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SYNTHESIS OF FUMARONITRILE-CONTAINING QUATERPOLYMER DETERMINATION OF STRUCTURAL AND THERMOMECHANICAL PROPERTIES

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Abstract

In this study, an electron-acceptor monomer Fumaronitrile (FN), and 3 electron-donor monomers; Trans-Anethole (ANE), Vinyl-iso-butylether (VIBE) and Trans-Stilbene (Stb) were polymerized by free radical polymerization and charge transfer complex (CTC) mechanism. Fumaronitrile content ratio, FT-IR, H-NMR, average molar weight, thermal and mechanical analyzes of the obtained FN-ANE-VIBE-Stb quaterpolymer were performed. The synthesized quaterpolymer was obtained in resin form. The rate of fumaronitrile in the chain was determined as approximately 50%. The thermal and mechanical properties of the obtained quaterpolymer were better than some common polymers.

Keywords: Charge transfer complex, Electron donor-acceptor monomers, Fumaronitrile, Quaterpolymer.

Özet

Bu çalışmada, elektron alıcı bir monomer olan Fumaronitril (FN) ile elektron verici 3 monomer; Trans-Anethol (ANE), Vinil-izo-bütileter (VIBE) ve Trans-Stilben (Stb), serbest radikal polimerleşmesi ve yük transfer kompleksi (CTC) mekanizması üzerinden polimerleştirilmiştir. Elde edilen FN-ANE-VIBE-Stb kuaterpolimerinin, monomer içerik oranı, FT-IR, H-NMR, ortalama mol kütlesi, ısısal ve mekanik analizleri yapılmıştır. Sentezlenen kuaterpolimer reçine şeklinde elde edilebilmiştir. Zincirde bulunan fumaronitril oranı yaklaşık %50 olarak belirlenmiştir. Elde edilen kuaterpolimerin ısısal ve mekanik özelliklerinin diğer bazı yaygın polimerlere göre daha iyi olduğu görüldü.

Anahtar Kelimeler: Elektron alıcı-verici monomerler. Fumaronitril, Kuaterpolimer, Yük transfer kompleksi.

1. Introduction

Fumaronitrile is a compound with many applications, especially in organic chemistry. (Kalka et al. 2022) Free radical co-polymerization of electron donor-acceptor monomers has attracted increasing attention in recent years. (Imren, 2010; Imren et al., 2008)

While these electron acceptor monomers do not form homopolymers on their own, they easily form co-polymers when combined. (Kismet , 2017; Kismet and Wagner, 2018; Kismet and Wagner 2019) Fumaronitrile, which is an electron acceptor monomer, does not homopolymerize alone, but can easily form co-polymers with electron donor monomors under free radical conditions by the charge transfer complex (CTC) mechanism. (Shirota et al., 1974; Price and Gilbert, 1975; Schuler and Heusinger, 1975; Braun and Hu, 2002; Xie et al., 2017). There are studies synthesizing the co-polymers of fumaronitrile for solar cell cells (Wan et al., 2013) and lithium-metal batteries (Sun et al., 2022) and terpolymers for carbon fiber precursor materials (Jamil et al., 2014). In this study by Jamil et al., when Fumaronitrile is added as a third co-monomer to Acrylonitrile-butyl acrylate (AN/BA) and Acrylonitrile-Ethyl hexyl acrylate (AN/EHA) monomer pairs, the synthesized terpolymers have higher carbonization efficiency (char yield) than co-polymers, and therefore has been shown to have higher stability in thermal applications.

In this study, Fumaronitrile-trans Anethol-Vinilizobutylether-trans Stilbene (FN-ANE-VIBE-Stb) quaterpolymer was synthesized.. Structural, thermal and mechanical analyzes were made and compared with some common vinylic polymers.

2. Material and Methods

2.1 *Chemicals*

Azo-bis-isobutyronitrile (AIBN)is a Sigma product, Fumaronitrile, trans-Anethol, trans-Stilbene, Tetrahydrofuran (THF) and Dimethyl formamide, diethyl ether are Merck product, Vinyl iso-butylether is a Aldrich product, all of analytical grade. Ethyl alcohol is a product of Isolab.

