

Radiation Cross-Linking of Ethylene Vinyl Alcohol Copolymer Functionalized with *m*-Isopropenyl- α,α -Dimethyl Benzyl Isocyanate

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SYNOPSIS

An ethylene vinyl alcohol copolymer was functionalized with *m*-isopropenyl- α,α -dimethyl benzyl isocyanate using reactive processing in a mixer. The functionalization introduces pendant unsaturation to the polymer, which allows radiation cross-linking to gel contents > 70% at radiation doses below 100 kGy. Unfunctionalized ethylene vinyl alcohol copolymer, on the other hand, forms no gel upon irradiation. The functionalization was completed within a few minutes of reactive mixing, which was confirmed with both FTIR and ^{13}C -NMR measurements.

The oxygen permeability of ethylene vinyl alcohol copolymer increased with increasing degree of functionalization, and irradiation of the samples formed trapped radicals, which act as oxygen scavengers. Consequently no oxygen permeability was detected. However, radical activity was inhibited by annealing the samples at 110°C resulting in a 24% higher oxygen permeability value for the irradiated unfunctionalized copolymer. The oxygen permeability values of the irradiated functionalized samples were approximately 13% lower.

Laminates of *m*-isopropenyl- α,α -dimethyl benzyl isocyanate functionalized ethylene vinyl alcohol copolymer and *m*-isopropenyl- α,α -dimethyl benzyl isocyanate functionalized ethylene hydroxyethyl methacrylate copolymer acquired improved adhesive strength both at dry and wet conditions as well as at elevated temperatures upon exposure to radiation.

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INTRODUCTION

The preparation and radiation cross-linking of ethylene copolymers containing pendant unsaturation has been discussed in earlier communications from this laboratory.^{1,2} Enhanced cross-linking at low doses has been achieved via this technique, in particular in polymers that upon exposure to radiation predominantly undergo main-chain scission (e.g., vinyl alcohol polymers). This technique is extended here to study the barrier and adhesion characteristics upon irradiation of a functionalized ethylene vinyl alcohol copolymer.

Ethylene vinyl alcohol copolymers have found widespread use as oxygen barrier layers in food

packaging and even in hot water pipes. The excellent gas barrier properties of these polymers are caused by inter- and intramolecular hydrogen bonds, and because these bonds are moisture sensitive the gas permeation increases with increasing humidity. At high humidity water enters the polymer and interrupts the forces holding the polymer chains together and thus permeation increases because of greater ease of moving the polymer chains.³

Cross-linking of a polymer, on the other hand, will inhibit the diffusion process because the polymer chains will be tightly bound together and thus resist the formation of voids necessary for the transportation of a diffusing molecule. The major conclusions from various studies⁴⁻⁵ on cross-linked polymer films are that cross-linking reduces the gas permeability, and that permeation is little affected until the polymer is highly cross-linked. Kita et al.⁶ found that the permeability coefficients of the gases CO₂, He,

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O₂, CH₄, N₂, and SF₆ did not decrease for electron beam irradiated polybutadiene until the average molecular weight between cross-links was less than 10³ g/mol, corresponding to approximately 25 C—C bonds between two cross-links.

Efforts to reduce the moisture sensitivity of vinyl alcohol polymers have been made by cross-linking polyvinyl alcohol with glyoxal, urea-formaldehydes, or melamine-formaldehyde,⁷ while irradiation of vinyl alcohol polymers have been reported to primarily result in main-chain scission, although highly dependent on the experimental conditions. For example, gel fractions of 70% have been obtained by irradiation of polyvinyl alcohol in the presence of allyl methacrylate.⁸ Recently the irradiation of ethylene vinyl alcohol copolymers was reported to markedly improve the oxygen barrier properties even at high humidity.⁹ Trapped radicals that are formed during the radiation react with oxygen permeating through the film, and as long as there are radicals present the polymer film will have zero oxygen permeability.

In most applications, however, the problem with moisture sensitivity is dealt with by protecting ethylene vinyl alcohol copolymers by coextrusion with polyolefins. On the other hand, the highly polar EVOH resin has poor adhesion to the nonpolar polyolefins, and therefore an adhesive layer must be used in order to tie the polyolefin to the EVOH resin. In every joint between polymers the adhesive strength is not necessarily determined only by the interfacial forces (van der Waals forces, chemical bonding, or electrostatic attraction) holding two phases together, but also on the nature of existing flaws and viscoelastic properties of the bulk phases. Viscoelastic dissipation is in fact considered to be the major component of the fracture energy,¹⁰ and the magnitude of viscoelastic dissipation depends in turn on both molecular entanglement and the magnitude of intermolecular forces.

