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Synthesis and Thermomechanical Analysis of Some Primer Alcohol Derivatives of Maleic Anhydride/Styrene Copolymer

Maleik Anhidrit/Stiren Kopolimerinin Bazı Primer Alkol Türevlerinin Sentezi ve Termomekanik Analizi

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Özet. Bu çalışmada, Maleik anhidrit/Stiren (MAS) kopolimeri sentezlendi. Sentezlenen kopolimer karakterize edildi ve iki farklı primer alkol (propil ve bütil) ile modifiye edildi. Kopolimer ve iki modifiye türevinin çözünme, FT-IR ve termomekanik (TMA) analizleri gerçekleştirildi. Türevlerin ester sayıları hesaplandı. Alkoller ile modifiye edilen türevler MAS kopolimeri ile aynı çözünme davranışları gösterdiyse de, daha hızlı çözündükleri saptandı. Modifikasyon işlemi FT-IR ile doğrulandı. Ester türevlerinin MAS kopolimerine göre daha elastik ve düşük camsı geçiş sıcaklığına sahip olduğu görüldü. Türevlerin ester sayılarının birbirlerine yakın olduğu hesaplandı.

Anahtar Kelimeler: Aşılama, kopolimer, maleik anhidrit, modifikasyon.

Abstract. In this study, Maleic anhydride/Styrene (MAS) copolymer was synthesized. The synthesized copolymer was characterized and then modified with two different primary alcohols (propyl and butyl). Dissolution, FT-IR and thermo-mechanical (TMA) analyzes of the copolymer and its two modified ester derivatives were

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performed. The ester numbers of the obtained derivatives were calculated. Although the ester derivatives showed dissolution behavior in the same solvents as the MAS copolymer, they dissolved faster. Modification was confirmed in the FT-IR spectra. It was also found that the derivatives were more elastic than the MAS copolymer and had a lower glass transition temperatures. The calculated ester numbers were also close to each other.

Key words: Copolymer, grafting, maleic anhydride, modification.

1. Introduction

Maleic anhydride is known as a reactive monomer and is often used as a compatibilizer in a polymer blend of two immiscible polymers [6, 25, 31]. Pairs of polymer blends prepared with grafted maleic anhydride result in interfacial adhesion and small areas in the blend matrix due to the use of maleic anhydride as a compatibilizer. The presence of free MA in the blend matrix had a plasticizing effect by affecting the mechanical and thermal properties of the blend [5]. Maleic anhydride is often preferred in the functionalization studies of alkenic polymers due to its low homopolymerization tendency and the formation of short grafts on the chain that allow the polymer to retain most of its physical and mechanical properties [1,8].

Maleic anhydride/Styrene (MAS) is a synthetic polymer composed of styrene and maleic anhydride monomers. The monomers form a [1:1] charge transfer complex, making the MAS copolymer an excellent alternative copolymer [12]. The polymer is synthesized by dissolving the monomers in an organic solvent followed by radical polymerization with the addition of an organic peroxide as the initiator. It is possible to obtain the MAS copolymer with different molecular weights and varying numbers of maleic anhydride contents [14]. High molecular weight MAS polymers are preferred in impact modified and glass fiber filled variants, advanced engineering plastic materials. In addition, MAS copolymer can be applied with other transparent materials such as PMMA without changing the transparency of the material [22]. By adding it to other commercial polymers such as ABS or PVC, it improves the thermal resistance of these materials [7, 23, 29].

One way to change the properties of polymers and obtain new materials is graft copolymerization. This kind of grafting with maleic anhydride has been done extensively in recent years [4, 20, 24, 26, 27, 28, 36]. The modified forms of maleic anhydride copolymers obtained by opening the anhydride ring with this grafting become functionalized polymers. Such functionalized polymers are used as compatibilizing agents in the reactive compatibility of incompatible polymer blends and can be obtained by graft copolymerization of functional monomers into the polymer backbone. Graft copolymers of maleic anhydride have been used as a compatibilizer to convert different immiscible polymers into compatible blends [3, 9, 16, 32, 37]. Graft polymerization reactions can be initiated by different methods such as high energy gamma rays or electron beams, ultraviolet rays from the middle energy region, peroxide initiators or polymer oxidation [2, 10, 11, 21, 30, 35].

Many works have been done to synthesize new polymer materials with improved performance or cost. Materials with desired properties can be produced by co- or terpolymerization of new monomers or by modifying or blending existing polymers [13, 15, 17, 18, 19].

