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Structural Modifications in an Irradiated Ethylene-Vinyl Alcohol Copolymer

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Abstract

Extraction experiments and calorimetric measurements have been performed on a commercial ethylene-vinyl alcohol copolymer irradiated in the dose range 0-20 Mrad.

The results support the idea that crosslinking predominates over chain scission at small irradiation doses and all together is the main effect in the explored dose range.

Introduction

The main effects of gamma radiation on polymeric materials are crosslinking and chain scission. Both processes usually coexist and the extent of either one depends on the chemical structure and morphology of the sample and on the conditions (temperature , environment, dose rate, etc.) under which the radiations are absorbed (1-3).

The effect of high energy radiation on a wide variety of homopolymers has been studied while relatively few investigations have been made on copolymers and homopolymer blends, in spite of their increasing industrial interest (4-6).

Aim of this work, which has to be cosidered a preliminary one, is on one side that of giving informations on the gamma radiation effect on a copolymer and on the other side that of exploiting the possibility of using a particular copolymer in the food packaging industry. A commercial ethylene- vinyl alcohol copolymer manufactured by Kuraray Co., has been taken under consideration. It is considered of interest for food packaging because of its very low gas permeability together with its good mechanical behavior (7). In view of food sterilization after packaging films from the above copolymer have been irradiated at least up to the needed dose (8) and some of the subsequent structural modifications have been evaluated through extraction experiments and calorimetric measurements.

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Experimental

The material used was a commercial ethylene-vinyl alcohol copolymer with about 25% ethylene, manufactured and kindly supplied by Kuraray Co.

Samples about 0.1 mm thick were obtained from pellets by compression molding at 240 °C with a laboratory Carver press. The pressure was 250 Kg/cm^2.

Before the irradiation the samples weredried for three days at 55°C under vacuum and in presence of silica gel; they were then sealed in glass tubes.

The polymer was irradiated by the IGS-3, a panoramic 3000 Ci ^{60}Co irradiator, already described elsewere (9). The dose rate, measured by the Fricke dosimeter, was 0.64 Mrad/hr. The investigated dose range was 0-20 Mrad: a variance of 5% in the radiation absorption was accepted.

A thermal treatment (post-irradiation) for three days at 55°C was made to remove the free radicals produced by the irradiation, which could cause an oxidative degradation when in presence of the air (10,11).

The gel content was determined by means of a soxhlet extractor. Approximately 0.5 g of irradiated polymer was exposed to refluxing ethylene glycol close to its boiling point. Extraction was continued until the sample attained constant weight as assessed after drying in a vacuum oven at 55°C. Maximum extraction times were about 48 hours.

Calorimetric tests were performed by a Perkin-Elmer DSC-1B on unfractionated samples and both on sol and gel fractions. The heating rate was 4°C/min up to the glass transition temperature. The sample was then heated up to the melting point at a rate of 16°C/min, cooled at a rate of 8°C/min and finally remelted at a rate of 16°C/min for determinations of melting enthalpy.

Results and Discussion

The gel extraction results were obtained using a liquid which is a typical solvent for the not irradiated polymer (12) and are reported in figure 1 as percent of gel vs radiation dose, d. They show a definite maximum at a dose of about 3 Mrad and values quite large also at the largest explored doses. This behavior indicates that, under the irradiation conditions here adopted, crosslinking predominates at small doses and chain scission at larger doses.

Support for the above indications is given by the calorimetric measurements and more strictly by the glass transition temperature data obtained on the unfractionated samples and reported in figure 2. Values larger than that corresponding to the not irradiated samples have been found in the range 1-3 Mrad while values slightly smaller have been observed at larger doses.

