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Preparation A Cross-Linked Copolymer By Using Unsaturated Poly (2-Butene Maleate) Polyester and Methyl Methacrylate

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Abstract

In this study, synthesis of unsaturated Poly(2-Butene Maleate) polyester by condensation polymerization and preparation of cross-linked graft copolymer with methyl methacrylate are presented. For this purpose, unsaturated polyesters were synthesized in four different time periods (12h, 24h, 36h, 48h) in the presence of hydroquinone using 1,4-Butanediol-2-ene and maleic anhydride. Then, the obtained unsaturated polyester was purified on the alumina column and used to obtain cross-linked copolymer with methyl methacrylate. Here in, methyl methacrylate acts as both co-monomer and cross-linking agent.

In the preparation of Poly(2-Butene Maleate), the optimization study of the molecular weight and yield ratios with the time parameter was carried out. In the results obtained, it was observed that the maximum molecular weight was reached after almost 36 hours (Mn=3400). It was observed that time did not have much effect on the yield. Structural characterizations of the obtained products were supported by FT-IR and NMR analyzes. In thermal analysis, it was observed that the thermal stability of Cross-linked graft copolymer is higher than unsaturated polyester but lower than pure Poly(methyl methacrylate). Elementals analyze was used to determine the quantity of C, H and O elements within synthesized polymers. According to obtained results, the percentage of H atom in the structure increased as expected by obtaining cross-linked copolymer using methyl methacrylate

Keywords: Cross-linked, Graft, Methyl methacrylate, Unsaturated polyester

1. Introduction

Unsaturated polyester resins are an important part of thermoset polymers and the third largest class of thermoset molding resins. They are commonly used due to their easy processability, low cost, availability in a variety of grades and good corrosion resistance [1-4]. They are generally produced by the condensation of a diol with anhydrides. The obtained condensation products form very durable structures and coatings when cross-linked with vinyl monomers such as methyl methacrylate, styrene [5-7]. The mechanical and chemical properties of the cross-linked resin depend on the types and amounts of anhydrides and diols used. Many commercial unsaturated polyester resins are derived from phthalic and maleic anhydride as the saturated and unsaturated component in the polymer and 1,2-propylene glycol as the diol [8,9]. Many other glycols and anhydrides or acids can be used to alter the character of unsaturated polyesters. E.g., terephthalic acid and isophthalic acid are chosen to obtain much better chemical and thermal resistance, whereas long-chain aliphatic acids, such as succinic acid or adipic acid, enhance the flexibility but reduce the thermal and chemical resistance [10,11].

On the other hand, despite the many advantages of unsaturated polyesters, when the disadvantages are considered, it has been seen that product improvement has been made in different ways. One of these ways is the cross-linking technique, as in this study. Because in this way, the low modulus, that is, stiffness, disadvantage of polyester can be eliminated, aging resistance can be increased, and the deformation time can be extended [12-14].

There are some studies in literature on cross-linked structures based on unsaturated polyesters as well as blends of commercial unsaturated polyesters with ready polymers. It is generally focused on the morphology, miscibility, and thermal properties in these studies [6, 15].

Studies in the literature have focused on similar techniques. Ready-made polyesters are generally cross-linked by the curing method. New types of products and product preparation methodology have not been given much attention in this regard. In this study, a new cross-linked unsaturated polyester was produced. Unlike previous studies, this product was obtained without using an auxiliary cross-linking agent and curing process.

2. Materials and Methods

2.1. Materials

2-butene-1,4-diol (97%, cis-isomer, Merck), Maleic Anhydride (for synthesis, Sigma-Aldrich), Hydroquinone (Reagent plus, ≥99%, Merck), Methylmethacrylate (99%, stabilized, Sigma-Aldrich), Benzoyl Peroxide (with %25 H_2O, for synthesis, Sigma-Aldrich), Chloroform (anhydrous, ≥99%, Merck)

2.2. Experimental

2.2.1. General Procedure

A stepwise polymerization method was used for the synthesis of polyester. At this stage, hydroquinone was used to protect the double bonds in the monomers.
An inert atmosphere was created by removing O_2 by applying vacuum to the reaction medium and passing argon gas. In the experiments carried out with maleic anhydride, to prevent the esterification reaction, which is an equilibrium reaction, from proceeding in favor of the reactants, the removal of the released water was provided by using the Dean-Stark adapter.

