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The Effect of Polyethylene Glycol and Nanoclay on the Rheological Behavior of Dispersing Cationic Polyurethane Nanocomposites

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ABSTRACT

Cationic waterborne polyurethane as a new dispersing polymer was synthesized by using relatively hydrophilic polyols. Dispersing cationic polyurethane (DCPU) nanocomposites were prepared using isophorone diisocyanate (IPDI), polyethylene glycol (PEG) with different molecular weights (M_n=200, 400, 600,and1000 g/mol), N-methyl diethanolamine (MDEA), dibutyltin dilaurate (DBTDL) and different percentages of nanoclay (1, 3, and 5%). The aim was to study the effect of polyol molecular weight and weight percentage of nanoclay on the extent of polarity, polymer flexibility, dispersibility of nanocomposite in aqueous phase, thermal stability and rheological behavior of the polymer. FT-IR and ^{1}H-NMR spectroscopy, Contact angle and thermal and rheometric analyzes were used to characterize the synthesized polymer and related nanocomposites. The results revealed that by increasing the molecular weight of polyethylene glycol, the following changes will be observed in the produced polymeric nanocomposites: particle size reduction, increase in dispersibility, contact angle, thermal stability and viscosity, as well as increase in semi-plasticity and elasticity properties of nanocomposites. Prog. Color Colorants Coat. 11 (2018), 33-46© Institute for Color Science and Technology.

1. Introduction

In recent years, many scientists have been looking for water-based resins to reduce pollutions and environmental concerns. Because of lower cost and easier application procedures for coating surfaces, their production and consumption are growing very fast [1-3]. A group of water-based coating resins includes "coatings soluble in water" and "coatings dispersible in water" (colloidal coatings) which contain small insoluble particles in water [4, 5]. In fact, the particles absorb water and the resin swells. Emulsifiers are added to resins in order to prevent coagulation and precipitation of particles. Dispersing polyurethanes are classified as anionic, cationic or non-ionic [6-8].

The common method for making water-based dispersing polyurethane resins is to prepare pre-polymers from isocyanates [9, 10]. Reaction with polyol will produce carboxylic acid groups, which after reacting with tertiary amines, produce ionic centers and stabilize polymeric particles. In the presence of a polyamine, the chain length of the polymer will extend [11, 12]. One advantage of water-based polyurethane

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suspensions is the completion of the reactions, so that at the end, no any traces of free isocyanate will exist. In coating industry, moving towards coating systems free from isocyanate is considered as a valuable advantage [13, 14].

Polyurethane chemical stability could be adjusted by a number of changes and modifications. By changing the molecular weight of the polyols used in the synthesis of polyurethane, the viscosity of the resin could also be adjusted, depending on the kind and condition of coating [15, 16]. Polymer-based nanocomposites gain more chemical and mechanical strength, due to the deposition of nanoparticles in their matrix. Nanoclays have various applications in producing polymeric coatings because of economical value. Three methods may be used for dispersing nanoparticles in the polymer matrix: *in situ* polymerization, combining and mixing nanoparticles with polymer solution, and dispersing particles into the molten polymer in the case of thermo plastic polymers [10, 15]. The specificities of the product depend on the applied procedure. Higher surface area of nanoparticles increases intermolecular bonding with polymer, which results in better strength, formability, thermal properties, lower gas permeability, and more resistance to oxidation, corrosion and degradation of nanocomposites [17, 18].

Nowadays, rheological analyzes are one of the most sensitive methods for studying the elastomeric behavior of polymers and semi-solid materials [19, 20]. These analyzes may be used for controlling polymerization parameters such as molecular weight, molecular weight distribution, and performance of final products. Rheological measurements will produce extremely useful information about certain behavior of materials used as coatings [21-23].

Different studies have been conducted regarding the properties of polyurethanes and the effect of nanomaterials on the microstructure of the polymer. However, researches regarding the synthesis and studying structurally different polyurethanes for various applications are limited. The objective of the current research is to synthesize cationic polyurethane dispersible in water with different flexibility and stiffness as a function of polyethylene glycol molecular weights and different percentages of nanoclay used in the synthesis of nanocomposites. In addition, other parameters such as nanoclay particle size, extend of dispersions, emulsions stability, hydrophilicity, elasticity, thermal stability and other rheological behavior are also evaluated.

2. Experimental

2.1. Materials and Methods

Isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), acetone and acetic acid were purchased from Merck Co., Germany. Polyethylene glycol (PEG) with various molecular weights (M_n=200, 400, 600 and 1000 g/mol) was purchased from Daejung of Korea and dried at 70 ^{o}C with vacuum pump at 1-2 mmHg for 6 hours before use. N-methyl diethanol amine (MDEA) was obtained from Aldrich-Sigma Co., USA, and nanoclay cloisite 15a from US Research Nanomaterials Inc. All materials were used without further purification.

2.2. Polyurethane Oligomer Preparation

Polyurethane (PU) oligomers were synthesized in a 100 mL glass reactor equipped with oil bath, stirrer, condenser, thermometer and nitrogen purge. 4.44 g (0.02 mol) isophorone diisocyanate (IPDI), 1.19 g (0.01 mol) N-methyl diethanolamine (MDEA), acetone as solvent and 0.03 g dibutyltin dilaurate (DBTDL) as catalyst were placed in a reactor and heated for 3 h at 60 °C. Then, polyethylene glycols (M_n=200, 400, 600, and 1000) (0.01 mol) were added to the prepared mixture and stirred (400 rpm) at 70 °C for 4 h. At the end, the mixture was neutralized by adding (0.01 mol) acetic acid and dispersing in the water (Figure 1).