The influence of covalent bonding at the interface on the strength of an adhesive joint is still a subject of dispute among scientists. Many scientists argue that interfacial chemical bonding indeed is essential for achieving high strength adhesive joints,^{11–13} while others claim that a high density of interfacial bonds will make the joint brittle and weak.¹⁴ On the other hand, most scientists agree that interfacial chemical bonding is necessary to make joints withstand high humidity or high temperature.

Encouraged by the enhanced cross-linking at low radiation doses of ethylene copolymers by introducing pendant unsaturation, we decided to study the possibility of improving the adhesive strength by

irradiation of functionalized polymers in multilayer constructions of ethylene vinyl alcohol copolymers and polyolefins. The presence of pendant unsaturation in the different layers would facilitate cross-linking and a change in the viscoelastic properties of the bulk and possibly give rise to interfacial chemical bonding upon exposure to radiation, resulting in an increased adhesive strength. Additionally, the change of the oxygen permeability by introducing pendant unsaturation and irradiating the functionalized ethylene vinyl alcohol copolymer was determined.

EXPERIMENTAL

Materials

An ethylene vinyl alcohol copolymer containing 44 mol % ethylene (SELAR-OH, 4416) was used as received from Du Pont. Prior to use the polymer was dried for 12 h at 80°C. An ethylene hydroxyethyl methacrylate copolymer (EHEMA) containing 10 wt % hydroxyethyl methacrylate was used as received from NESTE Chemicals (NTR-354).

m-Iso-propenyl- α,α -dimethylbenzyl isocyanate (TMI) was used as received from American Cyanamid.

Sample Preparation

SELAR-OH was functionalized with different amounts (3 wt %, 5 wt %, 10 wt %) of TMI by a reactive mixing in a Haake-Buchler mixer at 210°C and a rotor speed of 60 rpm. The polymer was allowed to melt for 1 min before the addition of the TMI monomer, which took approximately 1–2 min. The mixing time was 10 min during the sample preparation, but the functionalization was followed as a function of time.

EHEMA was functionalized with 2 wt % TMI by mixing at 180°C for 10 min. The functionalization of EHEMA and characterization of the reaction product are described elsewhere,² and are therefore not discussed in detail in this paper.

Film samples of SELAR-OH and functionalized SELAR-OH were prepared by compression molding for 1 min at 175°C and film samples of EHEMA and functionalized EHEMA were prepared at 120°C. The polymers were allowed to melt for 2 min before pressing and were cooled rapidly to room temperature after the pressing.

Preparation of Laminates for Peel Tests

Laminates were prepared by hotpressing together a film sample of EHEMA or functionalized EHEMA between two SELAR-OH or functionalized SELAR-OH films at a temperature of 160°C for 15 s.

Irradiation

Thin films, $140 \pm 10 \mu\text{m}$, of SELAR-OH and functionalized SELAR-OH for permeability tests were irradiated with an Electrocurtain® (Energy Sciences Inc.) electron accelerator under a nitrogen atmosphere ($< 200 \text{ ppm O}_2$) at an acceleration voltage of 175 kV. The laminates for peel tests were irradiated similarly but from both sides.

General Procedures

Fourier transformed infrared spectroscopy (FTIR) measurements were done on a Perkin Elmer 1710 spectrometer and differential scanning calorimetry (DSC) data was acquired on a Perkin Elmer DSC 4. Data was collected while heating the sample with a heating rate of $10^\circ\text{C}/\text{min}$.

^{13}C -NMR spectra, 400 MHz, were recorded with a Jeol 400 spectrometer at 80°C in 10-mm tubes. Sample concentration was approximately 20% (w/v) with perdeuterated dimethyl sulfoxide ($\text{Me}_2\text{SO-d}_6$, Aldrich) as solvent and as internal locking agent.

Wide angle X-ray diffraction (WAXS) patterns were recorded in reflection by a Siemens Diffrac 500 using $\text{Cu-K}\alpha$ radiation. The crystallinity of the SELAR-OH and functionalized SELAR-OH samples were determined according to

$$\text{crystallinity (\%)} = \frac{I_c}{I_c + I_a} * 100$$

where I_c is the total area of crystalline diffractions and I_a is the total area under the amorphous curve. The diffraction pattern is recorded between the scattering angles (2θ) 2° and 50° with the background subtracted. The background was measured under identical conditions with an empty sample holder. The integration of I_c and I_a are determined as described by Campbell and White.¹⁵ The crystallinity values are not exact since the amorphous diffraction pattern was drawn without data of the pattern from a totally amorphous state. However, the values of the different samples are comparable. The crystal size was determined from the peaks at both 20.4° (110) and 22.2° (200) scattering angles. The diffraction pattern was first resolved in two crystalline peaks and an amorphous maximum be-

tween the scattering angles 14° and 24° . The full width at half maximum (FWHM) was determined and the crystal size was calculated as described in Campbell and White.¹⁵

$$\text{Crystal size (\AA)} = \frac{0.94 * 1.54187}{\text{FWHM} * \cos\theta}$$

where 1.54187 (\AA) is the wavelength of the Cu-anode, 0.94 is a constant, and θ is the scattering angle.

