

Synthesis of Thermos responsive Polymeric Hydrogels

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Abstract—Polysulfone (PSU) is a specialty engineering polymer having various industrial applications. PSU is especially used in wastewater treatment membranes due to its good mechanical properties, structural and chemical stability. But it is a hydrophobic material and therefore its surface aim to pollute easily. In order to resolve this problem and extend the properties of membrane, PSU surface is rendered hydrophilic by addition of the sepiolite nanofibers. Sepiolite is one of the natural clays, which is a hydrate magnesium silicate Fiber, also one of the well-known layered clays of the montmorillonites where has several unique channels and pores within. It has also moisture durability, strength and low price. Sepiolite channels give great capacity of absorption and good surface properties. In this study, nanocomposites of commercial PSU and Sepiolite were prepared by solvent mixing method. Different organic solvents and their mixtures were used. Rheological characteristics of PSU-Sepiolite solvent mixtures were analyzed, the solubility of nanocomposite content in those mixtures were studied.

Keywords—Nanocomposite, polysulfone, rheology, sepiolite, solution mixing.

I. INTRODUCTION

NANOCOMPOSITES are one of the recent research fields of nanotechnology and greatly adopted by polymer science and technology. Nanocomposites of polymers are prepared in order to enhance the abilities of polymer by bringing together with the specialties of nanoparticles [1]. Nanocomposites have various application fields in specialty engineering products of aerocrafts, automotive, packaging, medical, energy and separation industries, due to their superior properties [2]-[4]. Nanocomposites provide good structural properties like heat resistance, mechanical strength and impact resistance or to decrease other properties such as electrical conductivity or permeability for gases like oxygen or water vapor [5].

In a polymer nanocomposite polymer creates the molecular matrix and nanoparticles penetrate into this matrix. Nanoparticles have large surface area comparing with equal amount of same material's particles having larger diameter. Larger surface area/volume ratio is beneficial for better attraction with polymer and for better combination. Therefore use of nanoparticles results better improved material properties and brings new and unique abilities to the final

product [6]. And also, even small number of nanoparticles can make desirable changes for nanocomposite, as a result of surface area/volume ratio.

Nanoparticles can be generally divided in three groups according to their shapes; these are particle, fibrous and layered materials [7]. Clays and synthetic clays are the layered nanoparticles, used as nanofiller for polymer nanocomposite production. Especially montmorillonites are one of the most studied clays in polymer nanocomposite production [2].

Sepiolite is a montmorillonite, belongs to the phyllosilicate family [8]. It has hydrous magnesium silicate layered clays with $(\text{Si}_{12}\text{Mg}_8\text{O}_{30})(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$ theoretical unit cell formula. Moreover, it has excellent Fiber structure different than other montmorillonites of layered clays, which comes from its tetrahedral and octahedral oxide layers packaging [9]. This Fiber structure is consisting of various channels and tunnels that gives large surface are and porosity, resulting superior adsorption and surface features [10], [11]. Sepiolite has good mechanical qualities, resistance to humidity and low cost. Furthermore, sepiolite is also used for biomedical application since it is a natural and biodegradable product [11].

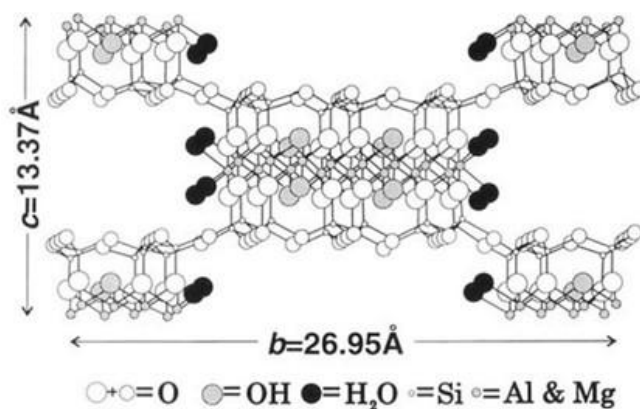


Fig. 1 Structure of sepiolite [10]

For composite matrixes metal or ceramic materials may also be used, but polymers are widely preferred, since not only they have a large range of usage area which still keeps growing; but also polymers have various mechanical and chemical properties. Thermoplastics, thermoplastic elastomers and thermosets are used in polymer nanocomposite production. Polysulfone (PSU) is one of the amorphous engineering thermoplastics that contain the sulfone groups (SO_2) in the main chain along with a variety of aromatic constituents like ether or iso-propylidene groups [12]. PSU is an excellent specialty engineering polymer since its great thermal stability, durability, high tensile strength, good chemical stability and pressure resistance [2], [13].

