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The castor oil based water borne polyurethane dispersion; effect of -NCO/OH content: synthesis, characterization and properties

DOI 10.1515/gps-2016-0144
Received August 19, 2016; accepted October 20, 2016; previously published online December 17, 2016

Abstract: In this work, a novel bio-renewable castor oil (CO) based aqueous polyurethane (PU) anionic prepolymer dispersion was prepared successfully using isophorone diisocyanate (IPDI) and dimethylol propionic acid (DMPA) as internal emulsifier maintaining NCO/OH molar ratios of 1 : 3 and 1 : 5, respectively. The intermolecular H-bonding change, type and intensity of the obtained films with change in molar ratio were investigated by analyzing with Fourier transform-infrared (FT-IR). The morphology of the films was recorded with scanning electron microscopy (SEM) and transmittance electron microscopy (TEM). The coating properties for the film were also studied and discussed. The structure-property relationship with different molar ratios of prepolymer revealed an increasing pattern showing increase in the hard segment content increases the physico-mechanical properties of the CO based PU prepolymer. The FT-IR deconvolution results are in agreement with the film properties. The excellent abrasion resistance properties of CO based films agree well with the surface morphology and FT-IR results. The outcome of the study also suggests use of CO as a better alternative to replace petroleum based polyol for feature perspective.

Keywords: bio-based polyurethane dispersion; coating properties; FT-IR; polyurethane prepolymer; SEM.

1 Introduction

Amid a growing clamor worldwide for green means of research, material scientists have helped this by restricting use of petroleum based polyol or synthesizing bio-based products with solvent-free synthesis methods. This achievement was fulfilled by means of waterborne, high solid, hyperbranched and radiation curable macromolecular products [1–3]. Amongst this, waterborne polyurethane (WPU) products are getting importance over relative conventional solvent borne coatings due to its eco friendliness, easy synthesis, and wide range of properties with customer satisfaction applications [4–8]. The technological advance behind WPU dispersion (WPUD) systems has been maintaining a perfect balance between its chemistry and on environmental credentials concerning the use of organic solvents [5–10]. Applications such as coating, adhesive, finishing agents, paper surface and fiber treatment agent are among the fields where WPUD is largely used [11, 12]. Certain property oriented applications such as flexibility, adhesion to a wide range of substracts, excellent resistance to chemicals, solvents, water, etc. makes WPU more prone to importance as a coating material [6]. Replacement of fissile fuel with plant or vegetable oil, and development of similar or enhanced properties are the prime demand from present research. By contrast, the properties of vegetable oil such as low toxicity, inherent biodegradability, and high purity, etc. emulate themselves for the production of bio-based thermosets [1–3]. In this scenario, WPUDs synthesized from renewable materials are gaining much importance due to their environmentally friendly systems with similar or improved properties and competitively low price [6]. Similarly, a large focus is employed on utilizing castor oil (CO) [6, 7, 12–21], for WPU synthesis as polyol has been largely replacing fossil feedstock. CO is the best among the vegetable oils due to its structural features, biodegradability, low cost, socially favorable advantage and availability.

García-Pacios et al. [22] investigated the synthesis of the WPU dispersions based on polycarbonate polyol, and they found that broader particle size distribution could result as the NCO/OH ratio increases, whereas both the dispersion viscosity and the dry film crystallinity decrease. Similarly, Otts and Urban [23] reported that changing the NCO/OH ratio from 1.0 to 2.2 could significantly affect the film morphology, and that the cast films with higher NCO/OH ratio might possess increased glass
transition temperature and surface roughness. More recently, Guo et al. [24] detailed the influences of the NCO/OH molar ratio and dimethyl propionic acid (DMPA) content on the properties of the WPU emulsions synthesized with 2,4-toluenediisocyanate (TDI) and isophorone diisocyanate (IPDI). Similarly, in another research the same group studied the properties of WPU emulsion synthesized from IPDI. This group concluded that the tensile strength increased with increase in NCO/OH molar ratio to 1.6 from 1.2, but a reduction in mechanical strength was recorded after the NCO/OH molar ratio increased to 2.0 from 1.6 [25].