2.2 *Quaterpolymer Synthesis*

For synthesis, 50 mL THF, 7.09 g (0.09 mol) fumaronitrile, 4.45 g (0.03 mol) trans-anethole, 5.40 g (0.03 mol) trans- stilbene, 3.90 mL (0.03 mol)) vinyl isobutyl ether, 3.05 mL and 8.2 milligrams ($1x10^{-3}$ $mol.L^{-1}$) of AIBN were added. All chemicals in the tube were mixed homogeneously. After the air was removed from the tube by vacuum, the tubes were immersed in a water bath at 70 ^{0}C. It was reacted for 10 hours under a nitrogen atmosphere. The tube was removed from the water bath and allowed to cool at room temperature. The cooled mixture was poured into beakers containing 500 mL of anhydrous diethyl ether and the polymer precipitated. The mixture in the beaker was separated from diethyl ether by passing through ordinary filter paper and left to dry. Weighed to calculate conversion rates. The dried polymer was dissolved in THF again and precipitated with diethyl ether. Polymers separated from diethyl ether by filtration were left to dry in an oven at 40 ^{0}C.

2.3 *Structural Analyzes*

Mattson 1000 FT-IR (UK) spectrophotometer was used for the FT-IR spectrum of the quaterpolymer. For this purpose, the polymer was first ground and powdered and pellets were prepared using KBr. Measurements were made with the spectrophotometer set to 4 cm-1 resolution, 16 scans.

UV/Vis spectra of the polymer were made with a Shimadzu UV-1601 (Japan) dual beam spectrophotometer. For analysis, 5 mg of sample was dissolved in 25 mL of dichloroethane ($C_2H_4Cl_2$) and measurements were taken at desired wavelengths between 200-320 nm.

Solubility of the obtained polymer in common solvents; THF was analyzed using dimethyl formamide (DMF), Benzene, Toluene, Acetone and water.

In order to make H-NMR analyzes of the quaterpolymer, 50 mg samples taken from the polymer sample were taken into NMR tubes containing deuterated dimethylsulfoxide (DMSO-d6) solution. In order to adjust the optimum concentrations of the prepared samples, solutions were prepared at a concentration of 10-20 mg/mL. Bruker Avance DPX-300 (USA) device was used.

For gel permeation chromatography (GPC), 0.1g/dL polymer solutions were prepared using THF. Prepared samples were injected into the Device (Waters HPGPC, with differential refractometer and UV detector, USA) at a flow rate of 0.5 mL/min.

2.4 *Thermal Analyzes*

Film samples were used in the thermal analysis of the obtained quaterpolymer. To obtain film samples, 0.5 grams of quaterpolymer sample was dissolved in 25 mL of THF. This solution was poured into petri dishes of the same size to obtain films of approximately the same thickness, and the solvent was expected to evaporate. Once the solvent was completely removed, the quaterpolymer films were allowed to dry further to allow the separation of the petri dishes. After drying, the films spontaneously separated from the containers.

Thermomechanical analyzes of the quaterpolymer in film form were performed on a Shimadzu brand TMA-50 (Japan) model TMA device. The stress-strain curves of the polymer sample were recorded under nitrogen atmosphere flowing at 25 mL/min.

In recording the stress-strain curves, the film sample was cut in (5x10) mm dimensions. Stress-strain curves were recorded at a loading rate of 5 g/min and a heating rate of 10 ^{0}C/min, applied on the film, in a nitrogen atmosphere. In addition, stress-strain curves were obtained at constant temperatures of 20, 40, 60 and 80 ^{0}C at constant temperatures of 20, 40, 60 and 80 ^{0}C at an increasing loading of 25 g/min and at a decreasing loading rate at the same rate in order to examine the effect of temperature on the stress-strain curves and to determine the amount of permanent yield.

2.5 *Nitrogen Micro-analysis*

Nitrogen microanalysis was performed using the Perkin-Elmer-2400 (USA) analyzer. For this, 100 mg of sample was burned at a temperature of 950-1000 ^{0}C, the gases formed were separated in the gas chromatography columns of the device. The fumaronitrile ratio in the sample was calculated with the method based on measuring the thermal conductivity of the gases formed.