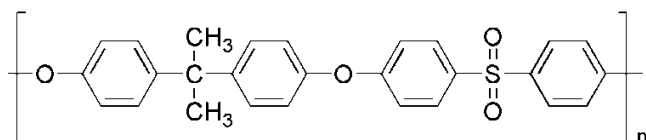


Fig. 2 Polysulfone

Basically there are three preparation methods for polymer/layered silicate nanocomposites. One of them is insitu method, where polymerization is carried on together with nanoparticles. Others are the physical methods: melt mixing and solution mixing [8]. Melt spinning process is the mixing polymer melt with nanoparticles via extrusion. Finally in solution mixing technique, solution of polymer or prepolymer and nanoparticles is prepared with proper solvent. This method can be employed for layered silicates. Intercalation of the polymer or pre-polymer is achieved through the solution. Hence solvent chose should be made as wherein the polymer or prepolymer is soluble and the silicate layers are swellable.

Afterwards solvent is removed and intercalated nanocomposite structure remains [1]. Also viscosity of the solution and other rheological parameters affect the intercalation and consequently nanocomposite structure [14][16]. Consequently understanding of the rheological properties of polymer-clay nanocomposites is crucial for obtaining improved material performance.

Within the scope of this paper we studied on the rheological properties of solution mixing method. The nanocomposite of PSU/Sepiolite is prepared by this method with the use different solvent mixtures. Their rheological features, solubility specialities and the effects of solvent chose were researched. For characterization infrared (IR) analyses were made.

II. EXPERIMENTAL

A. Materials

Sepiolite and PSU were commercially purchased. Sepiolite supplied by Tolsa Group from Turkey and polysulfone supplied from BASF. The solvents are dimethyl acetamide (Sigma-Aldrich, 99%), toluene (Alfa Aesar, 99.5%) and chloroform (Sigma-Aldrich, 99%).

For solution mixing, Heidolph magnetic stirrer (MR HeiStandart) was used.

Collection and evaluation of rheological data were accomplished by a rotational disc viscometer (Brookfield RVDV+II model with Brookfield Rheo-2000 V2.8 software Brookfield Engineering Co., US.).

Fourier transform infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer.

B. Preparation of PSU/Sepiolite Nanocomposite by Solution Mixing Method

First of all eight different solvent mixtures were prepared for solution mixing method. These solvent mixtures consist of dual combination of Dimethylacetamide (DMAC) with Chloroform and Toluene. Their volume fractions are represented in Tables I and II. For solvent phase of the method, 100ml of solvent combinations were prepared for each of ten mixtures.

TABLE I
VOLUME FRACTIONS OF DMAC-TOLUENE MIXTURES

Solutions	Dimethylacetamide	Toluene	Volume fractions of Toluene
A ^I			25%
B ^I			33.33%
C ^I			16.67%
D ^I			40%

TABLE II
VOLUME FRACTIONS OF DMAC-CHLOROFORM MIXTURES

Solutions	Dimethylacetamide	Chloroform	Volume fractions of Chloroform
A ^{II}	3	1	25%
B ^{II}	2	1	33.33%
C ^{II}	5	1	16.67%
D ^{II}	3	2	40%

In Tables I and II A, B, C, D referred as the volume fractions; I and II indexes show the dual solution type where solvent mixtures of DMAC and Toluene referred as I, solvent mixtures of DMAC and Chloroform referred as II.

For each 100ml solvent mixture 20g of composite phase was prepared. Composite phase contains PSU as the polymer matrix and sepiolite as the nanoparticles. During the preparation sepiolite is taken 1 wt.% of the polysulfone for all cases. Afterwards composite phases were added to the solvent mixtures. Solution mixings were proceed by magnetic stirrer, at room temperature, for 24h.

In the end of the solution mixing, firstly the solubility of the nanocomposite mixtures were observed, that while all of the solution mixtures of DMAC and Toluene dispersed well, only A^{II} and C^{II} solutions of DMAC and Chloroform were dispersed. Solubility of the PSU/Sepiolite nanocomposite in each solvent mixture is shown in Table III.

In the next stage, 2ml of samples were taken from dispersed nanocomposite solution. These samples were casted as film by spin coater and solvent removed from the film. Then thin films of PSU/Sep. nanocomposites are obtained.