In the present work, maleic anhydride/styrene polymer, which is a maleic anhydride copolymer, was modified with propyl and butyl alcohol by opening the anhydride ring, and its two ester derivatives were obtained. The modification was proven by FT-IR and thermo-mechanical analyzes were performed. It was observed that both ester derivatives obtained by the modification were more elastic, have higher coefficient of linear thermal expansion (CLTE) values, and have lower glass transition temperatures (Tg) than the MAS copolymer.

2. Materials and Method

2.1. Chemicals and instruments

Maleic anhydride, Styrene, and benzoyl peroxide used in the synthesis of MAS copolymer were at analytical grade and Sigma-Aldrich brand. Maleic anhydride was recrystallized by chloroform. Styrene was purified by vacuum distillation. Butyl and

Propyl alcohols were Merck brand. All of the primer alcohols and the organic solvents used are analytical grade. The solvents used were Sigma-Aldrich brand.

Thermo-mechanical measurements were recorded by Shimadzu TMA-50 instrument at a heating rate of 5 °C/min under air atmosphere. FT-IR spectra were recorded using a Unicam Mattson 1000 model spectrophotometer as KBr pellets.

2.2. Synthesis of MAS copolymer

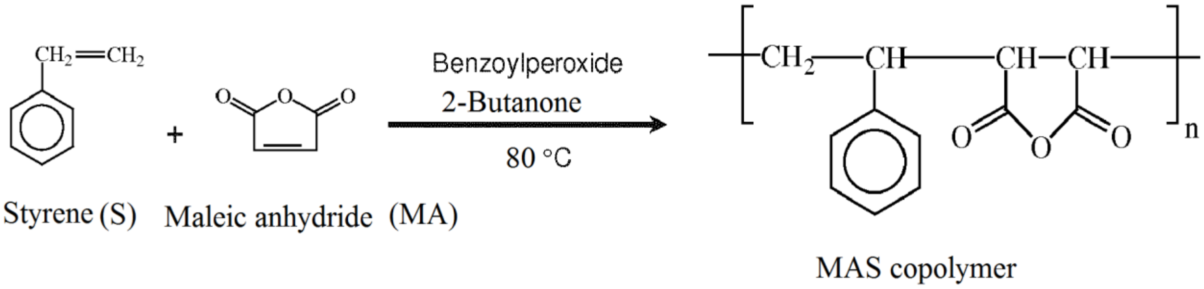

Figure 1. MAS copolymer sythesis reaaction

MAS copolymer synthesis was performed according to the reaction seen in Figure 1. Equimolar (0.1 mol) Maleic anhydride and Styrene were used. 9.8 grams of MA monomer was dissolved in 50 mL of ethyl methylketone. To this solution, 11.5 mL of styrene was added and mixed. 0.2 % benzoyl peroxide was added and dissolved. This mixture was made up to 100 mL with 2-butanone solvent. This solution was reacted at 80 °C for 2 hours. After 2 hours, the resulting viscous solution was allowed to cool, excess ethyl alcohol was poured and the MAS copolymer was precipitated. Then it was washed several times with ethanol and dried in an oven at 40 °C.

Styrene monomer is an electron donor monomer while Maleic anhydride is an electron acceptor monomer. When the two monomer are in the same reaction medium, they form a charge transfer complex (CTC). This charge transfer complex also causes them to form alternative copolymers. The copolymerization tendency of the charge transfer complex consisting of two monomers is higher than the homopolymerization tendency of the monomers.

2.3. Synthesis of MAS copolymer derivatives

2.02 grams of synthesized MAS copolymer (containing 0.01 moles of MA), 0.02 moles of propyl or butyl alcohol, was dissolved in a flask containing 100 mL of dioxane. A few drops of concentrated sulfuric acid were added to this solution. The solution was stirred at 85 °C for 24 hours. The solution was stirred while cooling at room temperature. The ester derivatives formed were precipitated with toluene. The derivatives were washed several times with ethyl alcohol and dried in an oven at 40 °C. The chemical reaction of derivatization is shown in Figure 2 below.

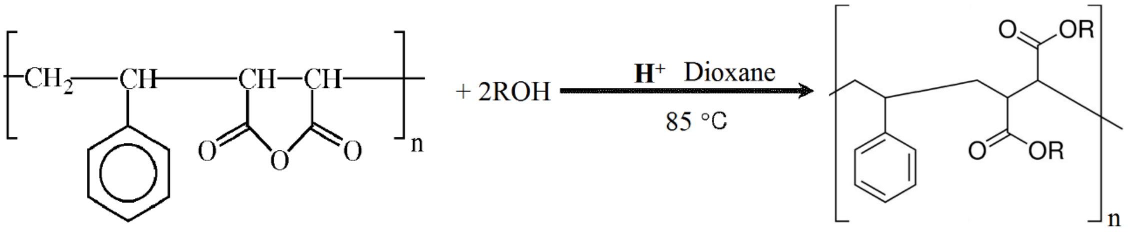

Figure 2. Derivatization reaction of MAS copolymer with primer alcohols.

