Avrupa Bilim ve Teknoloji Dergisi
Özel Sayı 34, S. 95-99, Mart 2022

Araştırma Makalesi

www.ejosat.com ISSN:2148-2683

European Journal of Science and Technology
Special Issue 34, pp. 95-99, March 2022

Research Article

Investigation of Thermophysical Properties of Polyester Composites Produced with Synthesized MSG and Nano-Alumina

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(2nd International Conference on Applied Engineering and Natural Sciences ICAENS 2022, March 10-13, 2022)

(**DOI:** 10.31590/ejosat.1072831)

ATIF/REFERENCE: Şahal, H. & Aydoğmuş, E. (2022). Investigation of Thermophysical Properties of Polyester Composites Produced with Synthesized MSG and Nano-Alumina. *European Journal of Science and Technology*, (34), 95-99.

Abstract

In this study, synthesis of a new compound, 4-[(E)-(5-Bromo-2-hydroxy-3-methoxybenzylidene) amino]-N carbamimidoylbenzenesulfonamide (MSG) has been carried out. The structures of MSG are characterized using spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR), and proton nuclear magnetic resonance spectroscopy (NMR). In experimental studies, synthesized MSG has been reinforced with 1 wt.% and 2 wt.% unsaturated polyesters. Besides, 1 wt.% and 2 wt.% alumina nanoparticles, 1.5 wt.% methyl ethyl ketone peroxide (MEKP), and 0.5 wt.% cobalt octoate (Co Oc) were used to produce polyester composites. Although alumina nanoparticles increased the density of the produced polyester composite, MSG supplementation decreased it. While nano-alumina raised Shore D hardness of the polyester composite, synthesized MSG went down it. Both nano-alumina and MSG reinforcement have been increased the porosity in the surface morphology of the polyester composite. Also, nano-alumina reinforcement raised the activation energy of the polyester composite and MSG decreased it. In other words, since the alumina filler raises the activation energy, the thermal stability of the polyester composite has gone up.

Keywords: Alumina, Synthesis, MSG, Polyester composite, Characterization.

Sentezlenmiş MSG ve Nano-Alümina ile Üretilen Polyester Kompozitlerin Termofiziksel Özelliklerinin İncelenmesi

Öz

Bu çalışmada yeni bir bileşik olan 4-[(E)-(5-Bromo-2-hidroksi-3-metoksibenziliden)amino]-N karbamimidoilbenzensülfonamid (MSG) sentezi gerçekleştirilmiştir. MSG'nin yapıları, Fourier transform kızılötesi spektroskopisi (FTIR) ve proton nükleer manyetik rezonans spektroskopisi (NMR) gibi yöntemler kullanılarak karakterize edilmiştir. Deneysel çalışmalarda, sentezlenen MSG, ağırlıkça % 1 ve % 2 doymamış polyesterlerle takviye edilmiştir. Ayrıca, polyester kompozitleri üretmek için ağırlıkça % 1 ve % 2 alümina nanopartiküller, ağırlıkça % 1.5 metil etil keton peroksit (MEKP) ve ağırlıkça % 0.5 kobalt oktoat (Co Oc) kullanılmıştır. Alümina nanoparçacıkları üretilen polyester kompozitin yoğunluğunu arttırmasına rağmen, MSG takviyesi bunu azaltmıştır. Nano-alümina, polyester kompozitin Shore D sertliğini yükseltirken, sentezlenen MSG onu düşürmüştür. Hem nano-alümina hem de MSG takviyesi, polyester kompozitin yüzey morfolojisindeki gözenekliliği arttırmıştır. Ayrıca nano-alümina takviyesi, polyester kompozitin aktivasyon enerjisini yükseltmiş ve MSG ise bunu azaltmıştır. Diğer bir deyişle, alumina takviyesi aktivasyon enerjisini yükselttiği için polyester kompozitin termal kararlılığı da yükselmiştir.

Anahtar Kelimeler: Alümina, Sentez, MSG, Polyester kompozit, Karakterizasyon.