2.3. Nanocomposites Preparation

Dispersing cationic polyurethane (DCPU) nano-composites synthesized from PEG 600, containing different percentages of nanoclay (1, 3, and 5%), were prepared as follow. Different amounts of nanoclay were soaked in acetone for 12 h and then dispersed for 60 minutes using an ultrasound apparatus. Then the dispersion was slowly added to polyurethane within 50 minutes using a mechanical stirrer. The resulting mixture was additionally mixed for 2h using a stirrer (1000 rpm).

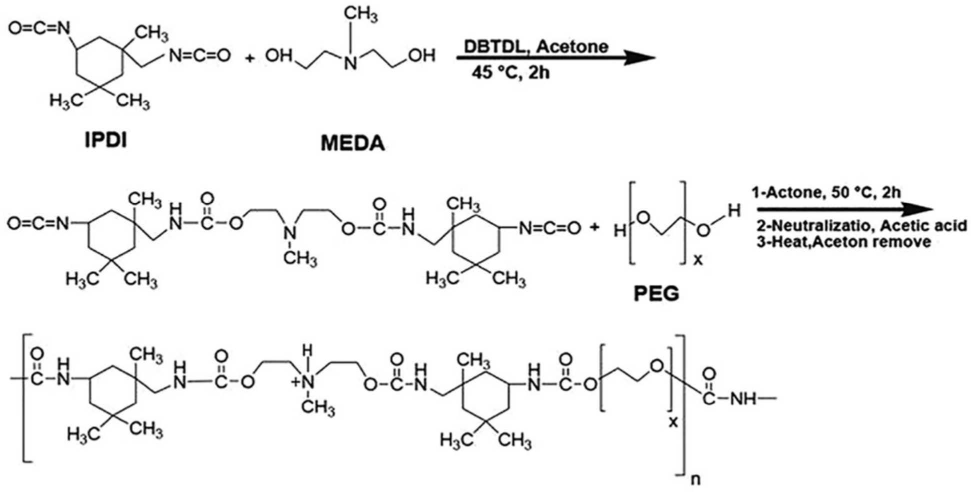

Figure 1: Synthesis scheme of dispersing cationic polyurethanes (DCPUs).

2.4. Measurements

Structural characterization of synthesized materials was done by using Perkin Elmer FT-IR spectrophotometer in the range of 4000-400 cm^{-1} using KBr tablets and ^1H-NMR Bruker 300 MHz spectrophotometer. Contact angles were measured by a Gl0 (KRUSS) instrument using Sessile Drop method. Particle size distributions were determined by Malvern particle size analyzer Master sizer 2000 model (UK). Thermal stability parameters (TGA/DTG) of the cationic polyurethane dispersion (DCPU) samples were measured by a Perkin Elmer Pyris Diamond instrument at nitrogen atmosphere from 25 to 550 ºC at a heating rate of 10 ºC/min. In order to study the viscosity and rheological properties, rheometer Anton Paar MCR300 device cylindrical TEZ180-C system was used at 25 and 50 °C.

3. Results and Discussion

3.1. Product Characterization

The cationic polyurethanes produced were identified by FT-IR and ^1H-NMR spectroscopy (Figures 2 and 4, and Table 1). The spectral data obtained are consistent with chemical structure of the products. Figure 3 shows that the FT-IR spectra of PEG 600 polyurethanes contain different percentages of nanoclay. As shown in the spectra, by increasing the amount of nanoclay, the vibrational band of N-H groups shifted from 1548 to 1544 cm^{-1} and the stretching band of C=O groups shifted from 1720 to 1716 cm^{-1}. These observations could be an indication of effective interactions between polyurethane and nanoclay particles [24].

Table 1: Data derived from bands in the FT-IR spectra of (DCPU's).

Functional	mode	cm^{-1}
C-O	Stretches	1060-1114-1148
C=O	Stretches	1720
C-N	Stretches	1244
-HN-CO_2-	-	1548
N-H	Stretches	3326

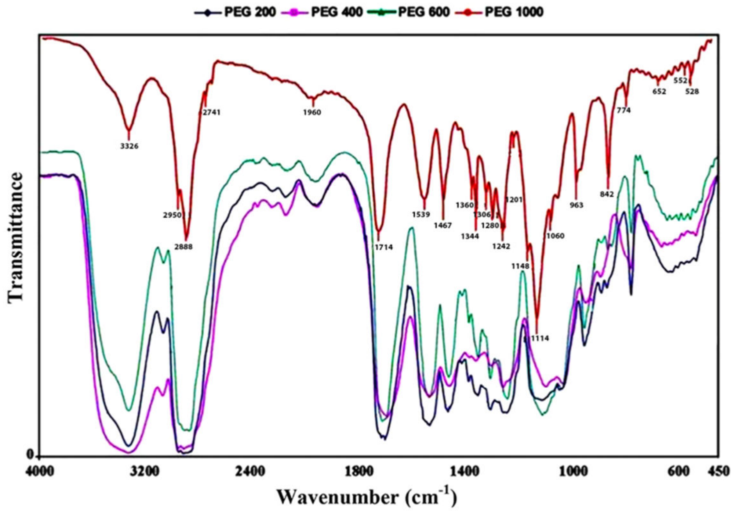

Figure 2: FT-IR spectral data of DCPU's.