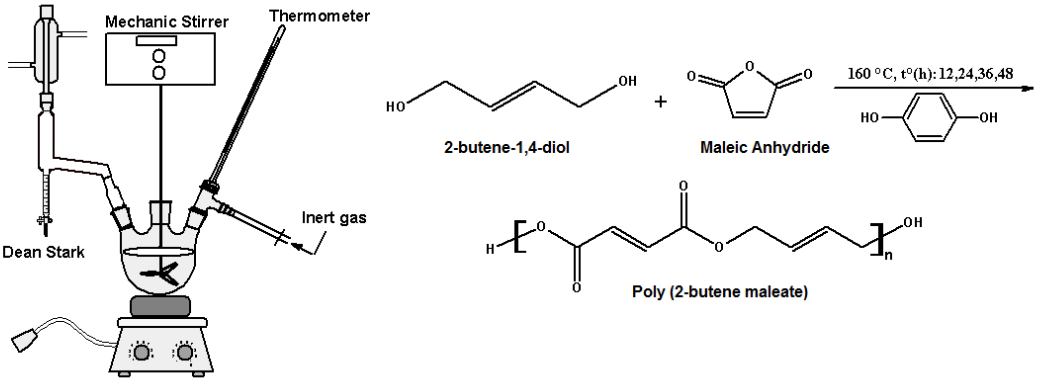

Figure 1. Synthesis of Poly (2-butene maleate) and reaction setup

2.2.2. Synthesis of Poly(2-Butene Maleate)

9.806 g maleic anhydride (0.1mol), 1.01 g hydroquinone (0.01 mol) and 9.30 ml 2-butene-1,4-diol (0.1 mol) were placed in a four-necked flask. Dean-Stark adapter and condenser were connected to one neck of the balloon and mechanical mixer was connected to the other neck. At the same time, argon gas was passed through the environment to ensure a continuous inert environment, while the temperature was monitored at 160 ^{o}C. The reaction was carried out under the conditions determined as four separate trials of 12, 24, 36 and 48 hours. The representation of the reaction setup is as in Figure 1.

2.2.3. Crosslinked Copolymer Synthesis

Hydroquinone was removed by passing the obtained Poly(2-Butene Maleate) through a column formed with unsaturated polyester alumina. One gram of the purified polyester was taken and cross-linked with equivalent moles of methyl methacrylate in the presence of chloroform. As the initiator, 3% of the total mole of benzoyl peroxide was used. Polymerization continued for 24 hours at a temperature of 75 °C. The synthesis of the cross-linked unsaturated copolymer is summarized in the Figure 2.

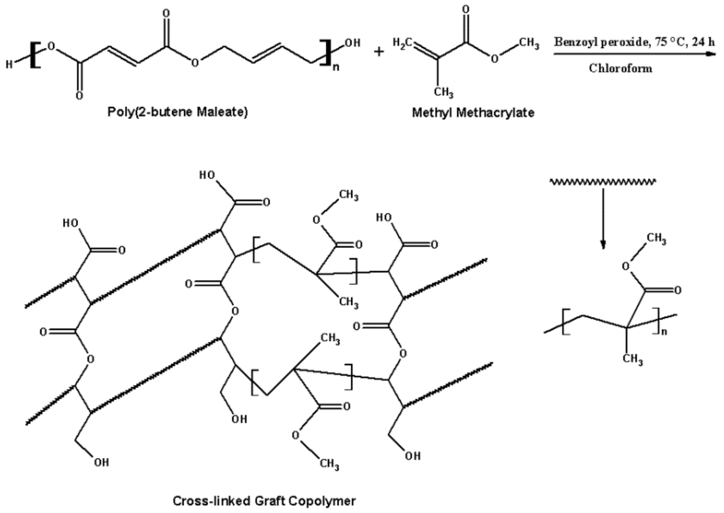

Figure 2. Synthesis of Cross-linked Copolymer

3. Results and Discussion

In this study, structural characterization was performed with FT-IR (Fourier Transform Infrared Spectroscopy, Perkin Elmer FT-IR Spectrum One-B spectrometer) and NMR (Nuclear Magnetic Resonance, ^{1}H-NMR spectra were recorded on Varian AS-400 spectrometers in $CDCl_3$ with $Si(CH_3)_4$ as internal standard). Molecular weight optimization of poly(2-butene Maleate) unsaturated polyester against time was performed. Molecular weight was determined by end group analysis. Thermal analysis of cross-linked graft copolymer obtained using poly (2-butene maleate) and methyl methacrylate was performed with TG (Thermogravimetry, performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C/min under nitrogen flow). It was supported the work with elemental analyzes was successful. Elemental analysis was performed by Perkin Elmer 2400 CHNS Organic Elemental Analyzer 100V

Determination of Molecular Weight

To perform the time molecular weight optimization of the synthesized unsaturated polyester, the experiment was carried out in 4 different periods, 12, 24, 36 and 48 hours. The molecular weights obtained in these time periods were determined as 1200 (12h), 2200 (24h), 2800 (36h), 2805 (48h). Calculation of molecular weight was carried out by end group analysis.
Figure 3 shows the molecular weight plot of the synthesized Poly (2-butene maleate) polyester versus time. Experimental results of end group analysis are given in Table 1. The formulation used in Equation 1 is given.