Determination of the Degree of Cross-Linking

The amount of polymer insoluble in DMSO at room temperature was chosen as a measure for the degree of cross-linking (gel content) of SELAR-OH and functionalized SELAR-OH. The procedure follows the standard ASTM D 2765, but since SELAR-OH is insoluble in xylene, DMSO was chosen as a solvent. Polymer film, $300 \pm 20 \text{ mg}$, was cut into pieces and immersed in DMSO for 24 h at room temperature. After extraction, the specimens were removed, rinsed in DMSO and acetone, dried to constant weight at 110°C , and reweighed. The gel content was calculated as follows:

gel content (%)

$$= 100 - \left[\frac{\text{weight loss during extraction}}{\text{weight of original specimen}} \right] \times 100$$

For each sample the gel content values were plotted as a function of irradiation dose.

Oxygen Permeability Measurements

The oxygen permeability was determined by using a Mocon Ox-Tran with 100% O_2 at different relative humidities. The tests were done at 23°C and it normally lasted 2 days to reach equilibrium at relative humidities between 0 and 50%, and 3 days between 50 and 90%.

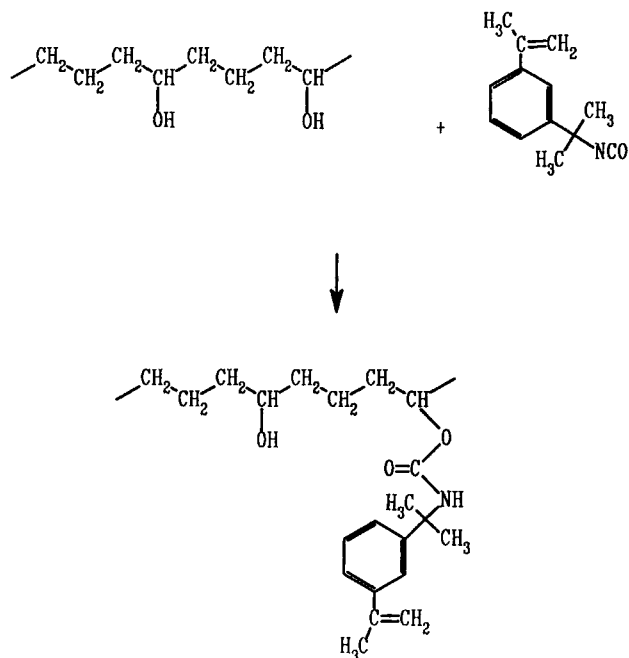
Peel Test

The adhesion of the laminates were determined by cutting out test specimens ($20 * 150 \text{ mm}$) from each laminate and measuring the peel force obtained in a 180° peel test with a delamination speed of 100 mm/min. The peel test was performed for dry samples at 25°C , 50°C , and 70°C . The wet strength of the laminates were determined after soaking the test specimens for 7 days in distilled water at ambient temperature.

RESULTS AND DISCUSSION

Functionalization of SELAR-OH with TMI

The functionalization of SELAR-OH with TMI follows the general reaction Scheme 1. The reaction of an isocyanate and an alcohol is usually considered to be a fast reaction, and in this work the reaction of TMI and SELAR-OH was found to be fast enough at 210°C to complete the reaction in a few minutes of mixing time. Three FTIR spectra that represent SELAR-OH and SELAR-OH functionalized for 2 min with 3 and 10 wt %, respectively, TMI are compiled and shown in Figure 1. There are no —N=C=O stretch vibrations present at around 2260 cm^{-1} in both spectra of the functionalized samples, indicating that all the added TMI monomers have reacted to SELAR-OH. Additionally, the formation of the carbamate in the functionalized samples can be detected at 1703 cm^{-1} (ester band), at 1540 cm^{-1} (amide band) and at 1266 cm^{-1} , which is the —C—O—C— vibration that possibly contains an absorption of associated —N—H groups.