1. Introduction

Since Schiff bases were discovered by Hugo Schiff in 1864, many specific properties have been discovered in studies of this class of compounds. For this reason, this group of compounds is used in optics, sensors, catalysis, biomedicine, composites, etc. areas that have been extensively studied. It has been reported that some Schiff bases with relatively stable structures can improve the thermal degradation of materials by forming ablative surfaces [1-3]. Meanwhile, polyimines/Schiff-base-based polymers with a system of conjugated –C=N– bonds exhibit valuable properties mainly associated with the presence of conjugated backbone and imine sites [4,5].

Composite materials can be produced by using organic and inorganic fillers in a pure polymer. In the study conducted in the literature, some thermal and mechanical properties have been investigated by adding a filler (borax) to the polyester composite. Borax reinforcement raised the thermal conductivity and elastic modulus of the polyester composite. Shore D hardness and limit oxygen value of the obtained composite also tend to increase compared to pure polyester. Besides, it has been determined that the porosity in the surface morphology increased as the percentage of the filler in the mixture raised [12].

In another article, both a waste polymer (polyethylene terephthalate) and synthesized modified palm oil have been reinforced to the polyester composite. As the waste PET ratio in polyester increased, the density, elastic modulus, and activation energy of the composite increased. Also, as the amount of waste PET raised, both the thermal conductivity coefficient and Shore D hardness of the polyester composite increased [11].

In another study in the literature, the thermal decomposition behavior of aerosil (SiO_2) reinforced polyester composite has been investigated. Nanoparticle (aerosil) reinforcement increased the activation energy of the composite, that is, its thermal stability. Moreover, when the aerosil ratio in the polyester composite went up, the thermal conductivity coefficient went down [13].

In another research, some nanoparticles (fumed silica, silicon carbide, graphene) have been reinforced to unsaturated polyester. Although graphene and silicon carbide supplementation increased the thermal conductivity of the polyester composite, fumed silica reinforcement decreased it. Fumed silica and silicon carbide have been raised Shore D hardness of the polyester composite. Also, fumed silica reinforcement decreased the density of the composite, the other nanoparticles raised it. Moreover, when the thermal stability of the polyester composites is listed from the largest to the smallest, it has been determined that they are fumed silica, graphene, silicon carbide, and pure polyester [14].

In this study, polyester composite materials have been obtained with newly synthesized MSG and nano-alumina reinforcement. The effect of alumina reinforcement with synthesized Schiff base (MSG) on some thermophysical properties of polyester composite has been evaluated. Some physical and chemical properties of the obtained polyester composite have been compared.

2. Material and Method

Unsaturated polyester (UP), methyl ethyl ketone peroxide (MEKP), and cobalt octoate (Co Oc) used in experimental studies have been supplied from Turkuaz Polyester. Alumina (Al_2O_3: 99.9 % purity) nanoparticle (<50 nm) has been also purchased from the Nanography Company. Also, other chemical components required for MSG synthesis have been obtained from Merck.

FTIR spectra have been carried out by a Shımadzu QATR-S (IR Spirit S1102SC) in the range of 4000–600 cm^{-1}. ^{1}H (400 MHz) NMR spectra were obtained in DMSO-d6 solutions by Bruker DRX-400 high-performance digital FT-NMR spectrometer.

The experimental work plan for polyester composite production is given in Table 1. First of all, after unsaturated polyester (UP) and fillers are homogenized, MEKP and Co Oc catalysts are added to the mixture. The mixture is poured into standard molds after mixing at 1000 rpm for 120 seconds. It has waited for 24 hours for the curing of the obtained polyester composites and then the necessary tests are carried out.

Table 1. Experimental working plan

Experiment No	UP (wt.%)	MSG (wt.%)	Alumina (wt.%)	MEKP (wt.%)	Co Oc (wt.%)
1	98	-	-	1.5	0.5
2	97	1	-	1.5	0.5
3	96	2	-	1.5	0.5
4	97	-	1	1.5	0.5
5	96	-	2	1.5	0.5
6	96	1	1	1.5	0.5

In Figure 1, polyester composite production and application method are expressed.

