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H. A. Abd El-Rehim^a; E. M. El-Nesr^a

^a National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

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Radiation Induced Crosslinking of Ethylene Vinyl Acetate Copolymers Hosting Sulfonic Acid Groups and Their Potential Applications

H. A. ABD EL-REHIM AND E. M. EL-NESR

National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

The effect of ionizing radiation on the properties of untreated ethylene vinyl acetate copolymer (EVA), sulfonated EVA and polyethylene-ethylene vinyl acetate blend (PE/EVA) was investigated. The crosslinking of the samples was studied on the basis of gel-content measurements, as well as some thermal and mechanical properties of the specimens. The results indicated that EVA and sulfonated EVA were more sensitive to the electron beam irradiation. The improvement in the measured gel content, tensile strength, and elongation at break and heat resistance of the EVA and sulfonated EVA has confirmed the positive effect of low doses electron beam irradiation on such copolymers. The crosslinked sulfonated EVA membranes were used for sucrose hydrolysis. The catalytic activity of the membranes was found to be dependent on the reaction temperature and the amount of the sulfonic acid groups hosted in the EVA membranes. The results of this work suggest that crosslinked sulfonated EVA membranes have a strong potential to replace liquid sulfuric acid and ion exchange resins in sugar hydrolysis processes.

Keywords crosslinking, radiation, EVA, characterization, catalytic activity

Introduction

The application of polymers for biotechnological and industrial purposes has become one of the principle challenges facing the polymer scientist. Recently, there has been an increasing demand for the development of low cost thermally and chemically stable novel proton exchange membranes to prompt the commercialization of polymer for industries (1–5). Sulfonic acid membranes have been found to be the most important membranes for different applications (6–9). In fact, unique properties arise from incorporating sulfonic acid (anionic group) into polymers via sulfonation, such as increased strength, hydrophilicity, and proton conductivity. These features of sulfonated polymers have led to an exploration of a variety of applications such as batteries, sensors, displays, as well as ion-exchangers and strong acid catalyst resins (10–14).

Sucrose is widely used in the food industry as a precursor of invert sugar through its hydrolysis. Invertase enzymes are the catalysts most often used on the industrial scale to transform sucrose into invert sugar. However, their use is restricted to the food industry as

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Address correspondence to H. A. Abd El-Rehim, National Center for Radiation Research and Technology, P. O. Box No. 29 Nasr City, Cairo, Egypt. E-mail: ha_rehim@yahoo.com

far as the products formed, glucose and fructose, inhibit the hydrolysis reaction (15), with a conversion of sucrose that does not exceed 95%. The current industrial approach for the production of inverted sugars syrups is based on the acidic hydrolysis of sucrose. Acid ion-exchange resins are also used and allow a complete conversion of sucrose in the temperature range compatible with their stability, but some of them invert sugar with a relatively high level of impurities (16).

Ion exchange resins composing of divinylbenzene crosslinked polystyrene network structure containing sulfonic acid groups, inhibit the access of reactants with sizes larger than the interstices of the polymer chains (17). It is unlikely that polystyrene–polypropylene fibrous ion exchange catalysts showed more effective catalytic activity towards sucrose hydrolysis due to the increase in their surface area together with the increase in the reactant molecular size accessibility (18). Very specific properties for the catalytic systems, as acidity, shape, selectivity, micro-porous sorption properties are required to obtain pure products. Therefore, attention has been made to prepare suitable catalysts of tailor properties for sugar hydrolysis at low or high temperatures (19, 20). Radiation has been found to be widely applicable in modifying the structure and properties of polymers, and can be used to tailor the performance of either bulk materials or surfaces. The process is based on grafting, degradation or crosslinking of polymer chains induced by ^{60}Co -gamma ray or accelerated electron beam irradiation.

Radiation-induced grafting using high-energy radiation has been found to be a powerful method to produce graft copolymers capable of hosting sulfonic groups and having more effective catalytic activity for hydrolysis processes (21, 22). Polystyrene sulfonic acid grafted microporous poly(tetrafluoroethylene) (PTFE) membranes and sulfonic acid containing hollow fiber membrane were prepared for sugar hydrolysis (18). Radiation-crosslinking of polyolefins has become commercially important because their properties are better than those of the parent homopolymers. Crosslinking by radiation causes improvement in modulus and strength, resistance against stress cracking corrosion, for the materials as well as creep and stress rupture properties.

The radiation crosslinking of EVA and PE/EVA blends have been extensively studied (23–25). In this respect, the aim of the present work was hosting sulfonic acid (anionic group) into EVA via sulfonation. The sulfonated EVA films were subjected to ionizing radiation for improving their properties. Such strong acid crosslinked EVA membranes were tested for hydrolysis of sucrose at various temperatures.