2.6 Scanning Electron Microscopy (SEM) Analysis

SEM analysis of the obtained polymer was carried out with a Philips XL-30 (Netherlands) electron microscope. For this, the samples were washed several times with acetone and dried in an oven at 40 0C. A few mg sample was taken and placed on an aluminum plate, and then it was covered with a gold layer by spraying method. Images of the samples were obtained under varying electron intensity.

3. Results and/or Discussion

Table 1. Dissolution in different solvents

Polymer	THF	DMF	Benzene	Toluene	Acetone	Water
1-FN/ANE/VIBE/Stb	+	+	-	-	-	-

(+) soluble (-) nonsoluble

Table 2. Determined percentage of Fumaronitrile by mass and mole

Polymer	% FN (w/w)	% FN (mol)
FN/ANE/VIBE/Stb	34,0	49,8

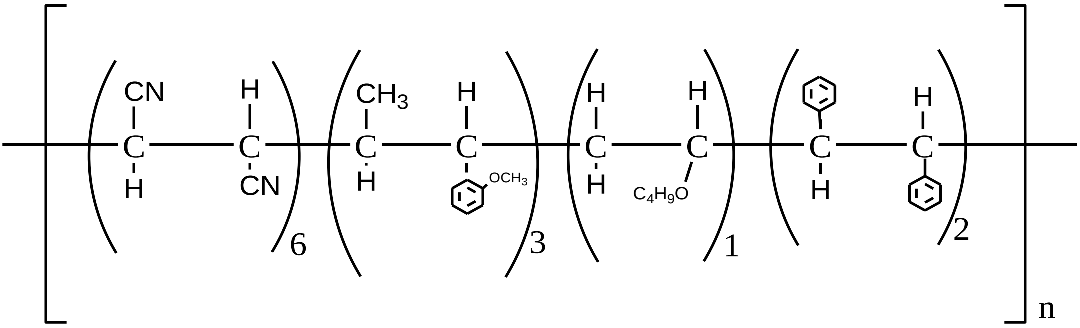

Figure 1. Calculated repeating unit of quaterpolymer

In order to examine the solubility of the synthesized polymer in common solvents, the solubility of tetrahydrofuran (THF), dimethyl formamide (DMF), benzene, toluene, acetone and water were examined and the results are given in Table 1. As can be seen in the table, the synthesized quaterpolymer dissolves in THF and DMF and is resistant to aromatic hydrocarbons such as benzene and toluene. This situation can be understood from the structural formula of the polymer, which was created in the light of the data obtained from Table 2 and given in Figure 1. The main chain has a vinylic structure and the number of fumaronitrile (FN) that does not contain aromatic structures is high.

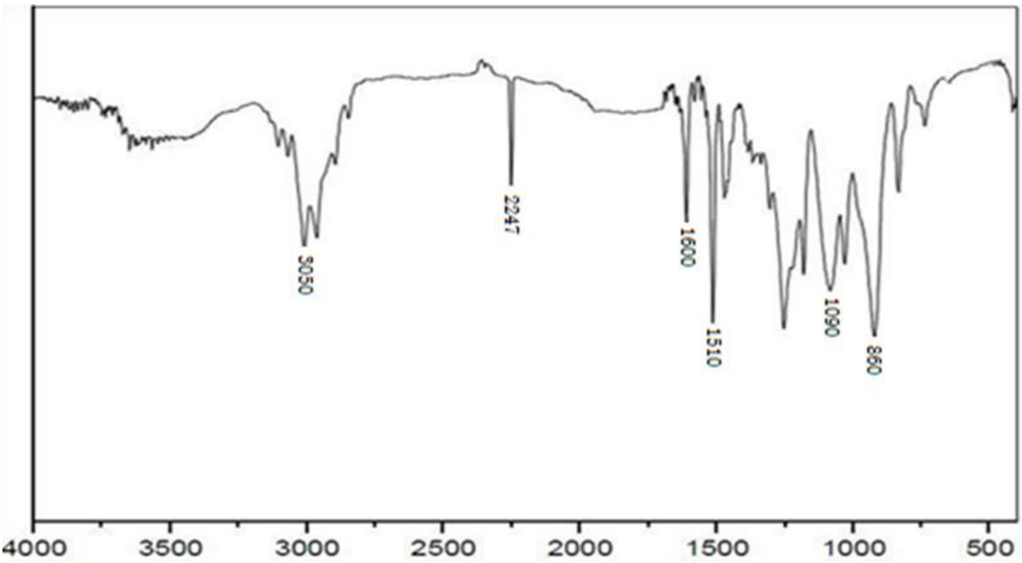

Figure 2. FT-IR spectrum of FN/ANE/VIBE/Stb (KBr Pellet)