Scheme 1

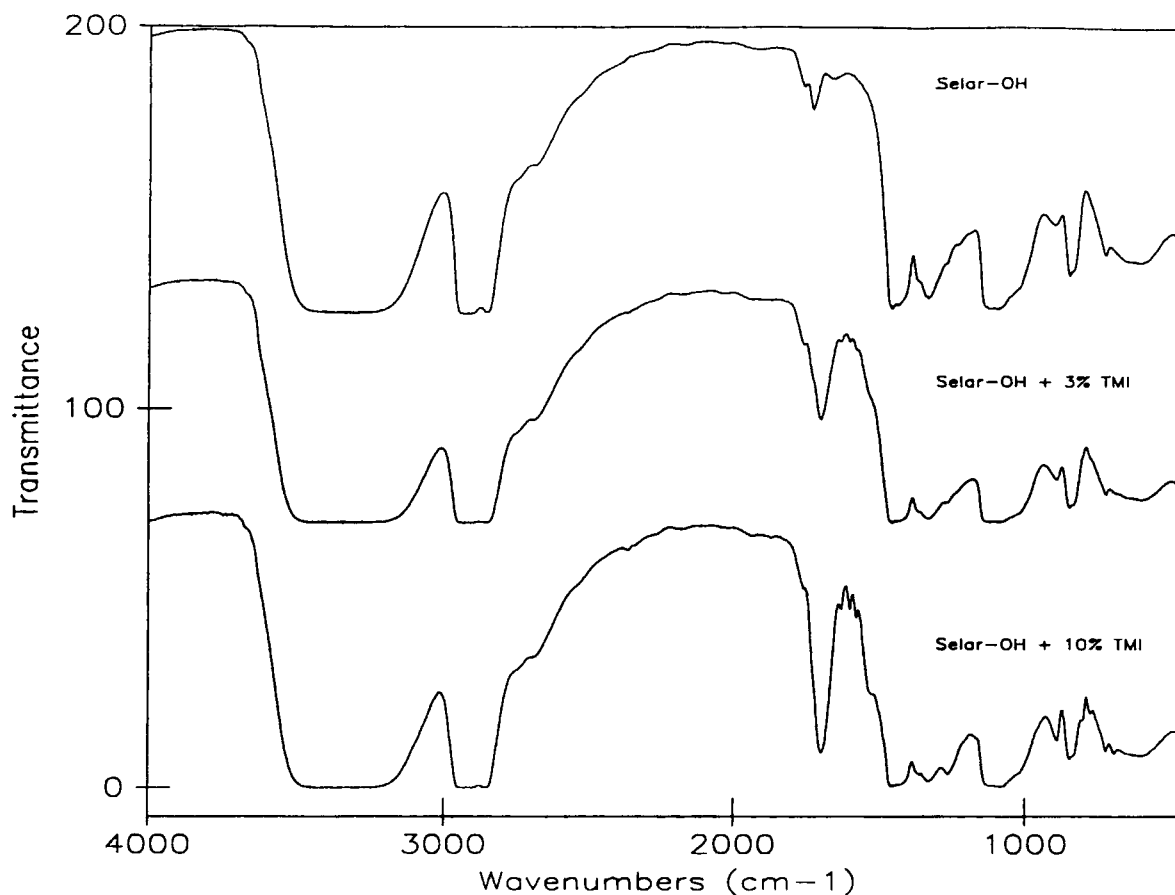


Figure 1 FTIR spectra of SELAR-OH and SELAR-OH functionalized for 2 min with 3 wt % and 10 wt % TMI, respectively.

During mixing the torque was followed to establish that no cross-linking of the polymer would occur. A polymerization of the pendant vinyl unsaturation or any other formation of cross-links would lead to molecule enlargement and an increase of the torque. No increase of the torque was noted however when SELAR-OH was functionalized with TMI, and we concluded that the pendant unsaturation is not reacting during the melt processing. Because all the added TMI monomers react to the polymer during the mixing, the composition of the functionalized SELAR-OH can be calculated, and these results are presented in Table I. Copolymers containing up to 2 mol % of pendant unsaturation were prepared.

Structural Analysis

The ^{13}C -NMR spectra of TMI and SELAR-OH functionalized with 10 wt % TMI are shown in Figures 2 and 3, respectively, and the corresponding spectral assignments are given in Tables II and III, respectively. The interpretation of the ethylene vinyl alcohol part of the spectra was done according to Ketels et al.¹⁶

From a comparison of the ^{13}C -NMR spectra of the TMI monomer and the SELAR-OH function-

alized with 10% TMI one can make the conclusion that all the added TMI monomers have reacted to SELAR-OH. That is, the resonance line at 123 ppm assigned to the isocyanate carbon disappears and a new resonance line (carbamate carbon) appears at 155 ppm in the ^{13}C -NMR spectra of the SELAR-OH functionalized with 10% TMI.

The ^{13}C -NMR spectrum furthermore reveals that the functionalized SELAR-OH contains the desired pendant unsaturation, that is, the resonance lines at 111.69 and 139.94 ppm, respectively.