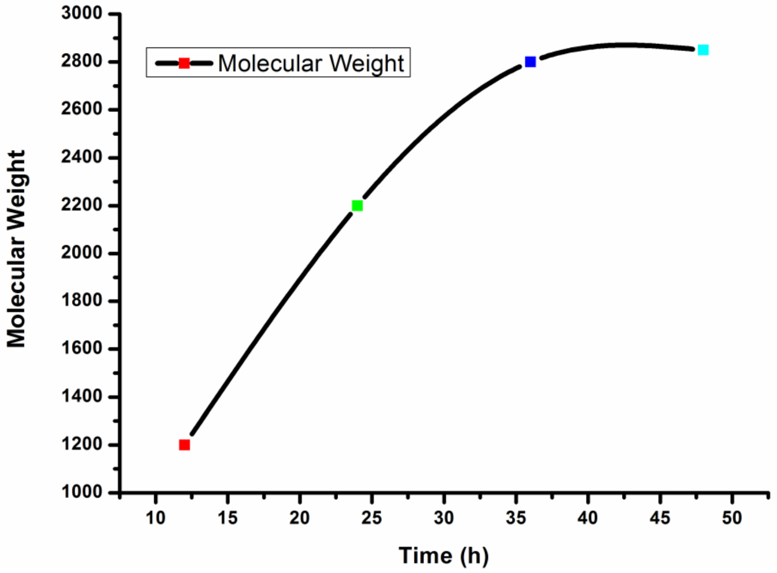

Figure 3. The molecular weight plot of the synthesized Poly (2-butene maleate) versus time

In the end-group analysis method, the number of chemical groups at the ends of the polymer chains is determined by an appropriate analysis method. In general, chains of cascading polymers have certain end groups suitable for analysis. For this reason, the method is mostly used to find the molar mass of cascading polymers such as polyamide, polyester, which have end groups such as $-H_2N$, -COOH. In the end-group analysis method, polymer samples were taken as 0.15 grams in all tests. According to the results obtained, the molecular weights of the polymers increased with enhancing time. According to the optimization, the maximum molecular weight was reached after 36 hours.

Moles of acid group in polymer = moles of spent base
Number of moles of acid group in the polymer = $0.025 \times 5.0 \times 10^{-3} = 125 \times 10^{-6}$ (experiment 1 sample calculation)

$$M_n = \frac{Amount\ of\ polymer\ sample\ used}{Number\ of\ moles\ of\ functional\ groups\ in\ the\ polymer} = \frac{0{,}15\ g}{125 \times 10^{-6} mol} = 1200\ g/mol \qquad (1)$$

Table 1. Experimental results of end group analysis

Experiment		End Group Analysis Results		Molecular Weight (g/mol)
No	Hours	Molarity of Titrant Used NaoH, (N)	Amount of Titrant Consumed (cm^3)	
1	12	0,025	5	1200
2	24	0,025	2,72	2200
3	36	0,025	≈2,14	2800
4	48	0,025	2,14	2805

FT-IR

Figure 4 shows the FT-IR spectra of monomers and polymers. According to this figure, asymmetric –C-O-C- stress at 1230-1236 cm^{-1}, symmetrical –C-O-C- strain at 1028-1036 cm^{-1}, CH_2 release at 1327-1340 cm^{-1}, =C-H- stretch at 3084 cm^{-1}, at 1644 cm^{-1} the -C=C- stretch was determined. In the spectrum of the final product, the cross-linked graft copolymer, it was observed that the peak of the double bond disappeared, as expected, and the carbonyl peak was very prominent at 1750 cm^{-1}.