When the IR spectrum in Figure 2 is read;

Multiple peaks at 2850 - 2950 cm^{-1} correspond to CH and CH_2 vibrations in the main chain and Stb monomer. Peaks at 2950-3100 cm-^{1} belong to aromatic CH stretches. The peak at 2245 cm^{-1} belong to CN stretching vibrations in FN. The multiple peaks at 1508-1607 cm^{-1} are the peaks of the aromatic C=C absorption of Stb, and the double peaks at 1031-1092 cm-1 are the stretching vibrations of the C-O bond of VIBE. (Boztug, 2004; Boztug and Basan, 2007; Boztug and Yilmaz, 2007; Kısmet and Wagner, 2012; Kısmet and Wagner, 2017; Yilmaz, 2022)

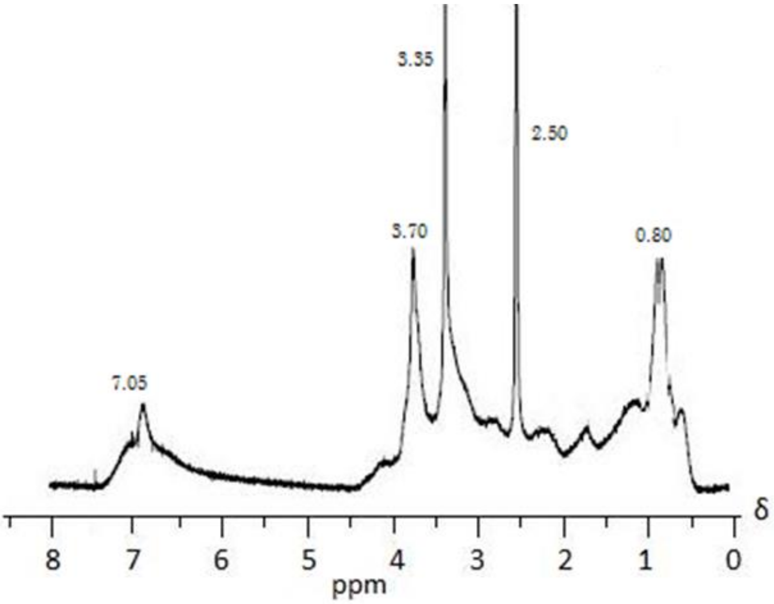

Figure 3. H-NMR spectrum of FN/ANE/VIBE/Stb (DMSO-d6)

When the H-NMR peaks in Figure 3 are read;

Chemical shift of non-deuterated methyl protons of DMSO at 2.50 ppm. Chemical shift of protons of fumaronitrile at 3.35 ppm. Chemical shift of methoxy protons of ANE at 3.7 ppm. Aromatic protons of ANE and Stb between 7-8 ppm. Chemical shift peaks belonging to ($-CH_3$) protons of VIBE were observed at 0.8 ppm. According to the results of both (IR and H-NMR) analysis, it is possible to say that the FN/ANE/VIBE/Stb quaterpolymer was successfully synthesized.