2.4. Ester number determination

For the determination of ester number; two ester derivatives (propyl and butyl) of 1.0 gram MAS copolymer, proMAS and butMAS, were placed in separate reaction flasks. 30 mL ethyl alcohol, 2 Molar 30 mL potassium hydroxide (KOH) in ethyl alcohol were added. This mixture was boiled for 2 hour under reflux condenser. The solution was cooled and titrated with 1M HCl, ester numbers of the ester derivatives of the copolymer were calculated using Equation 1.

$$n\ ester\ = \frac{Mw\ (KOH)(M1V1-M2V2)}{mp} \qquad \text{(Eq. 1)}$$

Where nester is the ester number of the derivative, Mw is mol weight of KOH, M1 is the molarity of KOH, V1 is volume of KOH in mL, M2 is the molarity of HCl, V2 is the volume of HCl in mL and mp is the weight of the derivative used in grams.

The determined ester numbers of MAS and its two ester derivatives were given at Table 1.

2.5. Solubility tests

Solubility tests of the synthesized MAS copolymer, proMAS and butMAS ester derivatives in different solvents were carried out. For this purpose, these experiments were carried out with some common organic solvents given in Table 1, and water using 10 mg sample taken from each polymer.

2.6. Tables and Figures

Table 1. Solubilities of MAS, its ester derivatives in some common solvents and water and their ester numbers

Polymer	Tetrahydro furan	Acetone	Chloroform	dimethyl formamide	Toluene	Water	Ester number
MAS	+	+	--	+	--	--	--
proMAS	+	+	--	+	--	--	655
burMAS	+	+	--	+	--	--	698

