

The Synthesis of Styrene-Oligoester Copolymer and Investigation of Their Physico-mechanical Properties

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Abstract

The copolymerization reaction of commercial propylene oxide with glycidylmethacrylate in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst have been investigated. The composition and structure of copolymerization products and anchored functional groups have been determined using IR and gel chromatographic methods. The physico-mechanical properties and utility of polyfunctional unsaturated oligoester were investigated. The obtained thermoset product via the reaction of the oligoester with both styrene and oligostyrene obtained from the bottom of column as a waste material during the rectification operation of styrene in the presence of radicalic initiator has a good adhesion capability, hardness and high heat and water resistance. Thus the waste material was converted to the high valuable polymeric material.

Introduction

The synthesis of the reactive polyfunctional monomers and new polymeric materials having complex properties has recently become of great practical importance for polymer chemistry and technology.

There are several research works [1-6] about the investigation and application of new oligoester materials with epoxy ester obtained from the reaction of acrylic and metacrylic acid with alkylene oxide.

In the previous studies [7,8] the unsaturated epoxy ester and unsaturated epoxy ketone with $-\text{COCH}_3$, $-\text{OCH}_3$, $-\text{COO}$, $-\text{C}=\text{C}-$ functional groups have been synthesized and it was pointed out that synthesized copolymers have a good adhesion capability and higher physico-mechanical properties. This study is carried out in order to extend our earlier papers, synthesize new styrene-oligoester copolymers and improve their physico-mechanical properties. In this study, firstly the unsaturated oligoester was synthesized via the reaction of glycidylmethacrylate with propylene oxide in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst. The synthesized oligoester was reacted both styrene and the oligostyrene that is a waste material from the rectification of styrene, thus copolymer with unsaturated oligoester fragment was prepared and the

chemical and physico-mechanical properties of obtained polymer were investigated.

Experimental

Materials

Propylene oxide (PO) ($d_4^{20} = 0,859$, $n_D^{20} = 1,3667$) was obtained from Industry as a commercial product and glycidylmethacrylate (GMA); ($d_4^{20} = 1,0728$, $n_D^{20} = 1,4505$, boiling point: 62°C at 2 mmHg) was synthesized via the reaction of potassium methacrylate with epichlorohydrine in the presence of tetra ethyl ammonium iodide [9]. $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst were commercial products and all of them were distilled under nitrogen atmosphere diluted with chloroform and sealed in glass ampoules.

Copolymerization

Cationic polymerization of propylene oxide with glycidylmethacrylate in the presence of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ catalyst at -10 to 0°C ($n_{\text{po}} : n_{\text{GMA}} = 0,5-10,0:1$) was achieved as follows; to synthesize the unsaturated oligoester at 0°C , the catalyst solution was added slowly to solution consisting of propylene oxide and glycidylmethacrylate mixture and stirred for 30 minutes. The amount of used monomer for the copolymerization reaction was controlled by chroma-

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tographic method. The yield is about 75-84 % for imsatuated oligoester synthesis reaction.

For graft polymerization reaction of oligoester with styrene in the presence of a radical initiator 0,5 g oligoester and 95 g styrene were mixed and stirred homogeneously. 0,5 g azo bis isobuturo-nitrile (AIBN) radical initiator was added to the oligoester-styrene mixture, then mixture was stirred again for 4 h at 80-120°C. After completion of the reaction, the product was dried under a vacuum at 1 mmHg, 20°C for 5 h. The modification of oligostyrene with imsatuated oligoester was done at the same reaction conditions as mentioned above.

Measurements

The IR spectra of oligomer films were recorded by use of a Unicam SP 1025 Spectrometer. The molecular weight and its distribution (MWD) with gel chromatographic method and the functional groups distribution (FGD) were determined.

Thermal Analysis

Thermogravimetry (TGA) and differential thermal analysis (DTA) experiments were carried out by use of a Paulik-Erday derivatograph system. The thermal stability of modified PS has been arbitrarily defined by initial loss observed with increase of temperature at 10 °C/min heating rate in the air atmosphere.

Differential Scanning Calorimeter analysis was realized by use of a Dupont TA 2000 at 10 °C/min heating rate in nitrogen atmosphere.

Physico-mechanical Analysis

The adhesion capability, relative extension and resistance to stretch were determined by RMI-250 apparatus. In this measurement, the samples were determined by stretching.