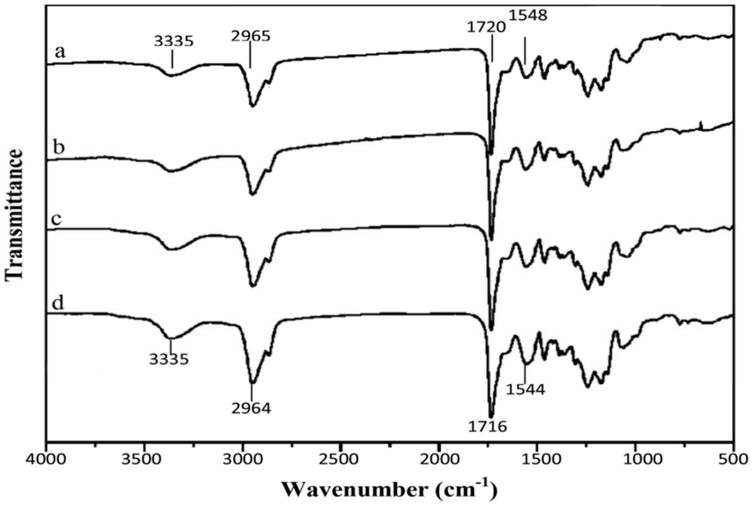

Figure 3: FT-IR spectra of DCPU/clay nanocomposites with different clay contact: (a) 0, (b) 1, (c) 3, and (d) 5 wt %.

3.1.1. ^{1}H-NMR Spectroscopy

Figure 4 shows the ^{1}H-NMR spectra of DCPUs. The strong peaks appeared at 1.13 and 1.18 ppm are assigned to hydrogen molecules of methyl groups in cyclohexane ring. Other peaks are in line with the expected structure for the product.

3.2. Particle Size Distribution

Figure 5 shows particle size distribution of polyurethane dispersions in aqueous phase. As can be seen from the curves, a sharp peak is visible for each sample. By changing the molecular weight of polyethylene glycol, major changes take place in hydrophilic part of polyurethane elastomer. By increasing the molecular weight of polyethylene glycol, the particle size of 10-100 micrometer eventually reduced to 1 micrometer. This means that by increasing the hydrophilic part of polyurethane chain, particle size of dispersed polyurethane is reduced. Polyurethane with smaller particle size has better dispersion in an aqueous phase and prevents particles from coagulation. Therefore, by increasing the chain length of polyethylene glycol, the length of the hydrophilic part of polyurethane increases, the particle size become smaller, and the viscosity also increases.

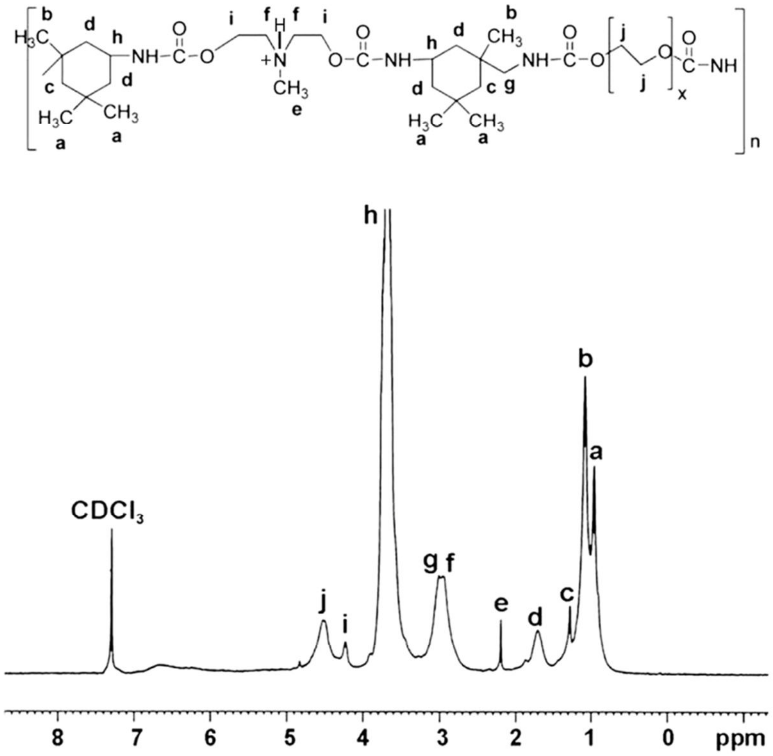

Figure 4: ^{1}H-NMR spectra of DCPU's.