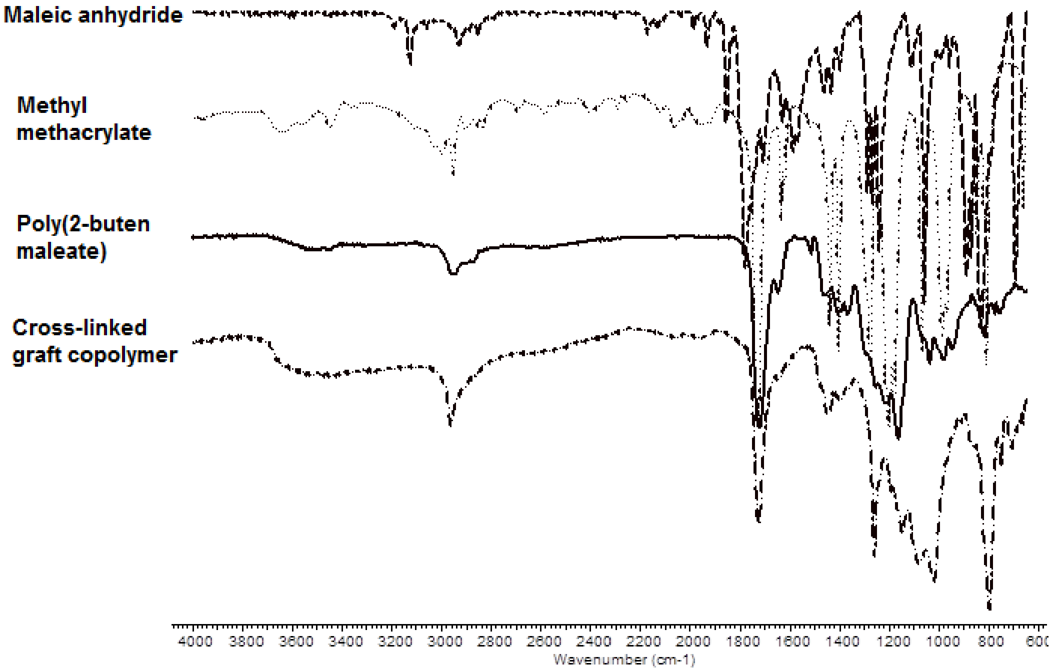

Figure 4. FT-IR spectra of monomers and synthesized polymers

^{1}H-NMR

The NMR spectrum of Poly(2-Butene Maleate) is shown in Figure 5. The positions of the protons are marked on the figure. The hydrogen atoms in the -$\mathbf{CH}_2$=$\mathbf{CH}_2$- structure between two carbonyl groups are approximately 6.8 ppm. The chemical shift value of the methylene group attached to oxygen, -O-$\mathbf{CH}_2$-, is around 4.2 ppm. The chemical shift value of the -$\mathbf{CH}_2$- group on the aliphatic chain was seen at 1.8 ppm. The result obtained supports the successful synthesis of poly(2-butene maleate).

TG

Thermal characterization of cross-linked graft copolymer was performed by thermogravimetry. Figure 6 shows the obtained thermogram. In this figure, the blue line represents pure PMMA, while the red line represents cross-linked graft copolymer. When we look at the thermal results of the products obtained under similar conditions to compare the results correctly, Poly(methyl methacrylate) (PMMA) showed one degradation step as seen in the literature [16,17]. It is seen that the decomposition, which started at about 320 ^{o}C, completely ended around 470 ^{o}C. PMMA decomposed sharply at 400 ^{o}C. This main degradation can be due to the cleavage of the backbone of the polymer. It is seen that the thermal stability of the obtained PMMA is higher than many similar ones in the literature. When the thermal degradation of the cross-linked copolymer is examined, it is clearly seen that there are significant differences compared to pure PMMA. According to figure 6 cross-linked copolymer has three main transition regions: the first one of these transitions is because of evaporation of CO_2 and water that occurs in the range of 80-180 °C. It has been observed that the second transition is between 230-430 ^{o}C. The cleavage of the backbone may be the cause of the degradation in this region. The third and final decomposition stage was determined to be between 450-580 ^{o}C. Although the thermal stability of the obtained cross-linked polyester is lower than PMMA, its thermal resistance is significantly better. In PMMA, decomposition completely ends at 470 ^{o}C, while in cross-linked polymer this value increased up to 600 °C.