Vegetable oil based anionic WPU dispersions using DMPA, an internal emulsifier, were successfully prepared followed by neutralization with triethylamine (TEA) [1, 2, 4, 9–13]. The carboxylate ion group provides surface charge to PU particles thereby stabilizing WPU in the aqueous phase. Moreover, two steric hindered carboxylic groups of DMPA minimized its reactivity with isocyanates during WPU synthesis [9]. The WPU reactions are generally carried out employing the acetone process, a prepolymer mixing process, a ketamine/ketazine process or a hot melt process [2, 4, 10, 11]. Acetone is mainly used as a solvent during the dispersion process to control the viscosity and emulsion particle size. According to a recent study, Guo et al. [25] reported that increase in acetone content decreases the particle size and viscosity, but the film water absorption capacity increases. WPUs are generally prepared in a mixture of two steps composed of synthesis of -NCO end capped PU prepolymer, followed by dispersion in water to obtain the emulsion [7–9, 26–30].

Lee et al. [26] utilized a modified dispersing procedure to prepare WPU by varying the molecular weight of the soft segment and the internal emulsifier dimethylolbutyric acid from 2.4 wt% to 11 wt% with respect to the prepolymer weight. The group reported that with increase in the ionic group content in the PU dispersion the particle size decreased, which influences the film properties. Negim et al. [28] prepared the WPUD using the acetone process by varying the NCO/OH molar ratio and reported the properties of the final film with variation of molar ratio. Cakić et al. [27] studied the influence of various ionic contents on thermal, mechanical and physical properties of WPUD. During the modified dispersing procedure, the ionic content was varied, changing the amount DMPA from 4.5 wt%, 7.5 wt% and 10 wt% to the prepolymer weight. The study concluded that with increase in the hard segment content, the properties of WPUD were influenced positively.

In this work, the preparation and characterization of CO based WPU was studied with different DMPA content. The structures of the casted films were confirmed from a Fourier transform-infrared (FT-IR) study. Scanning electron microscopy (SEM) and transmittance electron microscopy (TEM) were utilized to investigate the morphology of the obtained material, and universal testing machine (UTM) was employed to note the mechanical properties of the prepolymer film with variation of ionic content. The coating properties, such as hardness, abrasion, chemical resistance, gloss and contact angle of the dried films were also investigated to study the effect of ionic content on the physico-mechanical properties of the film.

## 2 Materials and methods

### 2.1 Materials

Table 1 shows various materials utilized for the purpose of synthesis of CO based WPUD. All materials were used as received without further purification.

### 2.2 Synthesis of CO based aqueous PU-prepolymer

Two WPU-prepolymer dispersions were prepared using a standard procedure discussed earlier [9] as per the reaction scheme shown in Figure 1. For all samples, the NCO/OH molar ratio (1.3 and 1:5) was considered for the formulation. It was defined as a molar ratio of IPDI and sum of the molar ratio of CO and DMPA in the starting formulation. Two-step procedures were followed for the synthesis of the prepolymer.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purchased from</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor oil (CO)</td>
<td>Aldrich Chemical Company (Milwaukee, WI, USA)</td>
<td>972.5</td>
</tr>
<tr>
<td>Isophorone diisocyanate (IPDI)</td>
<td>Aldrich Chemical Company (Milwaukee, WI, USA)</td>
<td>126.0</td>
</tr>
<tr>
<td>2,2'-bis (hydroxymethyl) propionic acid (DMPA)</td>
<td>Aldrich Chemical Company (Milwaukee, WI, USA)</td>
<td>134.13</td>
</tr>
<tr>
<td>n-dibutylamine and dibutylinlaurate (DBTDL)</td>
<td>Aldrich Chemical Company (Milwaukee, WI, USA)</td>
<td>631.56</td>
</tr>
<tr>
<td>Triethylamine (TEA)</td>
<td>Fisher Scientific Company (Fair Lawn, N, USA)</td>
<td>149.19</td>
</tr>
<tr>
<td>Acetone</td>
<td>Fisher Scientific Company (Fair Lawn, N, USA)</td>
<td></td>
</tr>
</tbody>
</table>
of WPUP-prepolymer. These are (a) synthesis of PU-prepolymer and neutralization and functionalization of the prepolymer and (b) during the final step, emulsification was done. The detailed synthesis procedure and mass of each chemical taken for synthesis are provided in Table 2. Initially, the IPDI was transformed to the 500 ml four necked reaction kettle in an inert atmosphere in order to avoid formation of urea linkages due to ingress of atmospheric moisture into the vessel. The four necked kettle was equipped with a mechanical stirrer, nitrogen inlet and thermometer. The CO, DMPA and 1 drop of n-dibutylamine and dibutyltin dilaurate as a catalyst were added to the reaction mixture and heated up to 75°C. Thereafter, the temperature of the reactor was raised up to 80°C in a stepwise fashion, and allowed to react for 1 h constantly at 1000 rpm. During this period, the viscosity of the reaction mixture was controlled by an addition of acetone (25 wt% of solid) to the bath. Then the reaction continued for another 2 h at 78°C. The stirring speed was maintained at 1000 rpm throughout the reaction. The DBA method was adopted to record the change in -NCO value during the reaction [4, 9, 28]. Isocyanate end capped PU-prepolymer, as obtained in the above step, was allowed to cool down to room temperature. TEA (2 equiv. per DMPA) was added to the PU prepolymer and stirred for 30 min to neutralize all the carboxylic acid groups, which was followed by emulsification with adding a calculated amount of distilled water (150 ml).

