Available online at www.sciencedirect.com
ScienceDirect
Nuclear Instruments and Methods in Physics Research B 258 (2007) 357–361
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Preparation and physical properties of enhanced radiation induced crosslinking of ethylene–vinyl alcohol copolymer (EVOH)

Pengyang Deng [a,c,*], Meihua Liu [a,b], Wanxi Zhang [b], Jiazhen Sun [a]

[a] *Changchun Institute of Applied chemistry, Chinese Academy of Science, 5625 Renmin Street, Changchun, Jilin 130022, China*
[b] *Department of Materials Science and Engineering, Jilin University, 142 Renmin Street, Changchun, Jilin 130025, China*
[c] *Graduate School of Chinese Academy of Science, 19 Yuquan Street, Beijing 100039, China*

Received 30 November 2006; received in revised form 25 January 2007
Available online 1 March 2007

Abstract

Preparation and physical properties of ethylene–vinyl alcohol copolymer (EVOH) crosslinked by enhanced radiation have been studied through various methods. It was found that the most effective agent for irradiation-crosslinking was triallyl isocyanurate (TAIC) among four kinds of polyfunctional monomers. Gel content (65.6%) was formed for EVOH-44 (content of ethylene is 44 mol%) at 200 kGy with 5% TAIC, but for EVOH-32 (content of ethylene is 32 mol%), only 37.4% gel content was formed under the same conditions. This result showed that the more the content of ethylene units comprised in EVOH, the easier the chemical bonds could be formed between different molecular chains. Tensile strength and elastic modulus increased after crosslinking at high test temperature and elongation at break decreased at the same time. Hygroscopicity of EVOH showed noticeable decrease after enhancement radiation-crosslinking.

PACS: 61.80.Fe; 61.82.Pv; 62.20.−x

Keywords: EVOH; Polyfunctional monomers; Radiation-crosslinking

1. Introduction

Ethylene–vinyl alcohol copolymers (EVOH) are constructed by random sequencing of hydrophobic ethylene (E) and hydrophilic vinyl alcohol (V) monomeric units. The properties of EVOH vary drastically with the copolymer composition [1]. When the content of E units is below 50 mol%, EVOH has outstanding gas-barrier properties under dry conditions compared to other polymeric materials [2]. So EVOH is used widely in various fields such as food packing and gasoline tanks [3]. And it is expected to work well as one of soft materials for ecology because of no emission of poisonous gas upon incineration.

However, EVOH is hygroscopic and the absorbed water in it lowers its glass transition temperature [4]. Consequently, EVOH loses much of its ability to inhibit oxygen diffusion, which is undesirable in food packaging. Introducing crosslinking bonds between polymer molecules by chemical or radiation treatments is a powerful method to reduce the hygroscopicity. But few studies have been on this subject. In our previous study [5], we found that neat EVOH was difficult to radiation-crosslinking when the content of ethylene was less than 50 mol%, because degradation occurred in the part of vinyl alcohol. The gelation dose increased from about 30 kGy of HDPE to 400 kGy for EVOH-89 (content of ethylene is 89 mol%) while the value was 800 kGy for EVOH-44 and about 1800 kGy for EVOH-32 by Co-60 irradiated in vacuum at room temperature.

Similar to the fact that PVA can be irradiated by crosslinking in solution [6], the efficiency of radiation induced

* Corresponding author. Address: Changchun Institute of Applied chemistry, Chinese Academy of Science, 5625 Renmin Street, Changchun, Jilin 130022, China. Fax: +86 431 85685653.
E-mail address: dpyang@ciac.jl.cn (P. Deng).

0168-583X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2007.01.300

crosslinking of EVOH-44 was found to be increased as 10% water existent [4]. But the crosslinking effect of EVOH on physical properties is not yet clear. In this paper, enhancement radiation-crosslinking of EVOH and treatment conditions for the most effective introduction of crosslinking agent was studied. And the mechanical properties and hygroscopicity of crosslinking EVOH were also investigated for the first time.