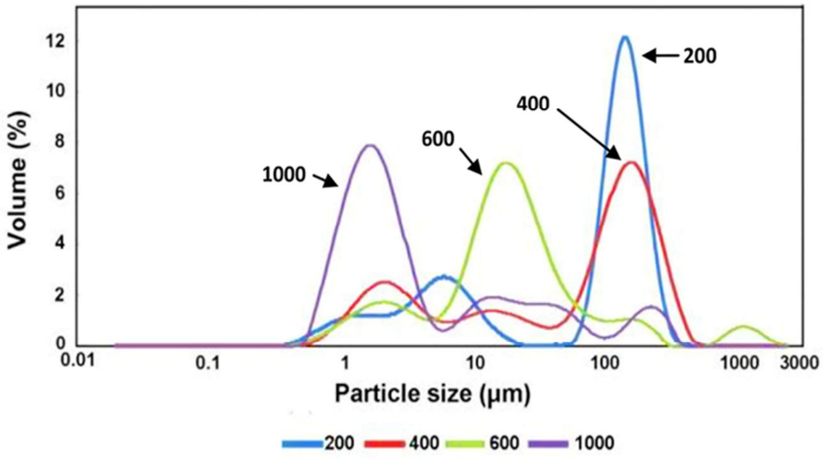

Figure 5: Particle size distribution of DCPU's in the aqueous phase.

3.3. Contact angle

The results of contact angle measurements for different dispersing cationic polyurethane nanocomposites with nanoclay percentages (1, 3, and 5%) and varying molecular weights (Mn=200, 400, 600, and 1000 g/mol) are shown in Table 2. From these observations, it could be concluded that contact angles are decreased by increasing the molecular weight of the polyethylene glycol, hence increasing the hydrophilic segment of the chains. On the other hand, contact angles are increased by increasing the amount of nanoclay. This is the result of reducing hydrophilicity of the polymer (Table 2).

Table 2: Results of contact angle analyzes for DCPU's nanocomposites.

Samples	Nanoclay(%)	Contact Angle (deg)
DCPU with PEG 200	0	82/9
DCPU with PEG 400	0	80/2
DCPU with PEG 600	0	79/4
DCPU with PEG 600	1	88/6
DCPU with PEG 600	3	88/5
DCPU with PEG 600	5	89/5
DCPU with PEG 1000	0	78/1

Table 3: Results of thermogravimetric analyzes for DCPU's.

Samples	TGA				DTG		
	*$T_{5\%}$	$T_{50\%}$	$T_{75\%}$	T_{Max}	T_d onset (°C)	T_d Peak (°C)	T_d offset (°C)
DCPU with PEG 200	159	300	329	365	105	317	402
DCPU with PEG 400	201	330	353	371	154	328	417
DCPU with PEG 600	195	350	381	390	156	378	421
DCPU with PEG 1000	223	376	398	410	160	398	427

3.4. Thermal Stabilities

The thermal stability of dispersing cationic polyurethanes was analyzed by taking TGA and DTG thermograms (Figure 6). The initial small weight loss in the temperature around 150 °C is related to the elimination of moisture, solvents and unreacted organic materials. The degradation of polyurethane chain appears around 310, 330, 350 and 376 °C for polyurethane dispersions with PEG200, 400, 600 and 1000, respectively. As can be seen, the thermal stability increases by increasing the molecular weight of polyol. In addition, data in Table 3 demonstrates that different percentages of weight loss of polyurethane dispersions are in accord with findings shown in Figure 6.

As concluded from DTG thermograms (Table 3), the initial degradation temperature (T_d onset) is increased by increasing the soft segment of the polymer chain [25, 26]. At the beginning, water and volatile materials are released and eliminated from dispersing cationic polyurethanes. At the highest temperature, the isocyanate groups (hard segment of the PU structure) will degrade. Finally, the main body of the PU will degrade. Regarding the DTG results, it can be concluded that polyurethanes synthesized with PEG 1000 and PEG 600 are the most stable products compared to other polyurethanes.

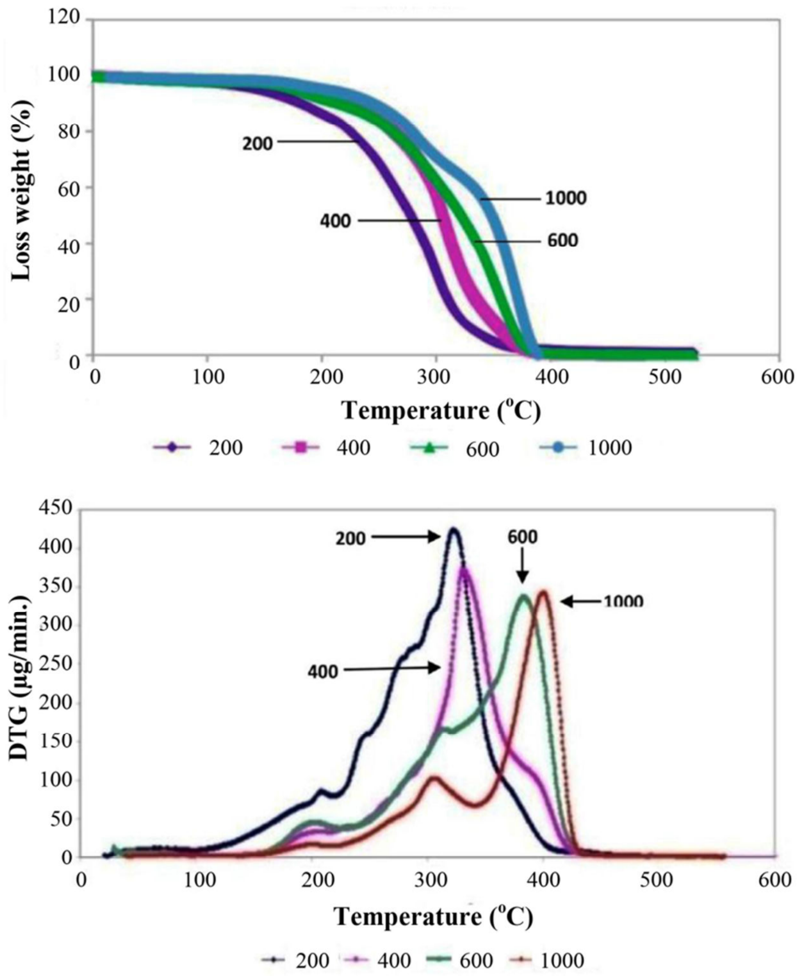

Figure 6: TGA and DTG thermograms of DCPU's.