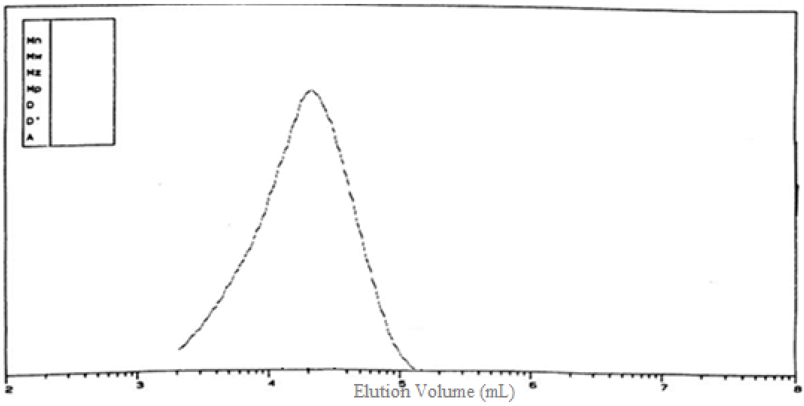

Figure 4. Gel permeation chromatogram (GPC) of FN/ANE/VIBE/Stb polymer

The data obtained from the GPC graph in Figure 3 is summarized in Table 3. It is understood that the molar mass of the FN/ANE/VIBE/Stb polymer is moderate and its dispersity index is relatively high. The formation of chains of different sizes during the chain growth stage is the factor causes this situation.

Table 3. Findings from GPC chromatogram

Polymer	Mn (g/mol)	MW (g/mol)	Dispersity Index
FN/ANE/VİBE/Stb	12.500	31.600	2,53

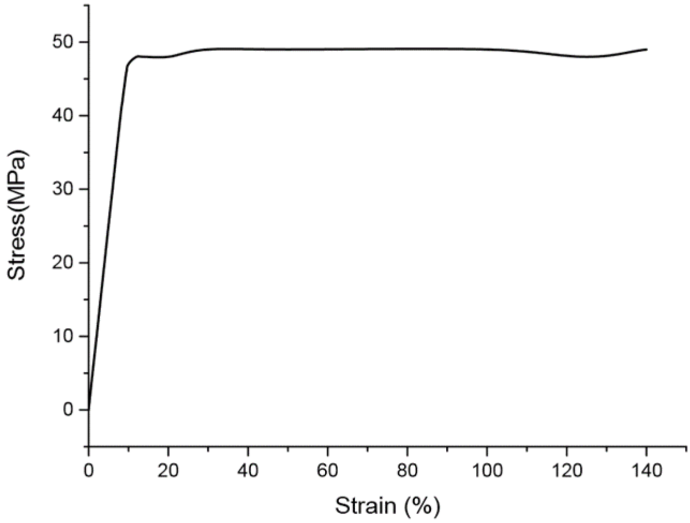

Figure 5. Stress-strain curve of FN/ANE/VIBE/Stb

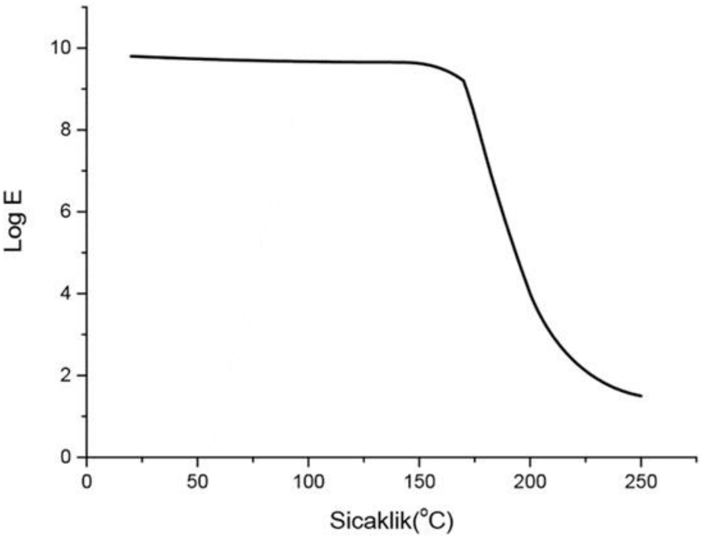

Figure 6. Temperature-LogE curve of FN/ANE/VIBE/Stb

With the curve given in Figure 5, the elastic modulus (E), thermal elongation coefficient (α) and the amount of stress and elongation at yield were determined. The elastic modulus (E) value, which is a measure of the stiffness from the slope of the linear part of the curve, is given in Table 4 below by finding the stress values that it can carry without permanent deformation and the elongation without permanent deformation from the starting points of the curve where the linear part ends and there are very large elongations at very small stresses. In addition, in order to find the Tg value of the quaterpolymer by elastic modulus method, elastic modulus values at certain temperatures were read from the device and a temperature-elastic modulus curve was drawn. This curve is given in Figure 6. In this curve, the mean of the temperature at which the elastic modulus decreases suddenly gives the Tg value. (Tucker et al., 1988). The Tg value calculated by this method is also given below in Table 5.