Further informations can be drawn from the calorimetric results obtained on sol and gel fractions also reported in figure 2. The gel

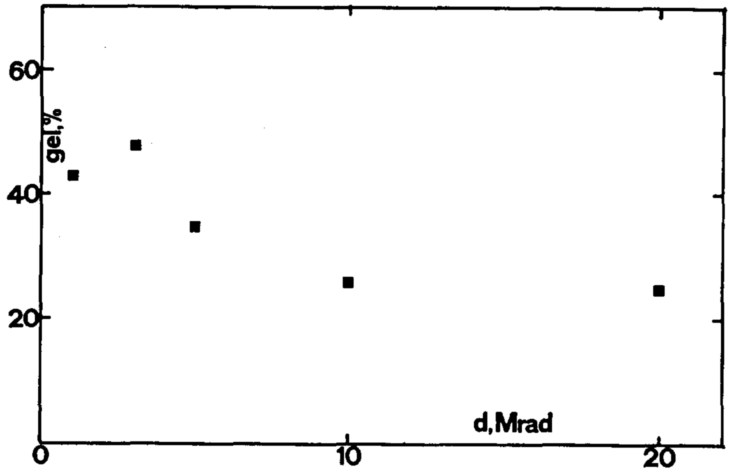

Fig. 1. Gel fractions vs radiation dose,d

fractions show a single glass transition markedly higher than that of the not irradiated sample and higher also than that of the irradiated unfractionated samples. On the contrary the glass transition temperatures of the sol fractions are always slightly smaller than those corresponding to the unfractionated samples, although in the range 1-3 Mrad are still higher than that of the control sample.

One may thus conclude that while the crosslinking effect enhances the properties of the observed material, possibly also the mechanical

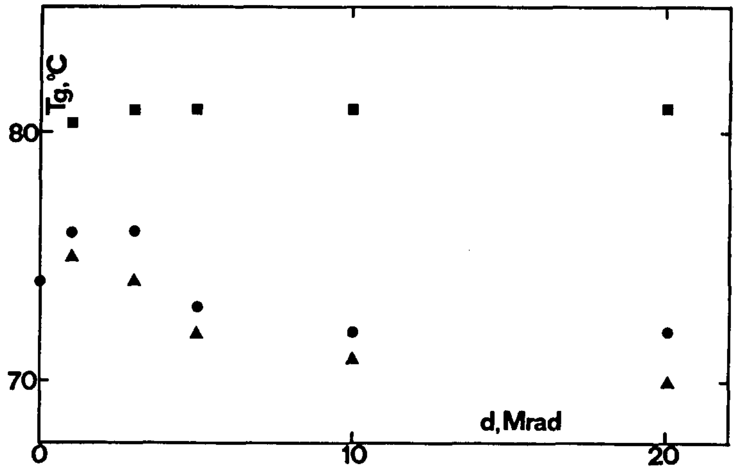

Fig. 2. Glass transition temperatures vs radiation dose, d. (●) Unfractionated samples, (▲) Sol fractions, (■) Gel fractions

properties, at small radiation doses, increasing the dose chain scission becomes more and more important giving rise to smaller gel fractions and lowering the molecular weight of the sol fractions. However , in the explored radiation dose range, the latter effect never seems to overcome the former.

Some final confirmations come from the calorimetric measurements made on the samples previously melted and then crystallized in similar conditions, as already mentioned in the experimental section. The results in terms of melting enthalpy are reported in the table, again both for unfractionated and fractionated samples. It can be observed that the control sample has a melting enthalpy, and possibly a degree of crystallinity, much larger than the irradiated unfractionated ones as a consequence of both crosslinking and chain scission effects. The decrease in molecular weight of the sol fractions is obviously responsible of the decrease of crystallinity with the increase of the radiation dose. The gel fractions show, in line with literature results (11,13), degrees of crystallinity much smaller and essentially independent from the radiation dose.

TABLE

Melting Enthalpies (cal/g)

Radiation	Dose	Unfractionated	Sol	Gel
0	Mrad	11.8		
1	"	7.5	9	4.1
3	"	7	8.2	4.2
5	"	6.7	8.2	4.1
10	"	6.5	8	4.1
20	"	6.2	7.7	3.4

Concluding Remarks

Both extraction and calorimetric results above reported on the irradiated ethylene-vinyl alcohol copolymer support the idea that crosslinking predominates over chain scission at small radiation doses and all together is the main effect in the explored dose range. Consequently the copolymer seems at the moment apt to the packaging and to the food after sterilization. Mechanical measurements are necessary for a direct proof, and more realistic irradiation conditions, namely in presence of air, are to be examined: work is in progress in these directions.

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