3.5. Rheological Properties of DCPU

The rheological behavior of polyurethanes was studied as a function of molecular weight of polyols at 25 °C and 50 °C. The loss modulus of four polyurethane samples at 25 °C and 50 °C is shown in Figure 7. The loss modulus of polyurethanes corresponding to PEG 200, 400 and 1000 continuously increases. But the loss modulus of polyurethane corresponding to PEG 600, initially decreases and then starts to increase by stress, which resembles the behavior of the semi-liquids in the samples. By increasing the temperature up to 50 °C, the polymers synthesized from polyethylene glycol with molecular weight of 600 and 1000, will keep the increasing trend of loss moduli, because of having higher molecular weights and higher chain lengths compared to other samples. This parameter prevents entanglement of polymer chains, resulting in better dispersion of polymer particles in liquid phase and lower adhesion of the particles. By increasing the temperature, viscosity reduces and the polymer behavior comes closer to semi-liquids. By increasing the chain length of hydrophilic portion of the polymer, and therefore, increasing the intermolecular interactions, these kind of behaviors are expected to be observed. In the case of cationic polyurethanes synthesized with PEG 200 and PEG 400, loss modulus moves from viscous state towards elastic state. This is because of lower molecular weight of polymers and higher possibility of inter-chain adhesions and higher particle size of polymer in the emulsion.

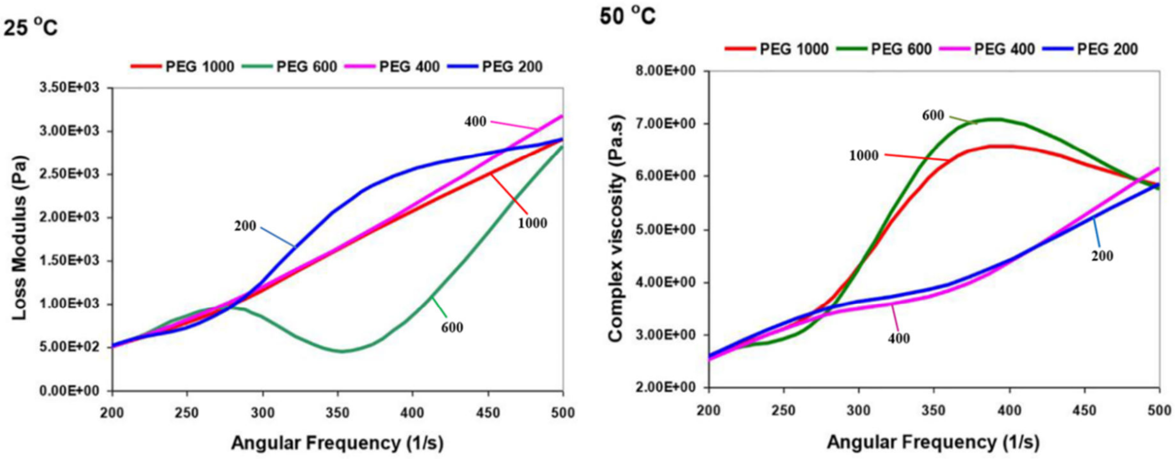

Figure 7: Loss modulus (G″) versus frequency (ω) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

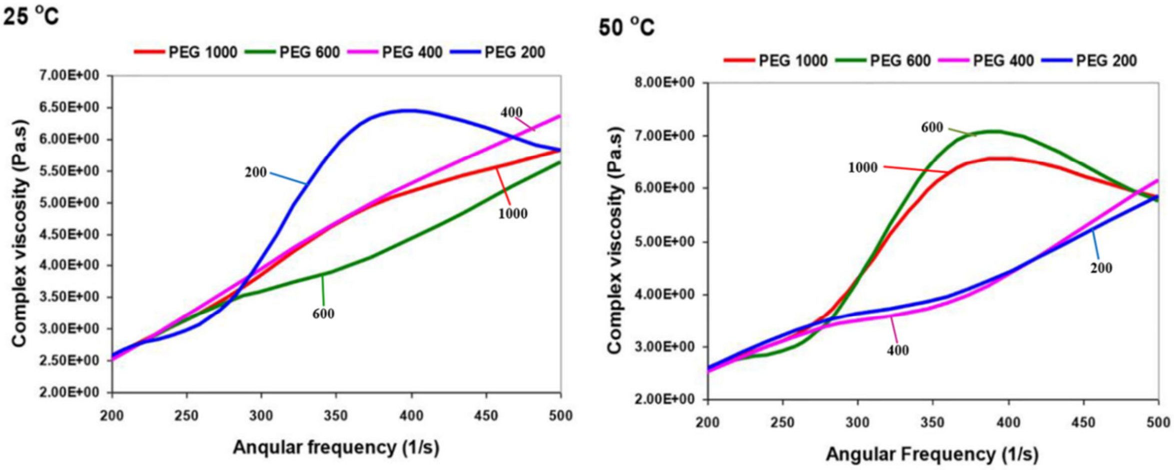

Figure 8: Complex viscosity (η) versus frequency (ω) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

As shown in Figure 8, by increasing the frequency at room temperature, the viscosity of all polymers increases and this trend changes by increasing temperature. The viscosity of two polyurethanes synthesized with PEG 600 and PEG 1000 increases, but began to decrease by increasing the applied frequency, reaching a relaxation point. This is because of changes in chain length and intermolecular interactions as well as changes in particle size.