Experimental

Materials

Ethylene vinyl acetate copolymer (EVA) containing 9% vinyl acetate was supplied by SNCI, France and LDPE was obtained from El-Naser Co. Chloro-sulfonic acid was obtained from Aldrich, Germany. The other chemicals were of reagent grade and used as received.

Film Preparation

EVA, PE and blended PE/EVA films were prepared using blow co-extrusion techniques with blow ratio 7. The co-extruder was used to obtain films from PE, EVA, or their real blend in a 1:1 ratio. The thickness of the blow co-extruded film was 160 μm .

Irradiation

The samples were irradiated at different doses with electron beam at a beam current of 2 mA and an acceleration energy of 1.4 MeV generated by accelerator (maximum current and voltage, 25 mA and 1.5 MeV, respectively).

Chloro-sulfonation

Chloro-sulfonic acid was chosen as a sulfonating agent. A suitable solvent was 1,2-dichloroethane as it is very miscible with chloro-sulfonic acid. EVA films were soaked in a flask containing 10 ml of chloro-sulfonic acid in 100 ml 1,2-dichloroethane at room temperature for 2–20 h. Sulfonyl chloride groups (—SO₂Cl) may be formed. Therefore, hydrolysis was directly carried out in distilled water at 80°C for 6 h in order to complete conversion of sulfonyl chloride groups to sulfonic acid groups.

Determination of Insoluble Parts

The insoluble part of the EVA and its copolymer was determined by refluxing the sample with xylene and DMF (80–20 v/v) for 24 h. The remaining insoluble sample was rinsed with methanol and dried in a vacuum oven at 70°C to a constant weight.

$$\text{Gel content (\%)} = (W_x/W_s) \times 100$$

where W_x and W_s represent the weights of dried after extraction and initial dry films, respectively.

Heat Resistance

Heat-resistance property of crosslinked EVA and its sulfonated derivative was measured at different temperatures using an oven. Film samples of area (0.3 × 3) cm² and thickness 160 μm were hung in the oven at a fixed load of 0.6 kg/cm³ and different temperatures. The time required to break the samples, which resulted from exposure at various temperatures, was determined.

Measurement of Ion-Exchange Capacity (IEC)

After immersing the samples treated with chlorosulfonic acid in distilled water, the sulfonated films were soaked in a 0.5 N HCl solution to change them into a H⁺ form. They were washed with distilled water to remove excess HCl and then equilibrated with an exact 50 ml of 0.01 mol dm⁻³ NaOH solutions for 24 h. IEC was determined from the reduction in alkalinity measured by back titration. IEC of the cation membranes was calculated by the following equation:

$$\text{IEC} = \frac{(M_{O, \text{NaOH}} - M_{E, \text{NaOH}})}{W}$$

where $M_{O, \text{NaOH}}$ is milli-equivalent (meq.) of NaOH in the flask at the beginning of titration, $M_{E, \text{NaOH}}$ is meq. of NaOH after equilibrium, and W is the weight of dry membrane (g).

Measurement of Water Swelling Ratio

After soaking the membranes in distilled water for more than 24 h, they were wiped with filter paper and weighed immediately. The samples were then dried at 60°C under a vacuum condition until a constant weight was obtained. The water swelling ratio (WSR) was determined by the following equation:

$$\text{WSR} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100$$

where W_{wet} and W_{dry} are wet and dried membrane weight, respectively.

Differential Scanning Calorimetry (DSC)

In the present study, the melting temperature of the first heating run (T_{m1}), melting temperature of second heating run (T_{m2}) and recrystallization temperature (T_{rc}) from a cooling molten state of crosslinked sulfonated EVA were determined using differential scanning calorimetry "DSC-7 Perkin-Elmer" with a heating and cooling rate of 10°C/min under nitrogen flow. Also, the heat of melting (ΔH_m), as well as recrystallization heat (ΔH_{rc}) from the area of the corresponding transition in DSC scans was determined.

Mechanical Properties Measurements

Tensile strength and elongation at break were estimated from stress strain curves measured by using a tension meter (carried out with the use of H10KS Hounsfield Co. UK), tension speed was 50 mm/min. Samples in a dumbbell shape (specimens of 50 mm long and 4 mm neck width of different degrees of crosslinking were used for a mechanical test.

Hydrolysis of Sucrose

The catalytic activity of the EVA membranes containing sulfonic acid groups was used for sucrose hydrolysis (inversion). The membrane of known degree of grafting was cut into small pieces (10 mm × 5 mm), soaked in 40 ml of a sugar solution having a concentration of 0.58 mol l⁻¹ hosted in a small glass reactor placed in thermostat controlled water bath and equipped with a condenser and round-shaped Teflon blade stirrer. At the prescribed time, samples (size 0.25 ml) were extracted and analyzed for the concentration of glucose. The size of the sample is negligible with respect to the total volume of sucrose solution. Analyses were detected by colorimetry using an enzymatic glucose kit as described in previous work (26). The analysis was made based on the variation in the reaction temperature from 40 to 70°C.