Table 4. Elastic modulus, Yield strength and Elongation at yield of FN/ANE/VIBE/Stb

Polymer	E (MPa)	Yield (MPa)	Elongation at yield %
1-FN/ANE/VIBE/Stb	4800	470	12

Table 5. Tg value of the quaterpolymer determined by the Elastic modulus method

Polymer	Tg / ^{0}C
FN/ANE/VIBE/Stb	208

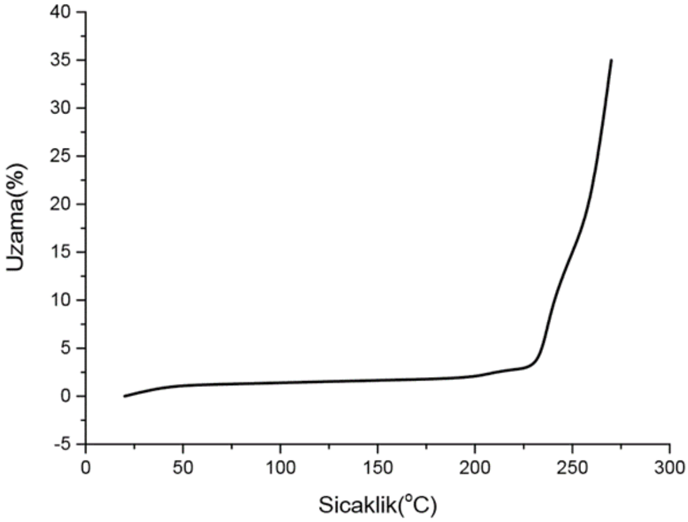

Figure 7. Elongation-temperature curve of FN/ANE/VIBE/Stb polymer

Table 6. Coefficient of Linear Thermal Expansion

Polymer	CTE (α) / elongation.^{0}C^{-1}
1-FN/ANE/VIBE/Stb	10,0x10^{-5}

The stress-strain curve of the quaterpolymer was recorded under increasing load and temperature conditions. By reading the elongation values against certain temperatures from this curve, the temperature-elongation curve of the polymer was formed and given in Figure 7. With the help of this curve, the thermal expansion coefficient which is often used to compare the thermal strength of the polymer can be obtained. The thermal elongation coefficient obtained from the slope of the linear parts of this curve is given in Table 6.

Table 7. Softening and glass transition temperatures of FN/ANE/VIBE/Stb by penetration method

Polymer	Softening point/^{0}C	Tg/^{0}C
1-FN/ANE/VIBE/Stb	173	210

The softening and glass transition temperature (Tg) of the polymer obtained by operating the thermomechanical analyzer in the entering mode are read as 173 ^{o}C and 210 ^{o}C, respectively in Table 7.

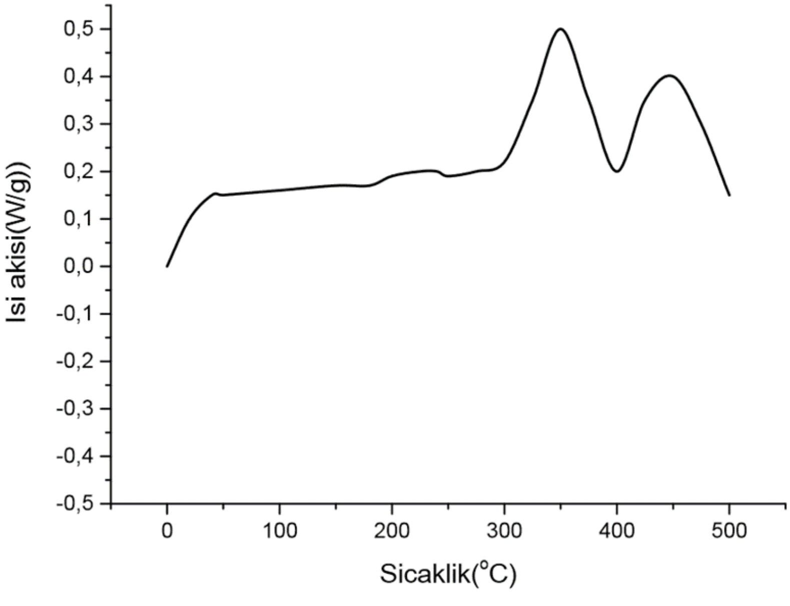

Figure 8. DSC thermogram of FN/ANE/VIBE/Stb polymer

Table 8. Thermal values obtained from the DSC curve and the energy values and peak temperatures obtained from the peak areas