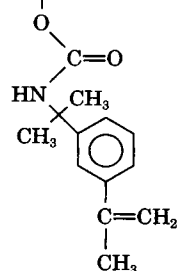
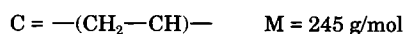
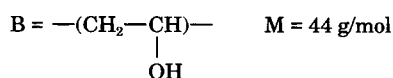
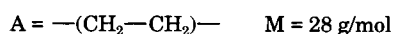
Crystallinity and Melt Enthalpies

The functionalization with TMI introduces a "bulky" pendant group to the polymer backbone and as a result of this the functionalized SELAR-OH samples will have quite different melt enthalpies and crystallinity than SELAR-OH. The results from DSC and WAXS measurements collected in Table IV show that both the melt temperature, melt enthalpy, as well as the crystallinity and the crystal size decrease with an increasing amount of pendant groups. The introduction of 2 mol % of pendant groups decreases the melt temperature from 160°C to 143°C and the crystallinity from 22% to 15%.

Table I Composition of SELAR-OH Functionalized with TMI

Amount of Added TMI to SELAR-OH		A		B		C		Weight ^a (g)
(wt %)	(mmol)	(wt %)	(mol %)	(wt %)	(mol %)	(wt %)	(mol %)	
0	0	33.3	44.0	66.7	56.0	0	0	50
3	7.5	32.3	44.0	64.0	55.4	3.7	0.6	50
5	12.4	31.6	44.0	62.3	55.0	6.1	1.0	50
10	24.9	30.0	44.0	57.8	54.0	12.2	2.0	50

^a Weight of the final sample after the functionalization:



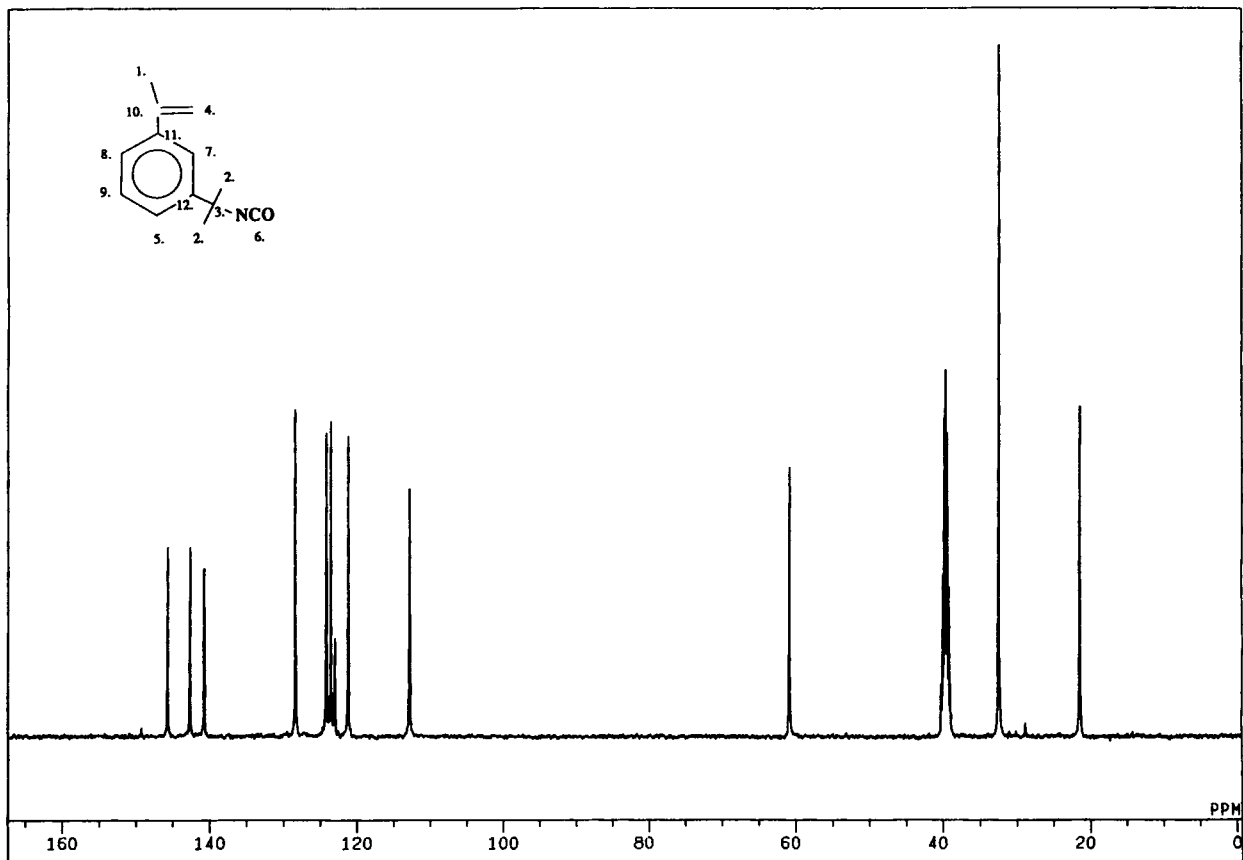


Figure 2 ¹³C-NMR spectrum of TMI.