Results and Discussion

Modification of EVA

The FT-IR spectra of the EVA and sulfonated membranes were studied and are shown in Figure 1. In the EVA, the absorption band assigned to the ester groups was observed at 1735 cm⁻¹. In the sulfonated membrane, the ester groups was also observed at 1735 cm⁻¹. The absorption band assigned to sulfonic acid groups was observed

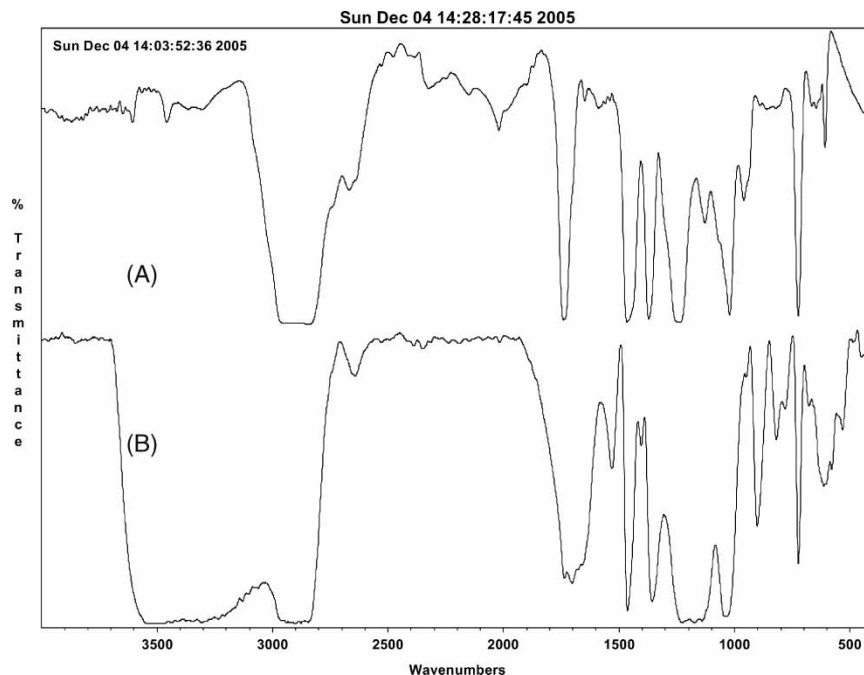


Figure 1. FTIR spectra of (A) EVA, and (B) EVA treated with chloro-sulfonic acid.

around 1040 cm^{-1} while the spectra for $\text{S}=\text{O}$ stretching vibration were detected at $1226\text{--}1141\text{ cm}^{-1}$ (27). The absorption broad band of OH groups was also observed around 3500 cm^{-1} . This confirmed that the sulfonic group was introduced into the membrane.

Ion Exchange Capacity and Water Uptake

The introduction of sulfonic acid groups into the EVA films created a pseudo two-phase, hydrophobic and hydrophilic. Ion exchange and water uptake properties were all due to the hydrophilic phase in the membrane. Chlorosulfonic acid was chosen as a sulfonating agent as it is highly reactive in substitutions of aliphatic chains and convenient for laboratory study.

Ion exchange capacity provides an indication of the content of acid groups in the membrane. The detected and calculated ion exchange capacity values of the obtained membrane, as a function of the reaction time are plotted in Figure 2. The ion exchange capacity increased with the increase in the reaction time. Therefore, the ion exchange capacity of the membrane could be controlled freely by changing the reaction time.

Treatment of different types of membranes namely, EVA, PE and EVA-PE blend with chlorosulfonic acid was performed and the ion exchange capacity was determined. As shown in Figure 3, the ion exchange capacity of treated membranes followed the order $\text{EVA} > \text{PE-EVA} > \text{PE}$. The presence of EVA improves the diffusion of chlorosulfonic acid to the polymer chains, and consequently, the introduction of sulfonic

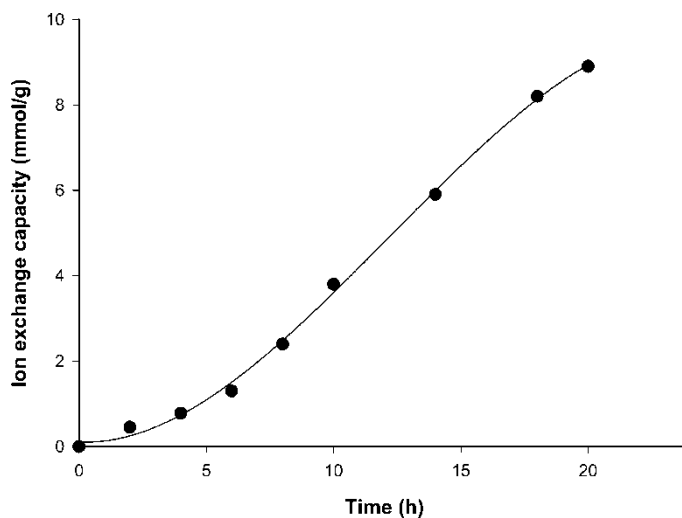


Figure 2. Ion exchange capacity values of EVA, treated with chloro-sulfonic acid as a function of the reaction time.

groups into the polymer takes place easier and faster. As a result, the ion exchange capacity increases.