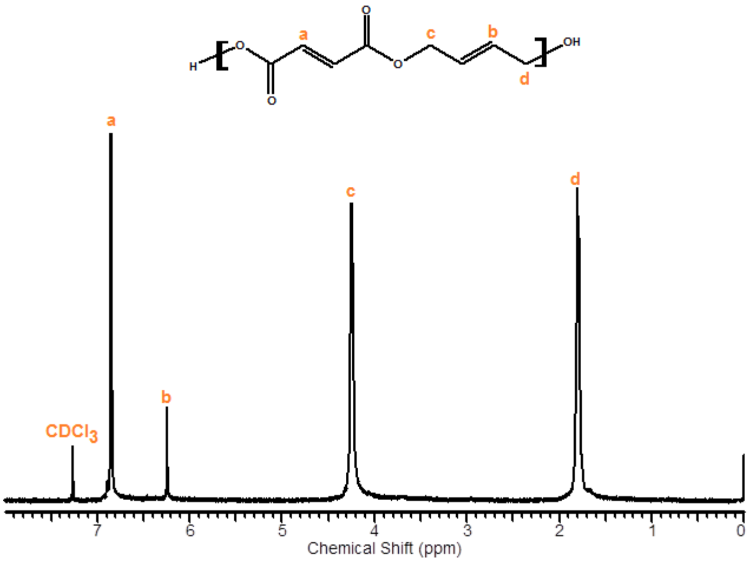

Figure 5. The ^{1}H-NMR spectrum of Poly(2-Butene Maleate)

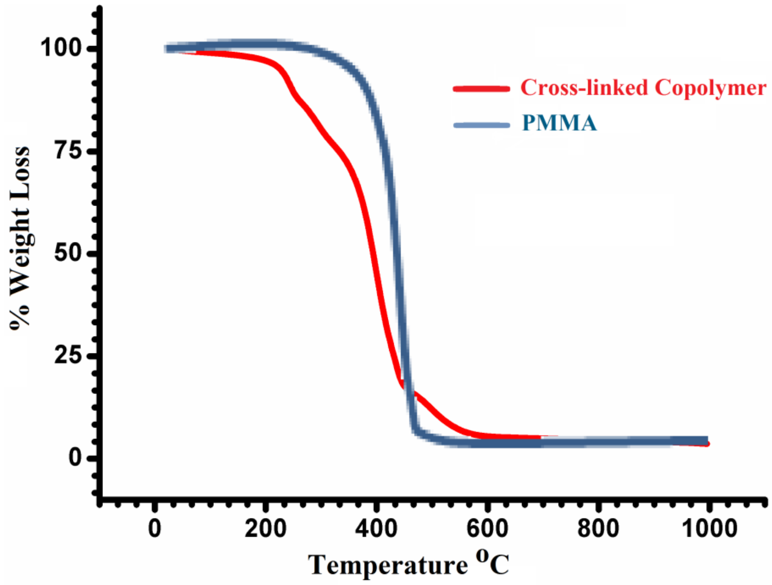

Figure 6. TG Curves of the PMMA and Cross-linked Copolymer

Elemental Analysis

Also, elemental analyzes of unsaturated polyester and cross-linked copolymer were carried out to determine the quantity of C, H and O elements within synthesized polymers. The data obtained are shown in Table 2. The highest molecular weight (2800 g/mol) Poly (2-butene maleate) was used in the analysis. An example of a cross-linked copolymer is the product obtained from this high molar mass polyester. The results of the C and H elements obtained from the analysis are in line with the theoretical expected results. The theoretically expected percentages (%) of C, H, and O in poly (2-butene maleate) are 57, 4, and 39, respectively. It was observed that the percentage of H atom in the structure increased as expected by obtaining cross-linked copolymer using methyl methacrylate.

Tablo 2. Elemental Analysis of the Cross-linked Copolymer and Poly (2-butene maleate)

Sample	Segment	Unit	Calculated			Found		
			C	H	O	C	H	O*
Poly (2-butene maleate)	-($C_8O_4H_8$)-	%	57	4	39	56	5	39
Cross-linked Copolymer	-($C_5H_8O_2$)-/-($C_8O_4H_8$)-/-($C_5H_8O_2$)	%				58	8	34

*Computed by difference

4. Conclusion

In this study, it was aimed to obtain a cross-linked copolymer by cross-linking methyl methacrylate with Poly (2-butene maleate) polyester obtained by condensation polymerization. Considering the thermal analysis of the cross-linked product, it was observed that although its thermal stability was not as high as Poly (methyl methacrylate), its thermal resistance was higher. In addition to being new in the literature, it is noteworthy that this product was obtained with very accessible, inexpensive materials and an easy method. Also, it was supported by FT-IR, NMR, and elemental analysis methods that the targeted materials were successfully obtained. It is thought that with further studies, the mechanical and thermal properties of the material will be improved, and it will allow the production of fire resistant materials.

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Author's Contributions

Fehmi Saltan: Drafted and wrote the manuscript, performed the experiment and result analysis.

Ethics

There are no ethical issues after the publication of this manuscript.

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