2.3 Preparation of the PU films

A leveled glass surface was chosen to cast the films with the help of an applicator of 90 μm to obtain a film thickness of 25–30 μm and films were allowed to slow evaporation of water at room temperature for 7 days [9]. Afterwards, the films were stored in desiccator to prevent absorption of moisture from the films. Table 2 shows the nomenclature of the films WPUDCO-1 and WPUDCO-2 prepolymer dispersion with their respective -NCO/OH ratios, which are used for this study. Similarly, coatings as obtained, were applied on the mild steel panel and allowed to dry before testing.

2.4 Solids content determination

To determine the percentage of solid content in the emulsion, the difference in weight both before and after the evaporation of an aqueous content was calculated. For this, about 1 g of emulsion was placed on an aluminum container and allowed to evaporate water at 105°C. To record a constant weight, the emulsion was kept for different time intervals. The reported data for solid content was an average of three experimental determinations.

3 Experimental techniques

3.1 FT-IR spectroscopy

FT-IR measurements were carried out in the attenuated total reflectance mode using a Thermo Scientific Nicolet 6700 spectrometer. IR spectra were obtained at 4 cm⁻¹ resolution between standard wave numbers ranging from 400 cm⁻¹ to 4000 cm⁻¹. In order to evaluate and identify underlying component bands of the N-H and carbonyl region, spectra were deconvoluted by curve-fitting stimulations using Origin software 6.0. This was done by considering peaks as Gaussian with a number of iteration to get the best fit peaks. An error of less than 5% was estimated to be associated with this.

3.2 SEM

SEM analysis of the film was captured employing a Zeiss EVO MA (UK) instrument. In order to improve the surface
conductivity, the samples were coated with gold using a vacuum sputter coater prior to testing.

### 3.3 TEM

The JEM 1400 TEM mode (JOEL, Japan) operated at an accelerated voltage of 100 kV was used to record the TEM images of the film. The dispersions prepared were diluted with distilled water on the coated side of a 200-mesh nickel grid and characterized after drying.

### 3.4 Gloss test

The gloss characteristics of the films were determined employing a gloss meter “Erichsen glossmaster” Model 507 according to ASTM D523. The resin coated glass place was kept at an angle of incidence of 60° and reflected light was measured. An average of three measurements was considered to obtain the final gloss values.