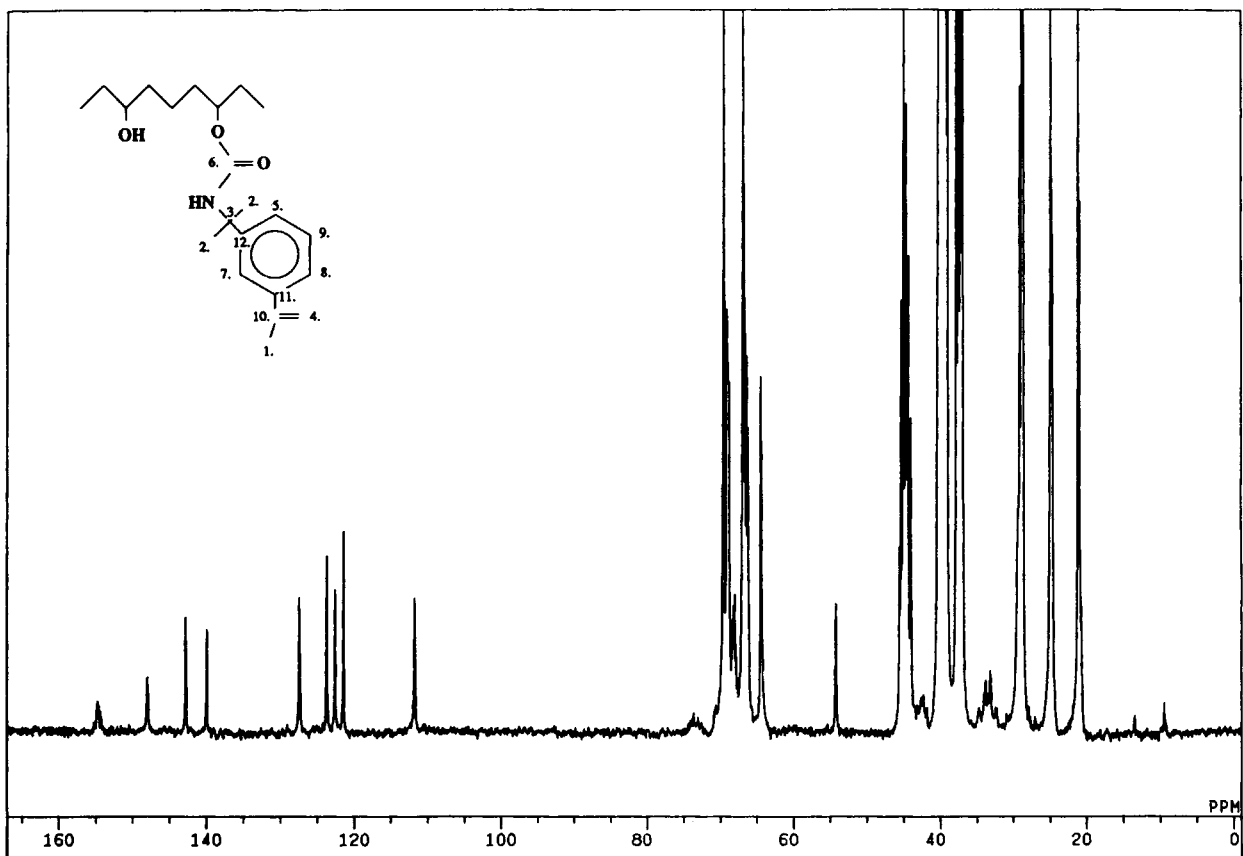


Figure 3 ¹³C-NMR spectrum of SELAR-OH functionalized with 10 wt % TMI.

Table II Spectral Assignments for TMI

Chemical Shifts ^a (ppm)	Carbons ^b
21.38	1
32.31	2
60.78	3
112.75	4
121.13	5
122.95	6
123.50	7
124.11	8
128.32	9
140.65	10
142.57	11
145.63	12

^a Chemical shifts given with respect to DMSO (39.50 ppm).

^b Denotes the carbons labelled in Figure 2.

There seem to be no changes in the melt enthalpies or the crystallinity upon irradiation of the functionalized samples, but a small increase of both the melt temperature and melt enthalpy of the irradiated unfunctionalized SELAR-OH can be detected. Furthermore, the crystal size of the samples remain largely unaffected upon irradiation except for the SELAR-OH sample functionalized with 10 wt % TMI, for which the crystal size changes from 75 Å to 67 Å after receiving a radiation dose of 250 kGy.