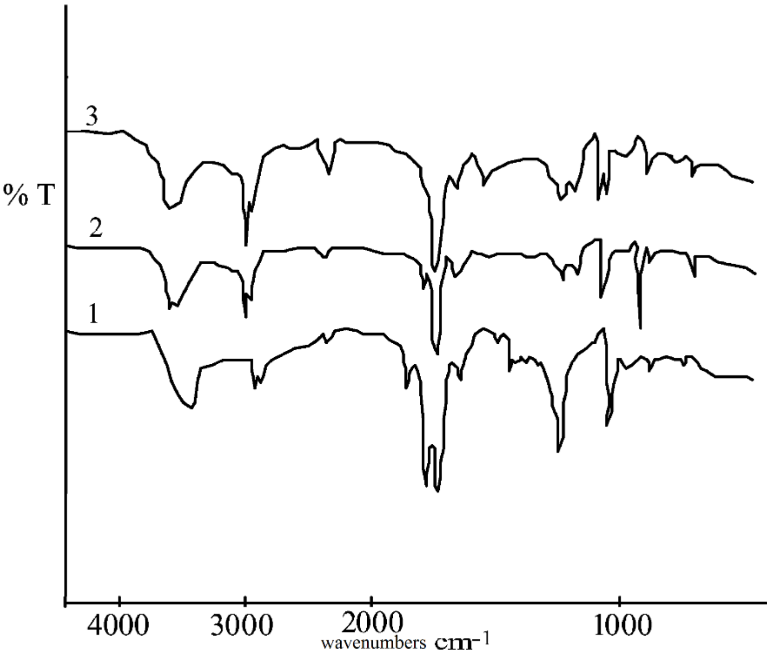

Figure 3. FT-IR spectra of (1) MAS (2) proMAS (3) butMAS

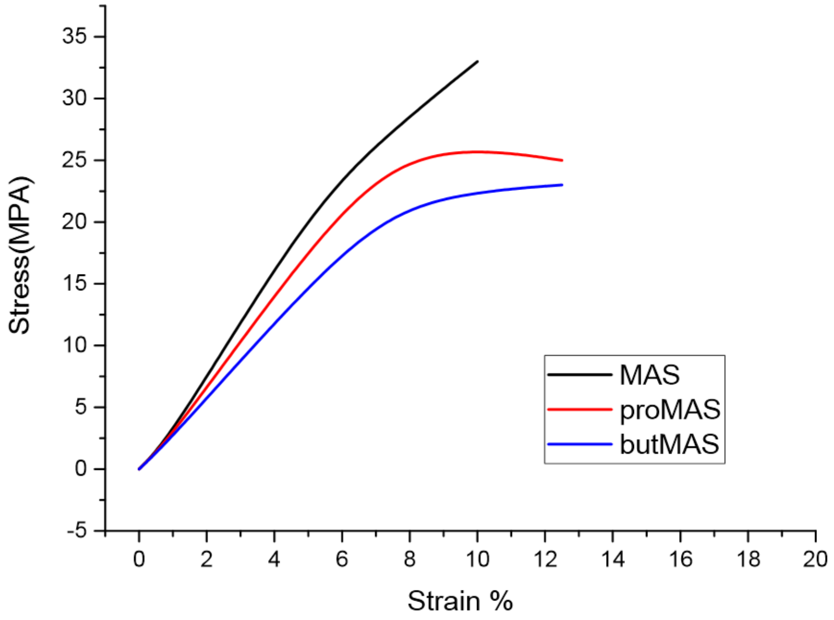

Figure 4. Stress-strain curves

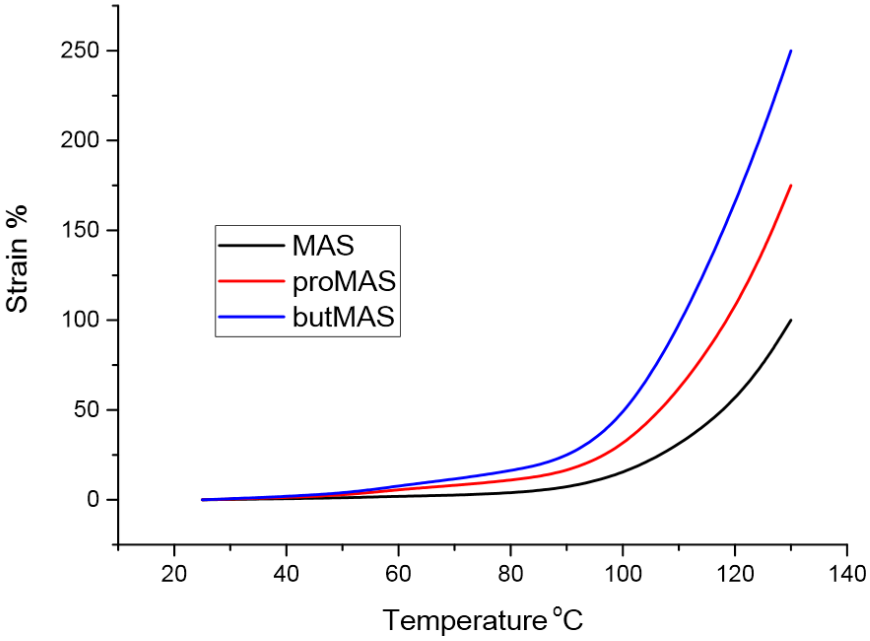

Figure 5. Temperature-strain curves

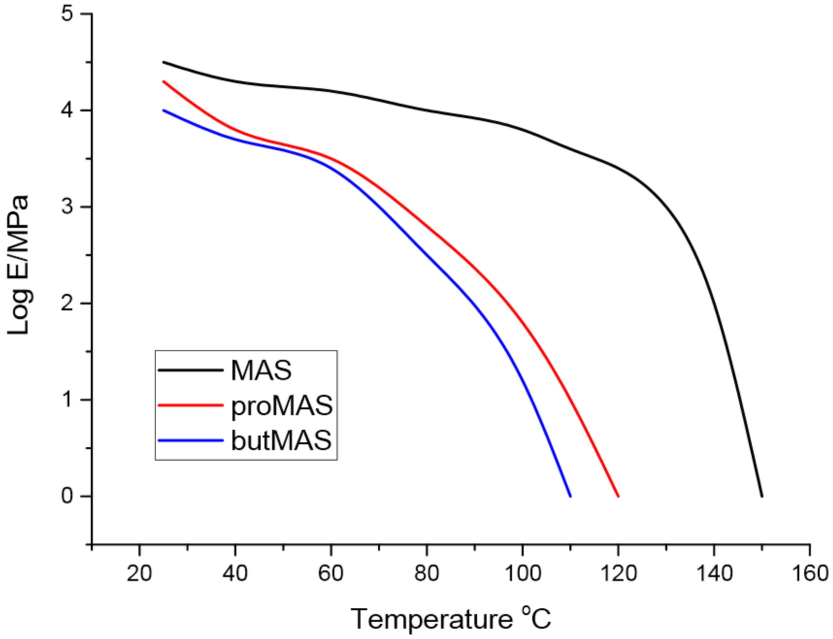

Figure 6. Log E - Temperature curves

Table 2. Some thermal and mechanic values of the MAS and its ester derivatives

Polymer	Young Modulus(MPa)	CLTE (α) ($^oC^{-1}$)	Glass Transition Temp (^{o}C)
MAS	3845	2.35	131
proMAS	2650	2.86	82
butMAS	2185	3.08	71