Dispersed solutions of nanocomposite were examined by viscometer. Further observation obtained by FTIR measurements.

TABLE III
SOLUBILITY OF PSU/SEP. NANOCOMPOSITE IN DMAC-TOLUENE AND DMAC-CHLOROFORM SOLVENTS

Solvent Mixtures	Volume Fractions	Solubility
	A ^I	+
	B ^I	+
DMAC-Toluene		+

C ^I		A ^{II}	+
		B ^{II}	-
D ^I	+	C ^{II}	+
		D ^{II}	-

C. Characterization spectrums of PSU/Sep. nanocomposites obtained from

Rheological measurements of dispersed PSU/Sep. nanocomposite solutions (AI, AII, BI, CI, CII and DI) were done by Brookfield RV-DV+II model viscometer. For analyses LV-3C type spindle was used. Measurements were preceded as 4 min periods between 3rpm and 60rpm. Obtained shear stress and shear rate data shown in Figs. 3 and 4.

dispersed solutions of DMAC-Toluene and DMAC-Chloroform.

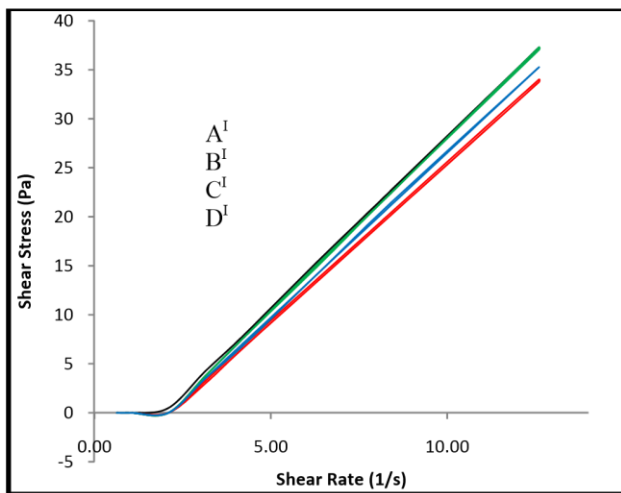


Fig. 3 Shear stress/ Shear Rate graph of DMAC-Toluene nanocomposite solution

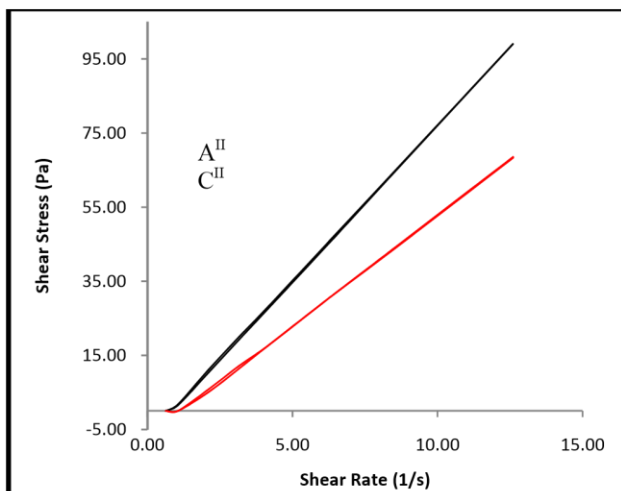


Fig. 4 Shear stress/ Shear Rate graph of DMAC-Chloroform nanocomposite solution

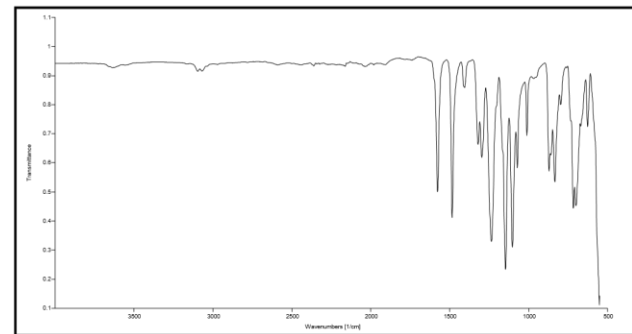


Fig. 5 Polysulfone