Degree of Cross-Linking

The gel content (insoluble fraction) of a polymer is generally considered as a measure of the degree of cross-linking, and the gel formation of radiation induced cross-linking is followed at different irradiation doses and plots of the gel content as a function of irradiation dose is presented.

Figure 4 depicts the gel formation when SELAR-OH and SELAR-OH functionalized with various amounts of TMI are irradiated. No insoluble fraction (Gel) is formed when SELAR-OH is exposed to radiation. SELAR-OH with pendant unsaturation cross-links to high gel contents already at irradiation doses below 100 kGy. These results show the benefits of introducing pendant unsaturation; a polymer that is otherwise impossible to radiation cross-link is by a reactive processing with a suitable monomer converted to an easily radiation cross-linkable polymer. Functionalizing SELAR-OH with more than 3% TMI does not significantly increase the gel content, but the density of the cross-links naturally increases with increasing amount of pendant unsaturation.

Peel Strength

Because both SELAR-OH and EHEMA can successfully be functionalized with TMI, the possibility of upgrading the adhesive strength of SELAR-OH-EHEMA laminates by introducing pendant unsaturation to the individual polymers and exposing the processed laminate to radiation was evaluated in comparison to unfunctionalized polymers. The peel force data in Table V suggest that the peel force increases from 430 N/m to 700 N/m by functionalizing SELAR-OH with 10 wt % TMI and EHEMA with 2 wt % TMI. Exposing the laminates containing the functionalized polymers to a radiation dose of 100 kGy increases the peel force to 1280 N/m; exposing the laminates of the unfunctionalized polymers to the same radiation dose decreases the peel force to 210 N/m.

Irradiation of the laminates containing unfunctionalized polymers have no effect on the wet strength (0 N/m), while irradiated laminates containing the functionalized polymers retained ~ 20% of the adhesive strength after a treatment in water. Furthermore, the peel force required to delaminate irradiated laminates of functionalized polymers at elevated temperatures is significantly higher than for the other samples. These results suggest the formation of interfacial chemical bonding upon exposure to radiation.

Table III Spectral Assignments for SELAR-OH Functionalized with 10 wt % TMI

Chemical Shifts ^a (ppm)	Carbons ^b
20.68–21.13	Methylene
24.64–24.88	
28.60–29.09	
36.84–37.69	
43.87–45.44	
54.12	3
64.27–64.41	Methine
65.96–66.85	
67.98–69.49	
111.69	4
121.38	5
122.51	7
123.64	8
127.37	9
139.94	10
142.81	11
155	6

^a Chemical shifts given with respect to DMSO (39.50 ppm).

^b Denotes carbons labelled in Figure 3.

Table IV Melt Temperature and Enthalpy, Crystallinity, and Crystal Size of Unirradiated and Irradiated Samples

Sample	Dose (kGy)	T_m^a (°C)	ΔH^a (J/g)	Crystallinity ^b (%)	Crystal Size ^b	
					110	200
SELAR-OH	0	160	63.8	22	152	123
	100	166	70.3	23	154	122
	250	158	66.0	23	152	118
SELAR-OH 3% TMI	0	154	55.3	21	149	110
	100	152	53.6	20	152	122
	250	152	47.6	20	153	115
SELAR-OH 5% TMI	0	150	48.6	19	143	107
	100	149	46.8	18	147	104
	250	149	46.9	20	143	102
SELAR-OH 10% TMI	0	143	36.8	15	133	75
	100	141	34.5	14	136	78
	250	142	36.5	15	131	67

^a Determined by DSC.^b Determined by WAXS.

Oxygen Permeability

Both functionalization of SELAR-OH with TMI and irradiation of SELAR-OH as well as irradiation of functionalized SELAR-OH have a pronounced effect on the oxygen permeability of the samples as shown in Table VI. As stated earlier (Table IV) the functionalization with TMI introduces a bulky pendant group to the polymer backbone and as a result of this the crystallinity decreases and the free volume increases with increasing amount of added TMI. Therefore, oxygen permeability will increase with increasing degrees of functionalization. Irradiated samples, functionalized or not, have no oxygen permeability as long as the free radicals formed during

irradiation are present and can act as oxygen scavengers.