The changes in viscosity as a function of applied shear stress are shown in Figure 9. It is observed that the viscosity of all dispersing cationic polyurethanes increases at 25 °C. Viscosity starts to decrease by increasing the applied shear stress, disruption in physical state of polymer, and increasing intermolecular interactions. By increasing temperature to 50 °C, lower friction between polymer chains and higher flexibility cause reduction of viscosity.

3.5.1. Rheological properties of DCPU Nanocomposites Produced with PEG 600

The rheological behavior of dispersing cationic polyurethanes synthesized with PEG 600, containing different percentages of nanoclay was studied at 25 °C and 50°C. Variations of storage modulus and loss modulus as a function of applied frequency are shown in Figures 10 and 11. As can be seen in the Figures, the storage modulus and loss modulus increase by the weight percentages of added nanoclay to polyurethanes. This is because of more interactions between nanoclay particles and polymer. At higher applied stresses, the polyurethane fills the spaces between the plates of nanoclay, separating them from each other. By increasing temperature to 50 °C, the intermolecular interactions will decrease and the viscosity will increases, therefore, better dispersion of nanoclay particles will be achieved.

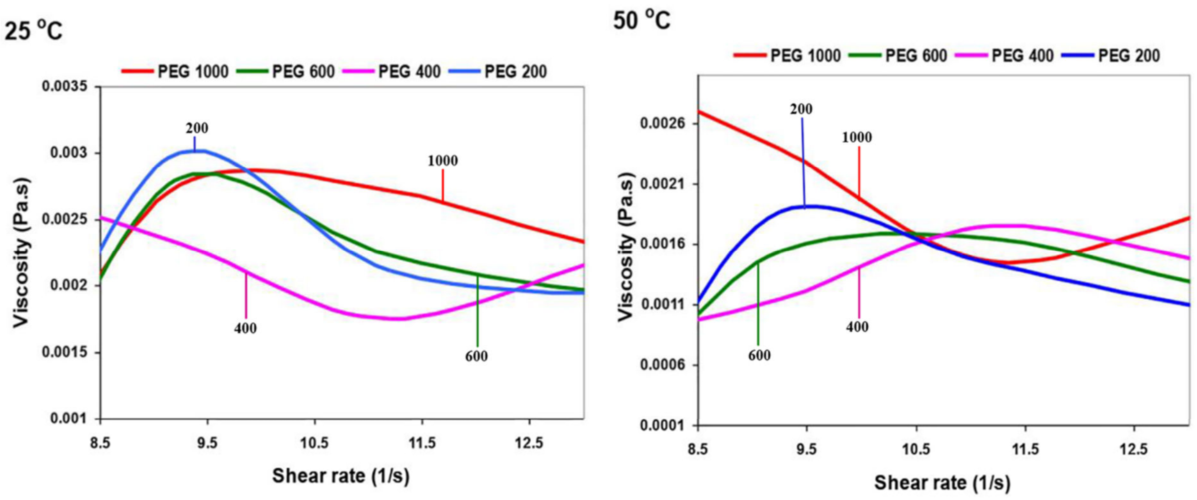

Figure 9: Viscosity (η) versus shear rate (γ) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

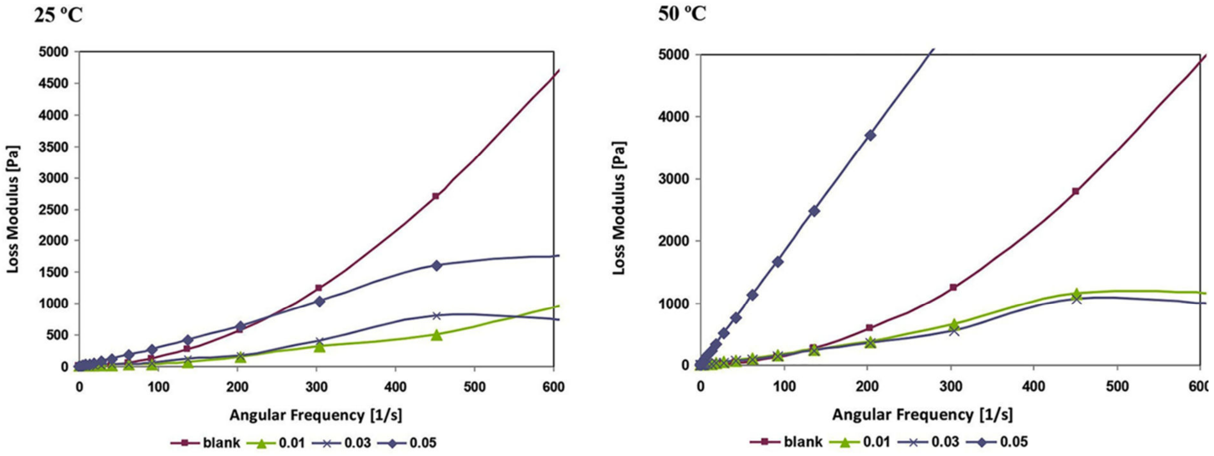

Figure 10: Loss modulus (G″) versus frequency (ω) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