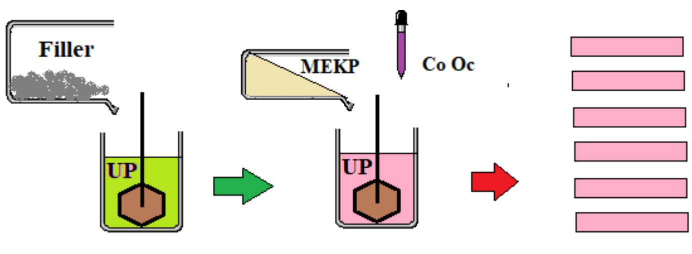

Figure 1. Polyester composite production scheme

2.1 Synthesis MSG

To a solution of 0.855 g (0.004 mol) of sulfaguanidine dissolved in 50 mL of absolute ethyl alcohol, 0.924 g (0.004 mol) of 5-Bromo-3-methoxy salicylaldehyde dissolved in 10 mL of pure ethyl alcohol was added dropwise and dispersed in the sound bath under room conditions for 10 minutes. This reaction mixture has interacted at 130 °C for 12 hours using the hydrothermal technique. The sediments were filtered, washed with cold ethyl alcohol, and dried at room temperature. Then got the product $C_{15}H_{15}BrN_4O_4S$: M=427.27). Yield 1.54 g (90 %). IR (KBr), υmax/cm−1: 3435(O—H), 3330, 3301, 3230, 3145, 1617 (C=N), 1543, 1476 (C—O), 1401(—SO2 str), 1382, 1348, 1277, 1136, 1093, 974, 913, 861, 822, 781, 658, 634, 583, 541; 1H NMR(DMSO-d6), δ: 12.77(s, 1H, O—H), 8.95(s, 1H, CH=N), 7.83—7.30(m, 6H, Ar—H), 6.75—6.54(m, 4H, —NH, —NH2), 3.39 (s, 3H, -OCH3).

In Figure 2, the chemical reaction mechanism of synthesized MSG is shown.

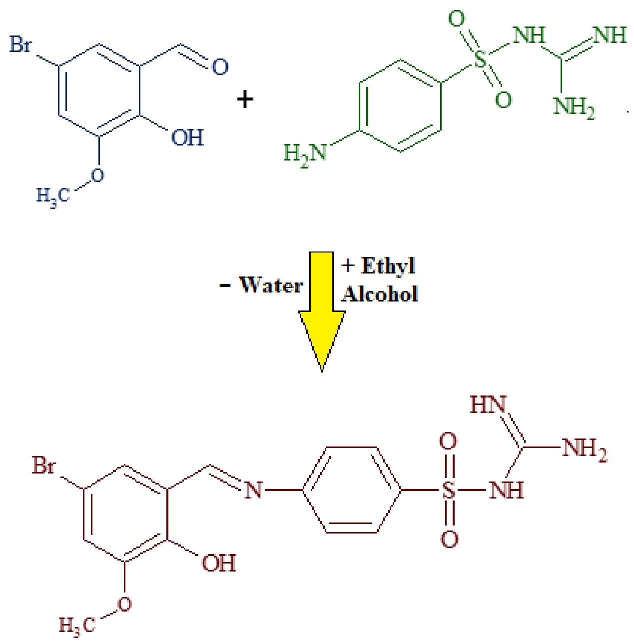

Figure 2. Chemical synthesis mechanism of MSG

3. Results and Discussion

3.1 Synthesis and characterization of MSG

In this study, a novel Schiff base derivative was synthesized by the reaction of equimolar amounts of sulfaguanidine with 5-Bromo-3-methoxy salicylaldehyde in absolute ethyl alcohol, then purified and isolated. The structures of the compounds were elucidated by general spectroscopic methods and elemental analysis, and the findings supported each proposed structure. The characteristic IR peaks of compounds are the peaks of C=N, C-O, O-H, S=O, and (C=N) Ar stretching vibrations. Others are C=C and C=O stretch vibration peaks, aliphatic C-H and N-H, and aromatic C-H stretch vibration peaks. When the IR spectrum of the compound (MSA) is examined, the OH stretching vibration of the phenolic –OH group is wide around 3435 cm^{-1}, while the C=N stretching vibration of the azomethine group is seen sharply at 1617 cm^{-1}. These bands support the completion of the formation reaction of (MSG) compound. These values agree with those found for similar compounds [6-8]. The most useful infrared spectral bands of the compound are listed in the experimental section.