Polimer	Tg	Tc	ΔH_c	Tm_1	ΔH_1	Tm_2	ΔH_2

	^{0}C	^{0}C	J/g	^{0}C	J/g	^{0}C	J/g
1-FN/ANE/VIBE/Stb	214	255	19,5	318	198	445	170

The Tg value given in Table 8, obtained from the DSC curve in Figure 8, is also seen as 214 °C. The glass transition temperatures obtained by these two methods seem to be quite close to the 208 °C temperature value obtained by the elastic modulus method given in Table 5. The crystallization temperature (Tc), melting temperature (Tm) and energy values of the quaterpolymer were determined from the DSC curve and given in Table 8.

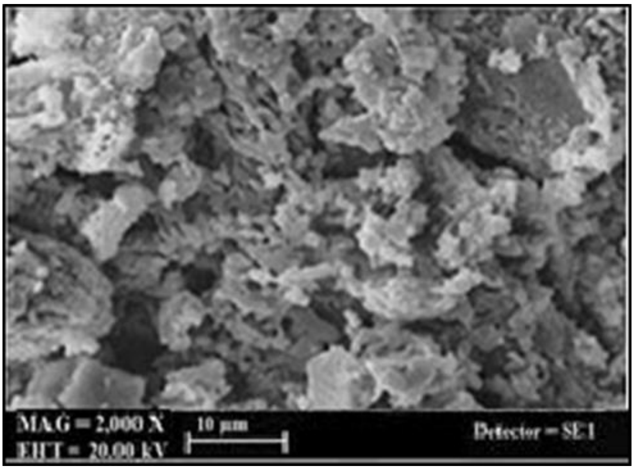

Figure 9. SEM image of FN/ANE/VIBE/Stb

When the SEM image of the quaterpolymer given in Figure 9 is examined, it is seen that it has a relatively rough surface. It is not possible to explain this situation with the chemical structure of the polymer. While the sample is being prepared for SEM analysis, it is inevitable that there will be breaks and cracks on the polymer surfaces during the grinding stage. Such surface deformations are more pronounced in hard polymers. The hardness of the quaterpolymer is thought to have caused this appearance.

Table 9. Tg, Tm, and Young's modulus of synthesized quaterpolymer and some vinylic polymers

Polymer	Tg (^{0}C)	Tm (^{0}C)	E (MPa)
FN/ANE/VIBE/Stb	**214**	**318**	**4800**
HDPE	-125	130	800
PP	-8	176	1500
PVC	81	227	2500
PS	100	240	3000
PAN	96	317	2500
PMMA	105	200	3100
PVA	85	220	2550
PET	72	265	2500
SBR Rubber	-50	-	2,5

4. Conclusion

FN/ANE/VIBE/Stb quaterpolymer containing fumaronitrile was obtained as a white resin.

The insolubility of the quaterpolymer in solvents that can dissolve many polymers such as benzene, toluene and acetone can be interpreted as a relatively good physical property. As a result of nitrogen microanalysis of the obtained quaterpolymer, the moles of polymer; It was found that it contains 50% Fumaronitrile and 50% other electron donor 3 monomers. This indicates that polymerization occurs following the mechanism predicted in the charge-transfer model. The peaks obtained in the H-NMR spectra were sharp, since the average molar mass of the polymer was not very high.

The glass transition temperatures (Tg), melting temperatures (Tm) and elastic modulus of the quaterpolymer and some vinylic polymers synthesized in Table 9 are given above.

As a result, considering both the above table and previous mechanical results, it can be said that the obtained polymer has superior thermal and mechanical properties compared to most common commercial polymers.

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Conflicts of interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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