Resistance to stretch (σ) was calculated as follows;

$$\sigma = \frac{P}{a \times h} = \frac{P}{A}$$

where P is the weight to which the sample is subjected, kgf; a is the width of sample, cm; and h is the thickness of sample, cm.

The relative extension (ϵ') (%) was calculated using the equation;

$$\epsilon' = \frac{l - l_0}{l_0} \times 100$$

where l_0 is the initial part of working sample, mm; and l is the breaking part of working sample, mm.

The adhesion capability (A) was calculated using the following equation:

$$A = \frac{P}{S}$$

where A is the adhesion (MPa); P is the force for stretch, kgf; and S is the surface area sample, cm².

$$S = a \times b$$

a is the width of signboard, cm, and b is the exposed adhesion area, cm.

Resistance to stroke (α) was determined by resistance to stroke using KM-15-1 apparatus. The resistance to stroke at the breaking time could be calculated (according to standard 120x15x10 mm) from the following equation:

$$\alpha = \frac{W}{a \times h}$$

where W is the work for breaking the sample, kgf/cm.

Brinell Hardness (H_B) was determined by AS-101/KM-2 apparatus and was measured as (N/mm²) according to the standard.

Resistance to heat (T_v) was determined by FWA model Vika apparatus. The heat rate was 50 °C/h.

The results of physico-mechanical, thermal and adhesion properties of the synthesized copolymers are given in Figures 1-2.

Results and Discussion

The unsaturated oligoester having the functional groups such as $-C=C-$, $-COO-$, and $-OH$ were synthesized via the reaction of the propylene oxide with glycidylmethacrylate in the presence of $BF_3 \cdot O(C_2H_5)_2$ catalyst, and their structure is characterized as shown in Scheme 1.

The structure and the amount of the functional group of the synthesized unsaturated oligoester were examined with chromatographic, spectroscopic and chemical analysis methods. By using gel chromatographic methods, it was found that M_n , M_w and polydispersion (M_w/M_n) of the oligomer is about 370-600, 540-1050 and 1,5-1,8 respectively. The unsaturated oligoester has some more functional groups and double bonds than that of oligoesters such as oligofumarate and oligomaleinate. This difference is caused by the crosslinkage between unsaturated

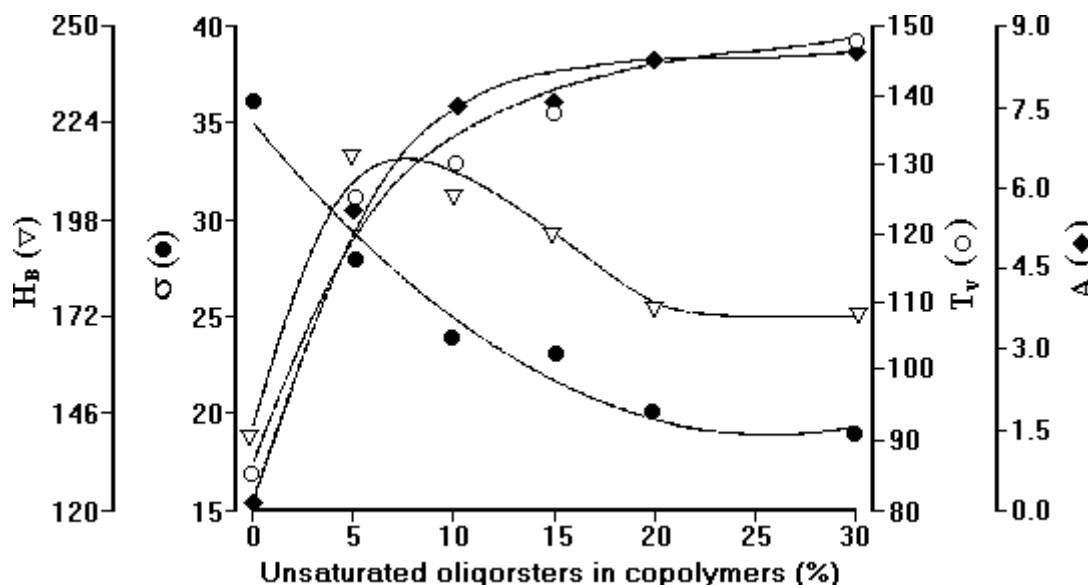
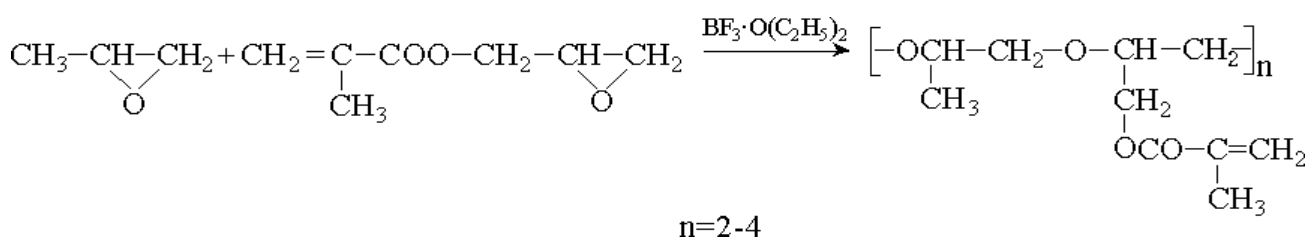


