 0,25, 50 , 75 , 100 , 125 KGy.
Reference samples were irradiated under vacuum with the same doses.

Solubility measurement to determine gel content was carried out as follow:
Samples were enclosed in a wire mesh container and the soluble fraction extracted by suspending the container in a large volume of xylen (110 ^{0}C) for 15 hours.

RESULTS

The results of the crosslinking measurements as a function of dose and atmosphere are shown in table 1 .

From this data the accelerating effect is shown clearly. The increment due to this process compared to irradiation under vacuum varies mainly by molecular weight and molecular weight distribution.

Polymers with high molecular weight is croosslinked more readily and therefore the accelerating effect increased inversely to molecular weight.

POE 8150 had a gel fraction of 90 % in Sor-Van method , comparing to gel fraction of 48 % under vacuum ,with the same dose of 125 KGy.

POE 8411 had a gel fraction of 86 % in Sor-Van method , while under vacuum no gel fraction was achieved,with the same dose of 125 KGy.

POE 8401 had a gel fraction of 80 % in Sor-Van method , while under vacuum no gel fraction was achieved,with the same dose of 125 KGy.

Table 1 : Crosslinking measurements as a function of dose and atmosphere

GEL CONTENT (%) : Under vacuum/ Sor-Van method						
Dose (KGy)	**0**	**25**	**50**	**75**	**100**	**125**
Material						
POE 8150 DuPont-Dow	0/0	0/14	33/72	42/88	48/90	48/90
POE 8411 DuPont-Dow	0/0	0/0	0/5	0/75	0/82	0/86
POE 8401 DuPont-Dow	0/0	0/0	0/5	0/68	0/76	0/80

Conclusions

As shown in the results, the accelerating effect of Sor-Van method on polymers with a high molecular weight such as POE 8150 (MW 140,000) is 87.5 % more than the vacuum method.

More significant are the results which obtained on low molecular weight polymers like the POE 8401 (MW 50,000).
While under vacuum no gel fraction was achieved, in Sor-Van method the gel fraction was 80 %.

In low molecular weight polymers, the results are unique, due to the fact that crosslinking is hardly achieved with other irradiation methods including Electron beam irradiation.

References :

1. Chapiro A., (1962) Radiation chemistry of polymeric systems. Wiley New York.
2. Dole M., (1974) Radiation chemistry of P.E. Advance Radiation chemistry Vol. 4 Wiley New York p. 307 .
3. Yashida H., E.S.E studies of free radicals in irradiated polymers, Advance in polymer science 105 Springer 1993 .
4. Hill J.T. David, Irradiation of polymers ACS 1994 , p. 130-138 .
5. Deng M., Irradiation of polymers ACS 1994 , p. 293-301 .
6. Hamilton J.V., Radiation physics and chemistry Vol. 52 No. 1-6 June 1996, p. 283-287.
7. Hiroshi Mitsui, Polymer Journal Vol. 6 No. 1 p. 20-26 (1974) .
8. Narkis M., J Macromol SCI -Pages. , B 26 (1) p. 37-58 (1987) .