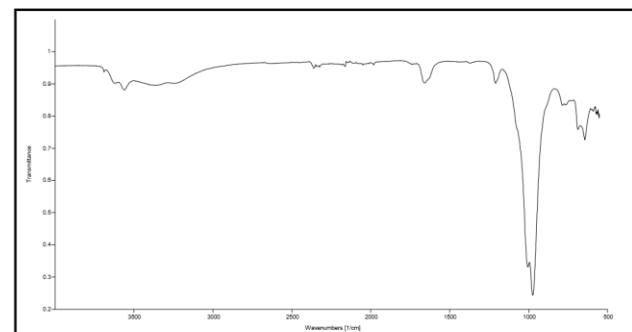


Fig. 6 Sepiolite

According to Figs. 7 and 8, FTIR data shows the characteristic bands for the polysulfone backbone and sepiolite structure weak peaks around 3435 cm⁻¹, indicates the presence of phenolic end groups. The formation of the new ester carbonyl peak at around 1735 cm⁻¹, less broad peak at around 3400 cm⁻¹ indicates that small amount of nonfunctionalized hydroxy groups comes from sepiolite.

III. RESULTS AND DISCUSSION

Sepiolite added polysulfone nanocomposites were prepared by solution mixing method. Eight different solvent mixtures were used for this method and rheological information of composite solutions was gathered. It was found from FTIR results that polymer nanocomposite combination was obtained for each dispersed composite solution.

Nanocomposite structure was examined by Fourier transform infrared spectra. Figs. 5 and 6 show the FTIR of the commercial sepiolite and PSU. Figs. 7 and 8 show the FTIR

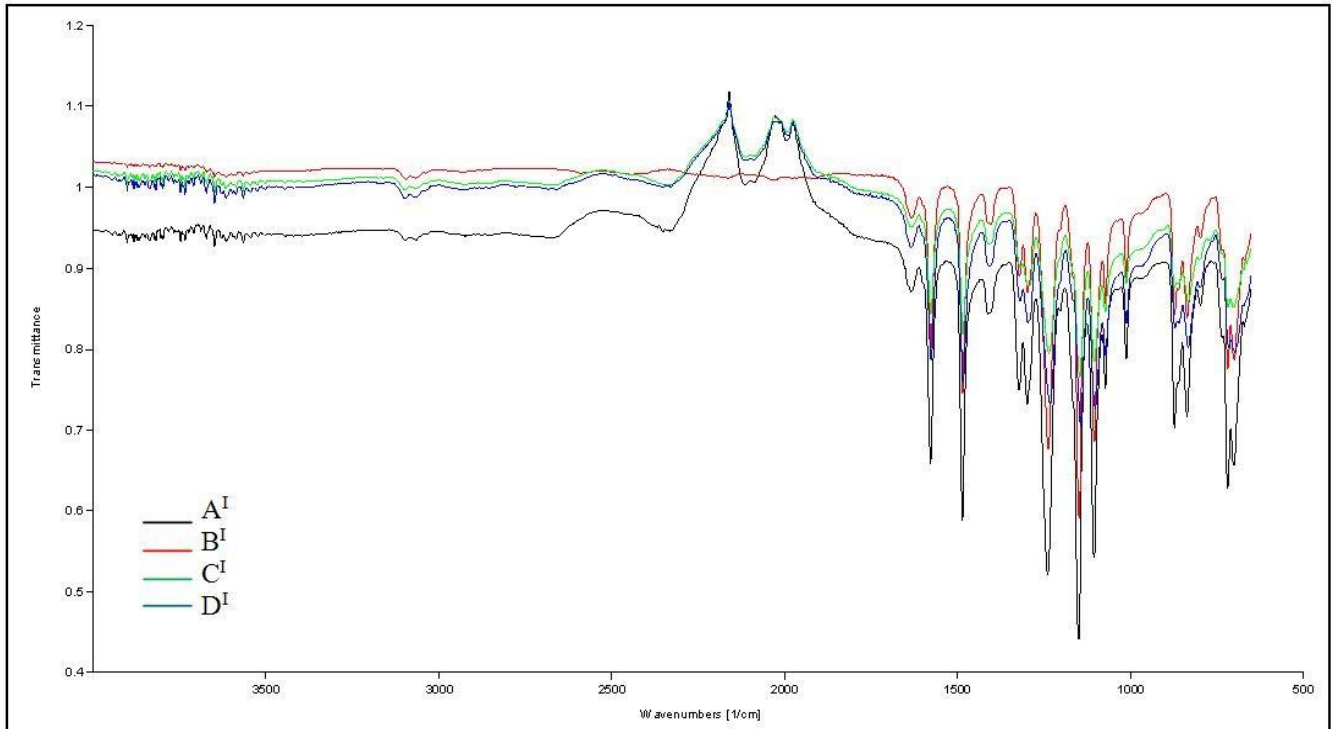


Fig. 7 FTIR Spectroscopy of PSU/Sep. nanocomposites prepared with DMAC-Toluene solvent mixture