Ion exchange capacity has a direct connection with the water uptake. The higher ion exchange capacity of a membrane, the higher the water uptake. Figure 4 shows the water uptake, of sulfonated EVA membranes as a function of the ion exchange capacity. It can be seen that the water uptake increases with the increase in ion exchange capacity, indicating the presence of hydrophilic sites within the hydrophobic EVA film.

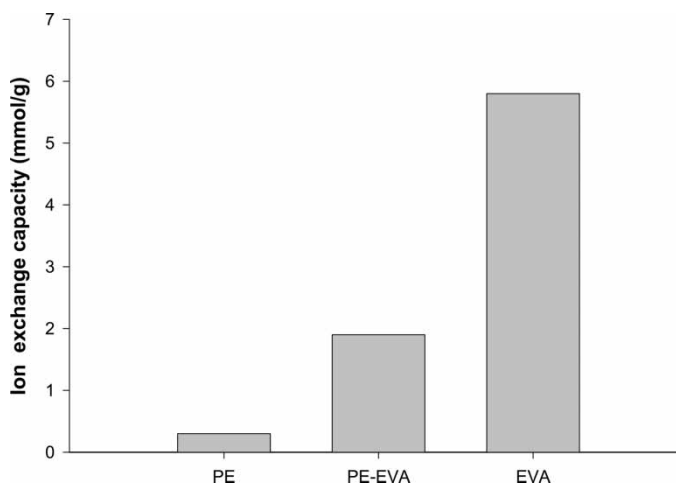


Figure 3. Ion exchange capacity of different types of membranes namely, EVA, PE and EVA-PE blend treated with chlorosulfonic acid. Reaction time 14 h.

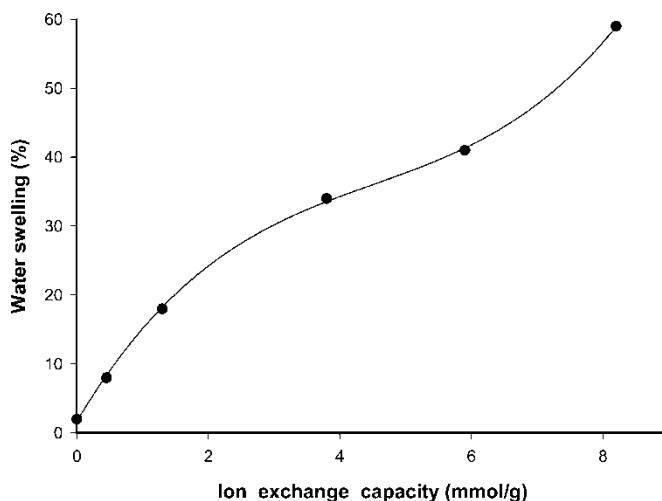


Figure 4. The water swelling ratio of sulfonated EVA membranes as a function of the ion exchange capacity.

Effect of Electron Beam Irradiation on the Properties of the EVA and Sulfonated EVA

Insoluble Fraction. The insoluble fraction of PE/EVA blend, PE and those treated via sulfonation as a function of irradiation dose is shown in Figures 5 and 6, respectively. For all cases, it is observed that the insoluble fraction increases with increasing irradiation dose. The sensitivity of the EVA, PE/EVA and those treated with chloro-sulfonic acid to crosslink is higher at low-radiation doses compared with PE and sulfonated PE. In all irradiation doses used, the amount of insoluble fraction of the treated and untreated EVA is higher than that of chloro-sulfonic acid-treated and untreated PE/EVA and PE.