### 3.5 Tensile strength, chemical resistance, pencil hardness and abrasion test

A UTM machine model 3382 (USA) following the ASTM-D 638 standard test method at 24°C, operated at a cross-head speed of 10 mm/min was used to measure tensile test of the film sample. The test specimens were prepared using a precision cutter with uniform thickness maintaining 10 mm width and 50 mm length. A cellulose tape was used to stick a 15 mm length on either end of the specimen leaving a clear 50 mm, and allowed for the tensile test. In most of the tests, all specimens were broken in the proximity of the center of the gauge length [4, 9]. Aqueous NaOH (10%), aqueous ethanol (10%), aqueous HCl (05%), and water were prepared to study the effect of chemical environment on the film. The standard procedure as per ASTM D 543-67 was followed for these tests. The small pieces of cured films were kept in 100 ml amber glass bottles containing the aforesaid media at 30°C. The percent of weight loss was measured after 21 days of test. Different graded pencils were used to determine the hardness for the PU-prepolymer film, according to the test method of ISO 15184: 1998 (E). For determination of abrasion resistance of the MS coated films, a similar procedure is discussed elsewhere [3, 9].

### 3.6 Contact angle

Contact angle measurement was carried out to determine the nature of CO based PU-prepolymer towards water (Phoenix, SEO, South Korea) using the sessile drop method, was used to measure contact angles for WPUDCO-1 and WPUDCO-2 prepolymer films at room temperature. For this, drops of water on different areas of the film surface were placed using a micro-syringe and the mean was taken as the real value for the contact angle study. The testing liquid, water, used for this study was deionized water prepared in the laboratory.

### 4 Results and discussion

#### 4.1 FT-IR analysis

The most well-established analytical technique for functional group analysis, phase separation behavior, elucidation structure property relation and H-bonding ability in polymers is FT-IR analysis. The noticeable shifting mid IR spectral band signifies the strength and intensity of the hydrogen bonding in macromolecules [9]. The translational, rotational, vibrational, and electronic energies of the functional group in the polymer contribute towards the total energy of a particular bond. Therefore, an interaction with radiation of the electromagnetic spectrum will result in different energy transitions of the bond or functional group involved in the macromolecule. Therefore, it is believed that during the formation of PU prepolymer, a significant and unique IR transmittance profile is expected, composed of both the hard segment mainly contributed from the urethane/urea-amide linkages and the soft segment derived from the macrodiol [29].

FT-IR spectra obtained for -N=C=O terminated PU prepolymer (A) along with the moisture cured PU prepolymer (B) are demonstrated in Figure 2. In this spectrum, (A) shows the formation consumption of -N=C=O group with the progress of reaction, whereas absence of a peak near 2270 cm⁻¹ shows completion of the reaction. The FT-IR spectra for the formation of moisture cured prepolymer for different -NCO/OH ratios are shown in Figure 3, showing the spectral zone between the range of 400–4000 cm⁻¹.

Further, when analyzing the spectral region, it is found that the N-H stretching vibration in the region (3150–3500 cm⁻¹), the C-H (methyl and methylene) stretching vibrations for both antisymmetric and symmetric stretching are pointed in the region 2800–3000 cm⁻¹. The scissoring and deformation band of methylene (CH₂) and methyl...
(CH₃) group are found at 1455 cm⁻¹. The rocking and stretching vibration of C-C and CH₂ groups are assigned between 1002 cm⁻¹ and 1012 cm⁻¹, respectively [29, 30].

The amide group formation during PU synthesis, [R-(C=O)-N-H₂] can be strongly tracked in the FT-IR spectrum and are shown in Figure 4. The C=O vibrations in amide-I (consisting of C=O, C-N stretching and C=C deformation vibration) are found in the region 1600–1800 cm⁻¹ and the δ N-H in plain bending + ν C-N stretching + ν C-C stretching for amide II are pointed in the region 1540–1700 cm⁻¹. This amide II mode is much more sensitive for both chain conformation and H-bonding formation in the network structure. The complex structural behavior indicates overlapping of peaks that share common vibrational bands. Further, the stretching frequency for ν C-N in amide III can be seen in the range 1226–1292 cm⁻¹, amide IV is assigned at 766 cm⁻¹ in the spectrum and amide-V band is assigned at 695 cm⁻¹, respectively [9, 29, 17–19].