^{1}H NMR spectra of the compound MSG were recorded in DMSO-d6 at room temperature. It belongs to a singlet -OH proton of one proton observed in the range of 12.77 ppm in the ^{1}H-NMR spectrum of compound MSG. In addition, the peak observed as a singlet at a proton intensity in the range of 8.95 ppm also belongs to the azomethine proton in the structure. Besides, the chemical shift observed in the spectrum in the range of 7.49 ppm belongs to the (-NH) proton(s) attached to the $–SO_2$ group in the structure (Figure 3). The most useful ^{1}H-NMR spectrum bands of the compounds are listed in the experimental section. The observed peaks are in agreement with the structure and literature [9,10].

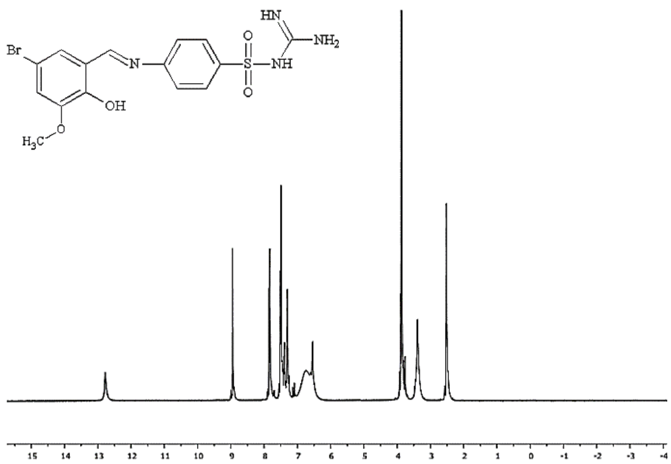

Figure 3. ^{1}H NMR spectrum of MSG

The variation of densities of polyester composites obtained with alumina reinforcement in Figure 4 and MSG reinforcement in Figure 5 are expressed.

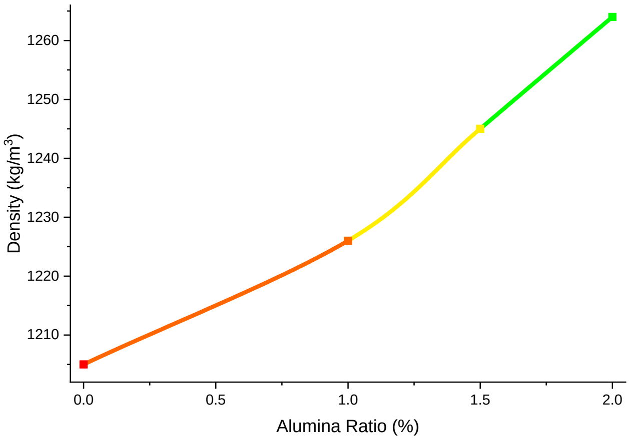

Figure 4. The effect of alumina ratio on the density of the composite

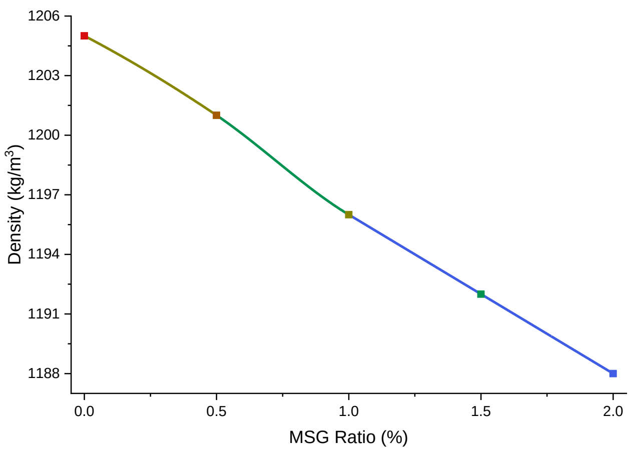

Figure 5. The effect of MSG ratio on the density of the composite

The effect of alumina and MSG ratios on Shore D hardness of polyester composite is shown in Figure 6 and Figure 7.