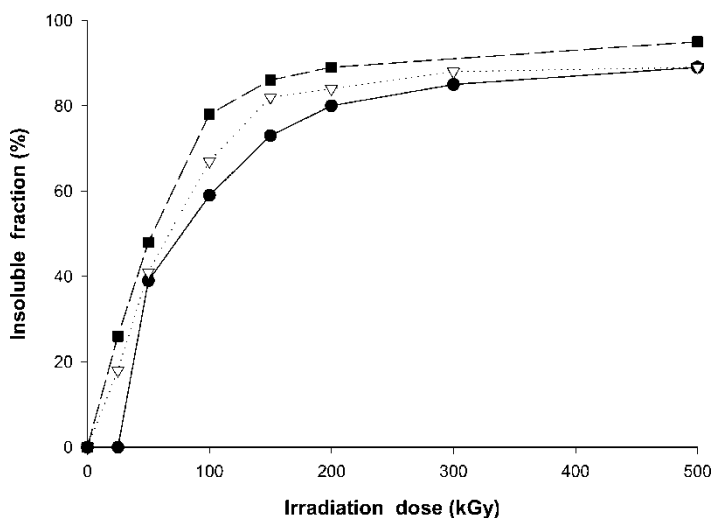


Figure 5. The insoluble part of (○) PE, (▼) EVA, (▽) PE/EVA blend at different irradiation doses.

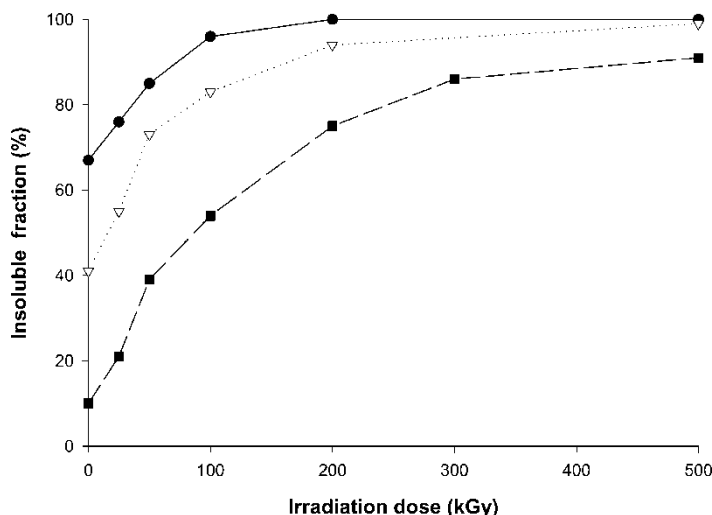


Figure 6. The gel insoluble part of, sulfonated (○) PE-IEC 1.1, (●) EVA-IEC 1.2, (▽) PE/EVA-IEC 1.25 at different irradiation doses.

It is also clear that the addition of EVA to PE improves the crosslinking process of the latter. This behavior is believed to be due to the nature of EVA, which easily crosslinks when exposed to electron beam irradiation.

From Figures 5 and 6, it can be seen that the irradiation with doses greater than 100 kGy for EVA, PE/EVA and their sulfonated derivatives leads to a slow increase of the insoluble fraction because the effectiveness of the gel forming process is lowered. This means that the crosslinking processes continue, and occur predominately between already crosslinked macromolecular chains. This leads only to increasing the crosslinking density (23).

Mechanical Properties

The changes in mechanical properties; tensile strength and elongation at break as a result of irradiation of the EVA and sulfonated EVA are shown in Figures 7 and 8, respectively. Each point from the curves given in the Figures corresponds to the average value of the property determined for a minimum of four samples. In Figure 7, it is observed that, at the same irradiation dose, the tensile strength of irradiated EVA is higher than that of sulfonated EVA. Upon irradiation, tensile strength of EVA and sulfonated EVA increased up to 150 and 100 kGy dose, respectively and then started to decrease with the further increase of irradiation dose. The reduction is most likely caused by the chain scission at high dose. It was reported that in order to get optimum mechanical properties from EVA, the irradiation dose should not exceed 150 kGy (28).

Figure 8 shows the relationship between elongation at break for EVA and sulfonated EVA and irradiation dose of the samples. Generally, increasing irradiation dose results in reduction in elongation at break of EVA and sulfonated EVA. This is similar to behavior of crosslinked PE by low-energy electron beam. The result can be attributed to the ever-increasing three-dimensional gel-like structure, which prevents the structural reorganization during drawing and brings about a decrease in internal chain mobility and elongation (29, 30). At a certain irradiation dose, the elongation at break for sulfonated EVA is lower