3. Results and Discussion

Figure 1 shows the reaction of the MAS copolymer, and Figure 2 shows the reactions in which the ester derivatives of the copolymer are obtained by using propyl and butyl alcohol.

In the FTIR spectrum of the copolymer MAS (1) in Figure 3, the peaks appearing at 1850 cm^{-1}, 1771 cm^{-1} are the carbonyl peaks belonging to the anhydride group (anhydride C=O). At 1220 cm$_{-1}$, the C-O-C stress peaks of the anhydride ring can be seen in the spectrum (cyclic C-O-C). Due to the ester conversion in the chemical reaction shown in Figure 2, a lower intensity was seen in the 1850 cm-1 and 1771 cm-1 anhydrous carbonyl peaks of proMAS (2) and butMAS (3) derivatives in the FT-IR spectrum. It is also seen in Figure 3 that the absorption peaks at wave numbers 2915 and 2838 of all three polymers correspond to the presence of methylenes ($–CH_2$). When all these peaks seen in the spectra of all three polymers and described here are evaluated together, it is seen that both the MAS copolymer and its ester derivatives have been successfully synthesized.

When Table 1 is examined, it is seen that the MAS copolymer and its ester derivatives exhibit the same solubility behavior in some solvents. By replacing an anhydride group with propyl and butyl ester groups, the number of side groups in the main chain has increased. Increasing the number of side groups causes ester derivatives to interact with solvent molecules. In this way, it is possible to explain that the ester derivatives of the polymer follow the same solubility pattern and dissolve easily.

As can be seen in Table 1, the ester numbers of both derivatives are close to each other. Ester numbers are highly dependent on the reaction conditions in which esterification occurs, and especially on the solvent [33]. Since the esterification reactions took place under the same conditions, and there was not much difference in carbon number between the primary alcohols used, there was not much difference in the ester numbers of the derivatives.

The stress-strain curves of the polymers were recorded to determine the thermo-mechanical properties of all three polymers. The Young's modulus (E), a measure of elasticity for three polymers, was calculated from the slope of the linear portions of the stress-strain curves seen in Figure 4. When the E values calculated from the stress-strain curves and given in Table 2 are compared, it is understood that the ester derivatives of the MAS copolymer have lower E values and therefore are more elastic than the original polymer.

Stress-strain curves of MAS copolymer and ester derivatives were also obtained with a dynamic measurement by increasing the temperature. Using these data, the stress-temperature curves of the polymers were drawn and shown in Figure 5. The linear thermal expansion coefficient (CLTE), a parameter commonly used to compare the thermo-mechanical properties of polymers, is found from the linear parts of the curves in Figure

5 and given in Table 2. Thermal expansion generally increases with decreasing bond energy, which also has an effect on the glass transition or melting point of a material so, materials with lower thermal transition temperatures are more likely to have a higher coefficient of linear thermal expansion (CLTE) [34]. This situation, which is seen in the CLTEs of polymers, is also seen at the glass transition temperatures (Tg) seen in Table 2. The Tg temperatures of the ester derivatives with higher CLTE were found to be lower than the MAS copolymer.

Chain mobility affects the Tg temperature. Polar side groups reduce chain mobility and increase Tg. Crowded side groups also reduce free volume, reducing chain mobility and causing high glass transition temperatures [4]. In Figure 6, the average temperature value at which the sudden decrease in the T-logE curves is detected is the Tg value. Although this method is an indirect method, it can be used to determine glass transition temperatures [5]. When the Tg values of MAS and ester derivatives given in Table 2 are compared, it is seen that the Tg value decreases as the linear side group gets larger (butMAS). It can be said that the butyl group, which is a longer side branch, increased the free volume of the main chain and increased the chain mobility, thus causing a lower Tg value.

In the final analysis, the two linear primary alcohols added to the MAS copolymer increased the free volume of the main chain, resulting in a softer, lower glass transition temperature and more expandable of the modified derivatives. With this study, it has been shown that the physical and thermal properties of a polymer can be changed with different alcohols grafted to the main chain.

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