Fig. 1. The physico-mechanical properties of styrene-oligoester copolymer, resistance to stretch (σ), hardness (H_B), resistance to heat (T_v), and adhesion (A)



Scheme 1

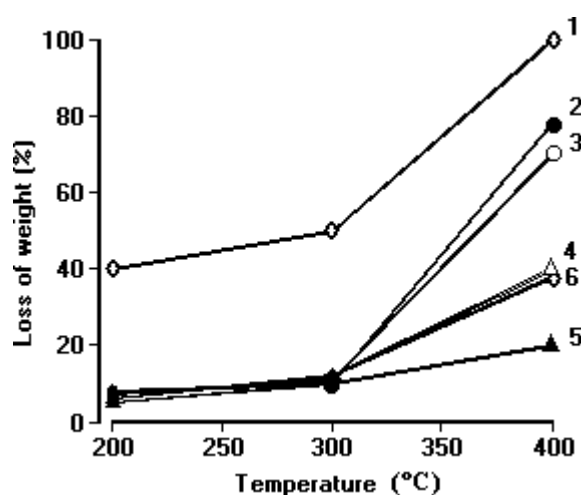


Fig. 2. The results of thermogravimetric analysis of styrene-oligoester copolymer: Oligoester:styren, % = 5 : 95 (2) ; 10 : 90 (3), 20 : 80 (4); 25 : 75 (6); 30 : 70 (5); Polystyren (1)

oligoester and styrene at lower temperature than that of saturated oligoester. The hardness rate of oligoester

with styrene in the presence of radicalic initiator is related to the amount of the double bonds (that is in glycidylmethacrylate fragment) in the oligoester. The hardness reaction is completely occurred in 5 hours.

The synthesized material via the reaction of oligoester with styrene in the presence of radical initiator has a good adhesion capability and thermostability and high physico-mechanical properties.

The results of physico-mechanical, thermal and adhesion properties of the synthesized polyfunctional polymeric materials are given in Table 1.

As shown in the Table 1, the adhesion capability of the copolymer increases from 5,6 to 8,5 MPA and thermostability increases from 125 to 140°C and the hardness of Brinel's decreases from 215 to 173 N/mm² with the increase of oligoester percentage in copolymer from 5% to 30%. The loss of weight at 300°C is about 11-19%. The thermostability of copolymer could be increased with the increasing of unsaturated oligoester percentage in copolymer.

As a result, the styrene and oligoestyrene obtained

Table 1

Physico-mechanical, Thermal and Adhesion Properties of Unsaturated Copolymers

Composition of Copolymer		σ MPA	T_V (°C)	H_B (N/mm ²)	A (MPa)	Loss of weight %		
Oligoester	Styrene					200 °C	300 °C	400 °C
0	100	36	85	140	0.05	40	50	100
5	95	28	125	215	5.6	8	10	78
10	90	24	130	205	7.5	7	11	70
15	85	23	138	195	7.6	6	12	40
20	80	20	145	175	8.4	5	10	20
30	70	19	147	173	8.5	6	12	38

from bottom column during rectification of the styrene is converted to the new material, which has high adhesion capability and thermal stability properties.

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