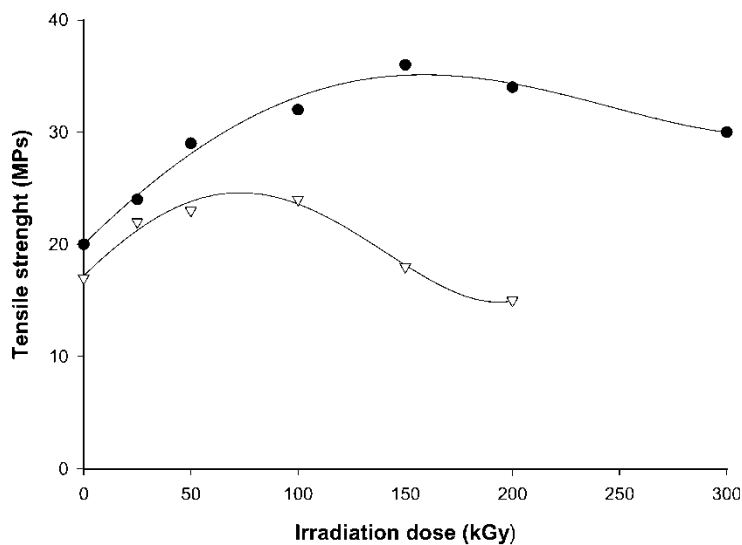


Figure 7. Effect of irradiation dose on the tensile strength of (●) EVA and (▽) sulfonated EVA-IEC 1.4.

than that for untreated one. This indicated the degradation process that takes place during the sulfonation of EVA.

Thermal Properties

The effect of radiation on the chemical and physical properties of sulfonated EVA was investigated by the DSC technique. The influence of irradiation dose on the thermal

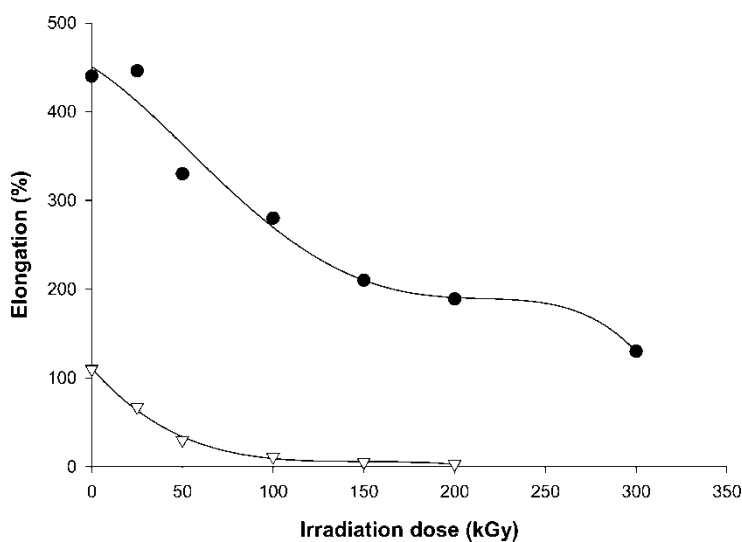


Figure 8. Effect of irradiation dose on the elongation at break of (●) EVA and (▽) sulfonated EVA-IEC 1.4.

parameters of EVA; T_m , T_{rc} , ΔH_m , ΔH_{rc} is shown in Table 1. In the first heating run, it is clear that the introduction of the crosslinking into sulfonated EVA results in a decrease in ΔH_{m1} and a slight increase in T_{m1} compared with those of unirradiated sulfonated EVA. Meanwhile, ΔH_{m2} of the second heating run decreases with an increase of the EVA crosslinking degree.

The apparent decrease in ΔH_{m1} is attributed to the presence of a network structure, which changes the polymer crystallite structure and reduces the energy to melt. The decrease in ΔH_{m2} and ΔH_{rc} values of crosslinked EVA compared with uncrosslinked ones can be also attributed to the network structure, which has considerable mobility with the molten EVA, retards the crystallization during cooling and interferes with the growth of its crystals.

The result obtained, suggested that the introducing of crosslinking structure into sulfonated EVA caused changes in its structure.

Heat Resistance

Certain mechanical properties such as the creep resistance and dimensional stability are improved by crosslinking. These properties are very important in industrial applications. Figure 9 shows the relationship between temperature and time for the breaking of EVA or sulfonated EVA under constant stress. It is observed that uncrosslinked EVA broke immediately when held at 120°C and converted to a viscous liquid. While crosslinked EVA and sulfonated crosslinked EVA show high heat stability at 100 and 120°C, respectively. The result also shows that crosslinked sulfonated EVA undergoes less heat deformation compared to irradiated EVA. They do not break even up to 180 min; however, at 200 and 220°C, the crosslinked EVA broke after 15 and 5 min, respectively, and the sulfonated EVA broke at 35 and 20 min, respectively.

The deformation of the EVA depends on the structure of the copolymer. The enhancement of the heat deformation property was due to the formation of the crosslinking network, which restricted the flow of the melted sample (29, 31). It was reported that the thermal expansion of the EVA continuously decreases with the increasing of the irradiation dose. A decrease in the thermal expansion can be related to the degree of crosslinking. Formation of an adequate crosslinking network in EVA renders the polymer with better elongation (32).