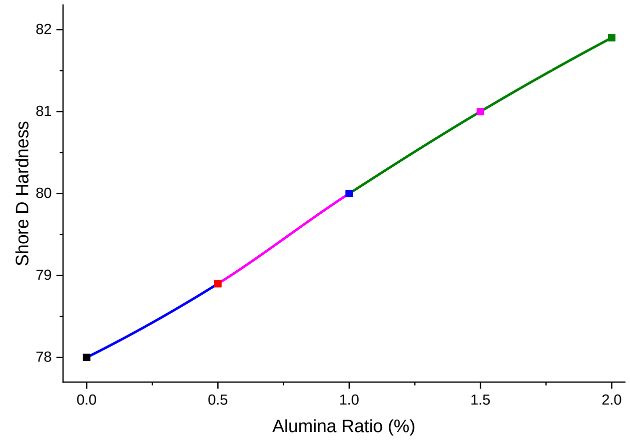

Figure 6. The effect of alumina ratio on the hardness of the composite

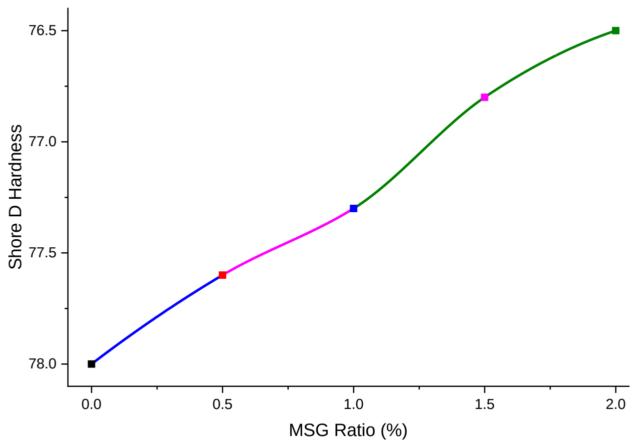

Figure 7. The effect of MSG ratio on the hardness of the composite

In Figure 8, the variation of the thermal conductivity coefficients of the synthesized polyester composite is seen. Alumina reinforcement has been increased the thermal conductivity of the composite more than MSG.

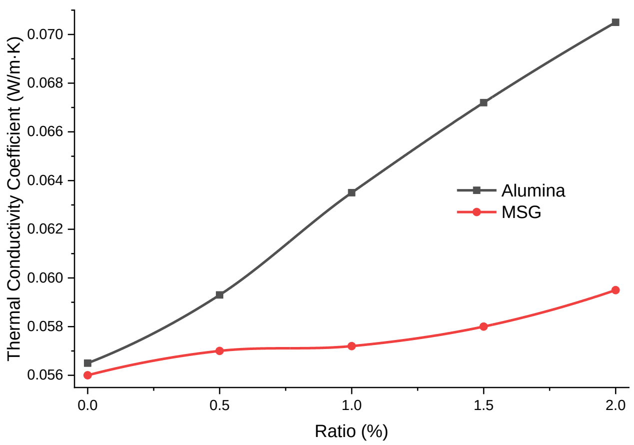

Figure 8. The effect of alumina and MSG ratios on the thermal conductivity of the composite

4. Conclusions and Recommendations

In this study, the effect of newly synthesized MSG and alumina reinforcement on the thermophysical properties of unsaturated polyester has been evaluated. Nano-alumina filler increased the density, thermal conductivity coefficient, Shore D hardness, and thermal stability of the polyester composite more than MSG. Also, alumina reinforcement has been raised the activation energy of the polyester composite more than MSG.

In this research, it has been seen that polyester composite can be obtained for the desired purpose by using organic and inorganic additives or fillers. It has been understood that organic and inorganic fillers could be used together, especially in the composite obtained in the 6th experiment.

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