2. Experiment

2.1. Material

The EVOH copolymers – E 151 (EVOH-44) and F 101 (EVOH-32) used in this work were obtained from Kuraray Co. Ltd., Japan, of which the ethylene contents are 44 mol% and 32 mol%, respectively.

Dimethyl acetamide (DMAc) and absolute alcohol used in extraction experiment were from Beijing Chemical Plant.

The polyfunctional monomers – diethylene glycol diacrylate (DEGDA), neopentyl glycol diacrylate (NPGDA), trimethlopropane triacrylate (TMPTA) – were obtained from Orient Organic Chemical Plant, China and TAIC was from Laiyu Chemistry Co. Ltd.

2.2. The mixture of EVOH with polyfunctional monomers

Two kinds of EVOH were blended with different polyfunctional monomers using Polylab System of Haake (RHEOMIX-600P), the blend temperatures were 185 °C and 200 °C for EVOH-44 and EVOH-32 mixture samples, respectively. The total blend time was 5 min. The mixture ratios of DEGDA, NPGDA and TMPTA with EVOH-44 were 1 wt/wt%, 2 wt/wt%, 3 wt/wt% and 5 wt/wt%. And the mixture ratios of TAIC with EVOH-44 and EVOH-32 were 1 wt/wt%, 2 wt/wt%, 3 wt/wt%, 5 wt/wt%, 7 wt/wt% and 10 wt/wt%.

2.3. Irradiation

The samples were molded to form 1 mm thick sheets using plate vulcanizing press. The working temperatures of EVOH-44 and EVOH-32 blend were 185 °C and 245 °C, respectively and the total holding time was 5 min. The samples were irradiated by electron beam and the radiation dose were 50 kGy, 100 kGy, 200 kGy, 300 kGy and 600 kGy, respectively, at room temperature. The dose rate was 600 Gy/s.

2.4. Determination of gel fraction

The samples covered with nickel-mesh were extracted by DMAc in a Sokhlet apparatus for 24 h and then they were dried to a constant weight in vacuum at 80 °C after washing with alcohol. The gel fraction was calculated by following formula:

$$G = \frac{W_1}{W_0} \times 100\%,$$

where G is the gel fraction (%), W_1 and W_0 are the masses of the samples after and before extraction, respectively.

2.5. Mechanical properties

Tensile strength, elongation at break and elastic modulus of the samples irradiated at different doses were tested with an Instron universal testing instrument (INSTRON 1121). The extension rate is 50 mm/min at room temperature (20 °C) and 200 mm/min at high temperature (200 °C).

2.6. Determination of the ratio of water absorption (R)

The samples were dried in a vacuum oven at 70 °C to a constant weight to eliminate the moisture from them and then put into high temperature stream around 100 °C and taken out at different times. The ratio of water absorption was calculated by the following formula:

$$R = \frac{W_1 - W_0}{W_0} \times 100\%,$$

where R is the ratio of water absorption, W_1 and W_0 are mass of the samples after and before being braised.

3. Results and discussion

3.1. Selection the crosslinking agent

Four kinds of polyfunctional monomers were mixed with EVOH-44 and irradiated by electron beam and their gel fractions are listed in Table 1. The results showed that the crosslinking network was formed in all mixture samples

Table 1
The gel fractions of EVOH-44 blend at different irradiation doses

Polyfunctional monomers	Weight (%)	Gel fraction (%)			
		0 kGy	50 kGy	100 kGy	200 kGy
TAIC	1	0	22.4	11.3	25.5
	2	0	35.0	26.8	45.5
	3	0	36.1	40.6	55.9
	5	0	43.3	42.4	65.6
		0 kGy	50 kGy	300 kGy	600 kGy
DEGDA	1	0	3.0	4.6	1.0
	2	0	3.0	6.0	3.1
	3	0	5.8	6.1	4.1
	5	0	8.2	14.8	4.6
NPGDA	1	0	5.3	3.0	2.9
	2	0	5.6	1.4	3.3
	3	0	5.2	6.0	4.8
	5	0	8.1	33.5	14.4
TMPTA	1	0	6.1	6.6	5.6
	2	0	6.3	6.1	6.2
	3	0	7.7	5.5	5.6
	5	0	11.0	5.1	8.2