Table 1
Thermal parameters of sulfonated EVA irradiated with different doses

Irradiation dose (kGy)	T_{m1}	T_{m2}	T_{rc}	ΔH_{m1}	ΔH_{m2}	ΔH_{rc}
0	102.2	88.3	73	49	20.3	-21.3
25	103.3	89.6	75	47	15.6	-16
50	103.5	89.1	74.8	46	15.2	-15
100	103.9	89.3	75.1	44.5	14.4	-15.4

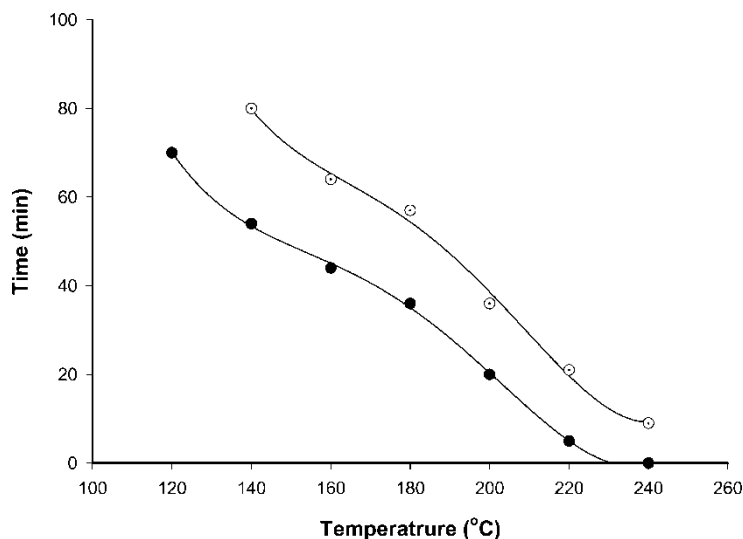
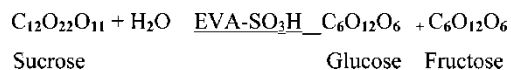


Figure 9. The relationship between temperature and time for (●) EVA and (○) sulfonated EVA of 1.2 IEC broken with an applied stress of 0.6 kg/cm³. The samples irradiated at 100 kGy.

Application of Crosslinked EVA Hosted Sulfonic Acid Groups for Sucrose Hydrolysis

The catalytic activity of the irradiated EVA membranes containing sulfonic acid groups was tested for the reaction of the hydrolysis of sucrose to glucose and fructose according to the following scheme:



Effect of Time on Sucrose Hydrolysis

An EVA membrane of 5.3 IEC was used as a catalyst and the reaction was conducted at a specified temperature and various time intervals. A small volume sample is extracted from the reaction vessel and analyzed for glucose. The effect of time on the hydrolysis of sucrose into glucose and fructose at different temperatures is shown in Figures 10 and 11. The % conversion of sucrose to glucose increases gradually with the increase of the reaction time for both sulfonated EVA and partially hydrolyzed sulfonated EVA (the latter was prepared by heating sulfonated EVA in a 3% NaOH solution at 70°C for 8 h, followed by soaking the treated membrane in a 0.5 N HCl solution). As the temperature increases, the sucrose conversion rate increases. The time needed for nearly 100% conversion of sucrose to glucose is 180 and 100 min at 50 and 60°C, respectively. When sulfonated EVA is used as a catalyst, the initial rate to convert sucrose to glucose and fructose is higher than that obtained when partially hydrolyzed sulfonated EVA is used as a catalyst. This may be due to the hydrogen bonds formed between SO₃H and OH groups, which are broken as the temperature, and/or reaction time increases.

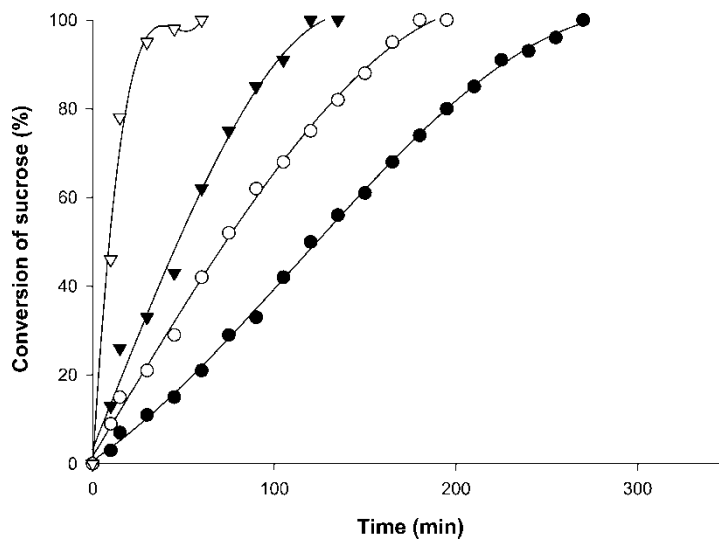


Figure 10. Effect of time on the hydrolysis of sucrose into glucose and fructose at different temperatures using sulfonated EVA. The samples irradiated at 100 kGy in exchange capacity 5.3 (mmol/g). Reaction temperature: (●) 40, (○) 50, (▼) 60, (▽) 70.