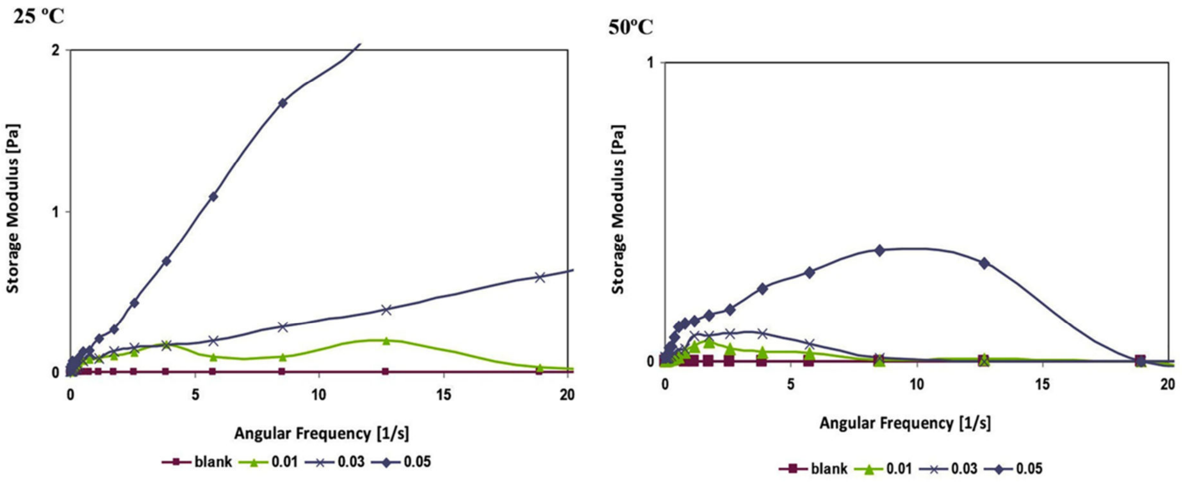

Figure 11: Storage modulus (G″) versus frequency (ω) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

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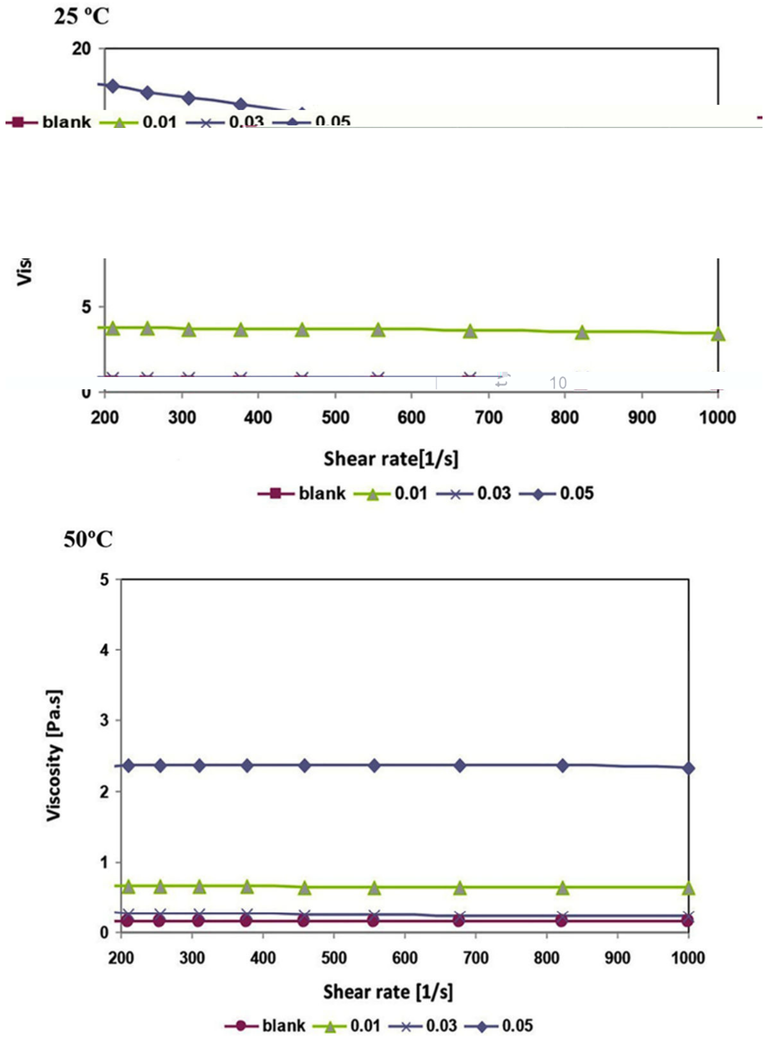

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Figure 13: Complex viscosity (η) versus frequency (ω) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