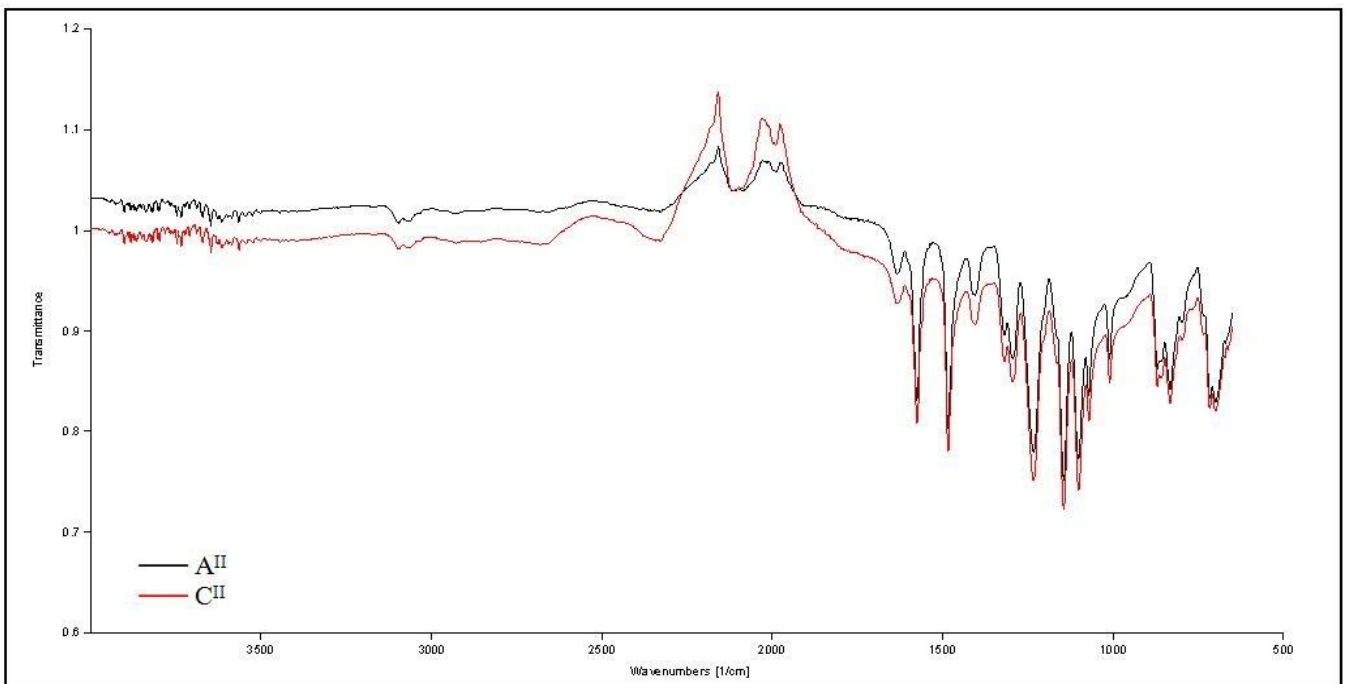


Fig. 8 FTIR Spectroscopy of PSU/Sep. nanocomposites prepared with DMAC-Chloroform solvent mixture

TABLE IV
RHEOLOGICAL PARAMETERS OF PSU/SEPIOLITE NANOCOMPOSITE SOLUTIONS

Rheological Parameters	A _I	B _I	C _I	D _I	A _{II}	C _{II}
Viscosity (Pa.s)	3.542	3.2477	3.5421	3.3715	8.4488	6.0225
Flow Index (Pa/s)	1.4475	1.4886	1.4475	1.3179	1.2506	1.2874

Moreover it is found that the increasing volume ratio of chloroform decrease the solubility of PSU composite phase. On the other hand increasing toluene volume fraction provides faster dispersion to the composite phase due to PSU has aromatic rings on its backbone helps dissolve in aromatic organic solvents like toluene. Other rheological parameters are shown in Table IV. According to the flow index values, which are greater than 1, one can say that the solutions show dilatent (shear thickening) shear flow. But solutions can be accepted Newtonian, since flow indexes are close to 1 and shear stress/shear rate graphs supports this.

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