Therefore, to be able to evaluate the effects on the oxygen permeability by cross-linking the functionalized SELAR-OH, irradiated samples were annealed at 110°C for 2.5 h and repeated permeability testing was performed. As indicated in Table VI, the oxygen permeability increases from 0 to measurable values when the irradiated samples are annealed at 110°C. Because the annealed samples contain no free radicals that can scavenge the oxygen, the permeability values of the samples may be compared with the unirradiated samples. The oxygen permeability of the irradiated/annealed SELAR-OH sample is ~ 24% higher than the value for the unirradiated sample, while the corresponding values for the SELAR-OH samples functionalized with 3 and 10 wt % TMI show a ~ 10% and ~ 13%, respective decrease in oxygen permeability. Irradiation of unfunctionalized SELAR-OH results in main-chain scission causing the oxygen permeability to increase. Irradiation of the functionalized SELAR-OH samples, on the other hand, results in cross-linking that will decrease the oxygen permeability.

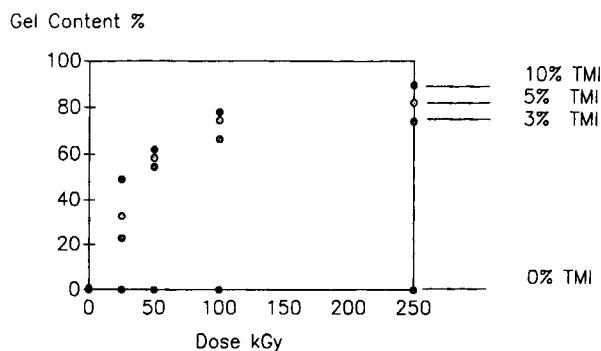


Figure 4 Gel content as a function of radiation dose for SELAR-OH and SELAR-OH functionalized with different amounts of TMI.

CONCLUSIONS

Introduction of 0.6–2 mol % of pendant unsaturation to an ethylene vinyl alcohol copolymer allows the

Table V Peel Forces Measured with 180° Peel Test on Laminates of Samples

Sample	Radiation Dose (kGy)	Condition	Peel Force (N/m)		
			25°C	50°C	70°C
A	0	Dry	430	108	22
	100	Dry	210	370	102
	0	Wet	0		
	100	Wet	0		
B	0	Dry	700	156	20
	100	Dry	1280	760	250
	0	Wet	0		
	100	Wet	250		

Sample A: SELAR-OH-EHEMA-SELAR-OH laminate. Sample B: SELAR-OH 10 wt %; TMI-EHEMA 2 wt %; TMI-SELAR-OH 10 wt %; TMI laminate.

radiation cross-linking of the polymer to high gel contents (> 70%), while the unfunctionalized ethylene vinyl alcohol copolymer forms no gel upon irradiation.

Both FTIR and ^{13}C -NMR spectroscopy confirmed the formation of carbamate units during the processing of ethylene vinyl alcohol copolymers with *m*-isopropenyl- α,α -dimethyl benzyl isocyanate as well as the introduction of the desired pendant unsaturation.

In comparison to laminates of unfunctionalized polymers, laminates of TMI functionalized ethylene vinyl alcohol copolymer and TMI functionalized ethylene hydroxyethyl methacrylate copolymer ac-

quired improved adhesive strength at both dry and wet conditions as well as at elevated temperatures.

The oxygen permeability of ethylene vinyl alcohol copolymer increased with an increasing degree of TMI functionalization. For irradiated samples, on the other hand, no oxygen permeability could be measured, because the trapped radicals that are formed during irradiation act as oxygen scavengers. Annealed irradiated samples, however, contain no free radicals that can scavenge the oxygen, therefore the degree of oxygen permeability is attributed to the structure of the polymers. Irradiation of unfunctionalized SELAR-OH results in main-chain scission accompanied with an increase in the oxygen

Table VI Oxygen Permeability for Functionalized and Irradiated SELAR-OH at Different Humidities

Sample	Radiation Dose (kGy)	Oxygen Permeability ^a (cc/m ² /25/ $\mu\text{m} \cdot \text{d} \cdot \text{atm}$)			
		0%	30%	60%	90%
Selar-OH	0	0.037	0.045	0.045	0.205
Selar-OH 3% TMI	0	0.066	0.067	0.062	0.248
Selar-OH 10% TMI	0	0.152	0.119	0.096	0.498
Selar-OH	150	0	0	0	0
Selar-OH 3% TMI	150	0	0	0	0
Selar-OH 10% TMI	150	0	0.01	0.005	0.487
Selar-OH	Irr. and ann. ^b	0.046			
Selar-OH 3% TMI	Irr. and ann. ^b	0.059			
Selar-OH 10% TMI	Irr. and ann. ^b	0.133			

^a Oxygen permeability is reported at 0, 30, 60, and 90% relative humidity.

^b Oxygen permeability of 150 kGy irradiated (irr.) samples after annealing (ann.) at 110°C for 2.5 h.

permeability, but irradiation cross-links the functionalized SELAR-OH samples resulting in a decrease in the oxygen permeability.

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