Effect of Ion Exchange Capacity of the Membrane on its Activity

Sulfonated EVA and partially hydrolyzed sulfonated EVA membranes with different ion exchange capacities were used for sucrose hydrolysis as shown in Figure 12. For both membranes, it is clear that as the ion exchange capacity increase the hydrolysis of

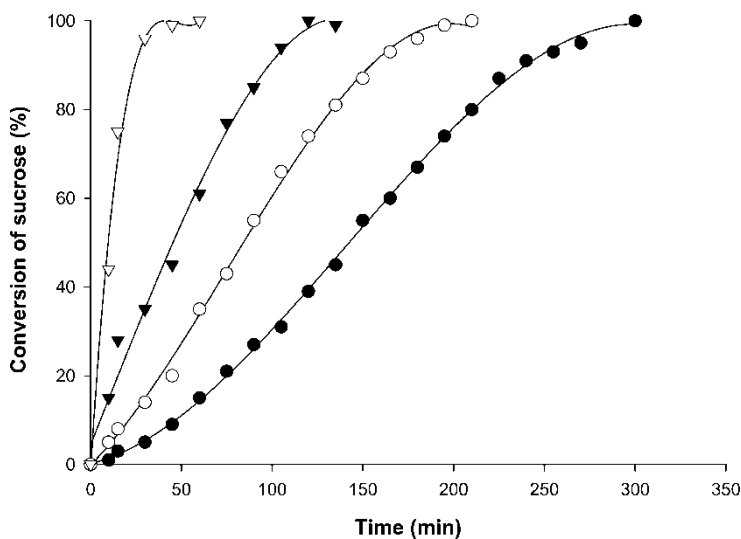


Figure 11. Effect of time on the hydrolysis of sucrose into glucose and fructose at different temperatures using hydrolyzed sulfonated EVA. The samples irradiated at 100 kGy ion exchange capacity of the prepared membrane 5.3. Reaction temperature: (●) 40, (○) 50, (▼) 60, (▽) 70.

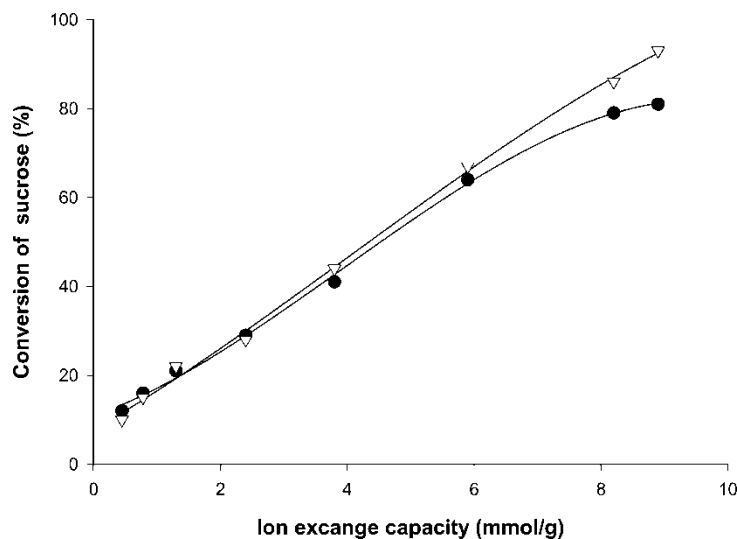


Figure 12. Effect of ion exchange capacity of the EVA membrane on its activity towards the sucrose solution. (●) sulfonated EVA (▽). Partially hydrolyzed sulfonated EVA, reaction time 60 min.

sucrose increases. The increase in ion exchange capacity means that increase in the number of SO_3H groups that is responsible for the hydrolysis process.

Conclusions

Radiation induced crosslinking of EVA and EVA hosted sulfonic acid groups was investigated. EB radiation has positive effect on the properties of EVA and sulfonated EVA. The irradiation dose has a great influence on the insoluble fraction content of EVA, PE/EVA blend and their treated ones. The tensile strength of EVA and sulfonated EVA increased when irradiated up to 150 and 100 kGy, respectively and decrease with further increase in dose. The catalytic activity of the sulfonated membranes is found to be high and enhanced as the concentration of fixed sulfonic groups increased. This work demonstrates the potential of radiation-induced crosslinking in preparing membranes for sucrose hydrolysis. The results suggest that crosslinked EVA membranes hosted-sulfonic acid groups could replace liquid sulfuric acid and ion exchange resins in sugar hydrolysis processes.

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