The results of vibrational shear stress tests of nanocomposites containing different percentages of nanoclay are shown in Figure 14. In all samples, storage modulus and loss modulus have reduced at both temperatures by lowering the applied frequency. As expected, in all frequencies, the modulus increases at higher nanoclay content. At higher frequencies, the modulus behavior of the composites are almost similar. But at lower frequencies, by increasing the percentages of nanoclay, the extent of changes of elastic modulus becomes uniform and plain. On the other hand, at low frequencies, the viscoelastic responses of all nanoclay-containing nanocomposites reduced by reducing the frequency. Their rheological behavior also became similar to that of semi-solid materials. In all nanocomposites containing low percentages of nanoclay, an intense non-linear behavior is observed. This is because of the penetration of polyurethane chains into nanoclay silicate layers. The result is weakening of Vander Waals interactions and strong hydrogen bonding between hydroxyl groups of the components of nanocomposite. The semi-solid behavior of nanocomposites at lower frequencies is assigned to the polar structure of nanoclay molecules and the extent of mixing with polymer. High storage modulus of dispersing cationic polyurethane nanocomposites prevents their precipitation in the polymer mat.

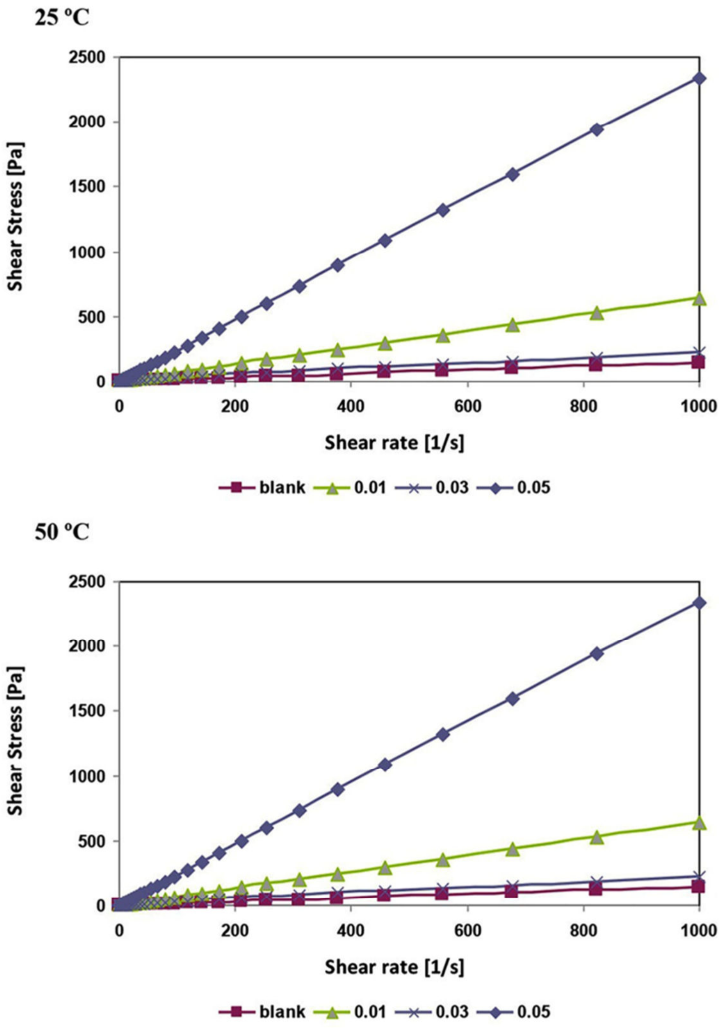

Figure 14: Shear stress (1/s) versus shear rate (γ) for DCPU with various PEGs measured in a rotary rheometer at 25 ºC and 50 ºC.

4. Conclusions

In this research, the effect of hydrophilic portion of polymer chain and the percentage of nanoclay on the properties of dispersing cationic polyurethane nanocomposites, including chain flexibility (elasticity), particle size, extent of dispersion in aqueous phases, thermal stability and other rheological behaviors, were studied. Spectral data (FT-IR and ^{1}H-NMR) were in accord with expectations, verifying the structure of synthesized polymers. Particle size analyzes showed that by increasing the molecular weight of PEG, the particle size of the polymer decreases. The reason can be the better dispersion of synthesized polymer in liquid phase, lower adhesion of particles, and lower precipitation in the emulsion. On the basis of thermal analysis, it was observed that viscosity and thermal stability of the synthesized polyurethane increase by increasing the molecular weight of PEG. Increase in molecular weight of polyol resulted in increasing of the length of hydrophilic segment in the polymer chain. Moreover, the molecular weight of the synthesized polyurethane also increased. Therefore, the flexibility and dispersibility as well as thermal stability of polymer are improved. Rheometric analyzes at 25 ^oC and 50 ^oC indicated the major changes in rheological behavior of dispersing nanocomposites. These behaviors are the result of changes in the molecular weight of polyols used in the synthesis of polyurethanes. Storage modulus, loss modulus and viscosity of polymer changed because of variation of molecular weight of polyethylene glycol. The nanocomposites also behaved as semi-plastic materials. In addition, viscosity of polymer increased due to the penetration of dispersing cationic polyurethane to the spaces between nanoclay plates and increasing the distances between the plates. Therefore, storage modulus and loss modulus are prevented from increasing, hence better dispersion was achieved in the liquid phase.

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