Among the other peaks, O-CH₂ stretching vibration is found at 2795 cm⁻¹, and C-O-C stretching vibration for ether groups is assigned at a frequency of 1110 cm⁻¹. The stretching vibration for carbonyl groups appeared at 1780 cm⁻¹ and the urethane hard segment (O-C=O) and esteric C-O stretching vibration were found near 1076 cm⁻¹. According to Otts and Urban [23] the band near 553 cm⁻¹ is assigned to the δ N-C-N of methylalkylureas. The lower band near 453–455 cm⁻¹ is assigned to C-O-C and C-C-O of the urethane moiety [9, 29].

4.2 Study of hydrogen bonding

The role of the hard and soft segment on reaction chemistry with structural changes was better understood by more detailed analysis of the υ(-N-H) and υ(-C=O) regions in the FT-IR spectra. The bonding activities in case of PU-prepolymer are mainly due to the donor proton are form N-H group of urea or urethane and acceptor proton can be from carbonyl of the urethane’s C=O, urea’s C=O or the oxygen atom of the ester or ether linkage when polyester or a polyether are present as the soft segment. The material properties of the macromolecule largely depend
on the strength and intensity of hydrogen bonding. Since our main aim is to study the role of the structure property relationship, considering hydrogen bonding, hence, two spectral regions carbonyl and N-H are further analyzed and a probable hydrogen bonding in PU prepolymer formation along with their FT-IR frequency are shown in Figure 5. The representative deconvolution curves for the $\nu$ (C=O) region for sample WPUDCO-2 are shown in Figure 6. The four different overlapping bands at 1735 cm$^{-1}$, 1730 cm$^{-1}$, 1700 cm$^{-1}$ and 1705 cm$^{-1}$ are obtained and assigned to free urethane, free urea, bonded urethane and bonded urea, respectively [29]. Moreover, the area associated with the bonded C=O is found to be more in both cases when compared to free C=O in the deconvolution curve. Similarly, the representative deconvoluted spectrum of $\nu$ (-N-H) regions for the moisture cured prepolymer is shown in Figure 7. The peaks as obtained from Figure 6 at 3521 cm$^{-1}$ and 3341 cm$^{-1}$ are associated with free N-H and hydrogen bonded -NH [-NH...O=C], respectively. The corresponding intensity of each peak is given in Table 3. Table 3 indicates that when the isocyanate content decreases, the free N-H intensity decreases, whereas hydrogen bonded -NH intensity continues to increase with increase in the -NCO/OH ratio. This suggests intermolecular interactions are increasing with increase in the segmental proportion [9].

### 4.3 Morphology studies

#### 4.3.1 SEM analysis

Factors like chemical structure of the soft segment, chain rigidity, viscosity of the prepolymer and cross linking within the polymer matrix are the prime factors ruling the particle size during degree of dispersion in the polymeric material. The surface morphologies of the film, as obtained from SEM analysis, are shown in Figure 8A and B. These morphologies indicate that a continuous phase without any agglomerates for the CO based waterborne dispersion was achieved. This suggests that hard segment domains are fairly distributed in the soft segment, resulting in a good phase mixing morphology. However, with increase in the hard segment content, the surface becomes rough in nature and agglomerations are observed (Figure 8B). This result suggests poor dispersion or interaction between the soft and hard segments. This interpretation is fairly in agreement with our FT-IR results. Thermodynamic miscibility between the hard and soft segments plays an important role in a uniform microstructure [10, 13, 20].
4.3.2 TEM analysis

The TEM micrograph demonstrates the degree of dispersion for the CO based PU dispersions. Several factors are influencing the degree of dispersion and particle size in the PU dispersions, such as hydrophilicity, prepolymer viscosity, etc.; however, the average particle size within a polymer matrix does not directly relate to physical efficiency of interaction, but, the dispersions having larger particle size are preferred in surface coatings for rapid drying and smaller particle size is required where deep penetration into the substrate is essential [29]. The obtained TEM images of PU prepolymer are shown in Figure 9A and B. A homogeneous dispersion in both hard and soft segments inside the polymer matrix can be seen in both of our images. However, with a higher hard segment,
the surface homogeneity was disturbed. These features are in correlation with the results obtained from Figure 8B.

4.4 Mechanical properties

4.4.1 Tensile test and % of elongation at break

The mechanical properties of CO based PU-prepolymer depend on the degree of cross linking, the hard segment content and the intermolecular interaction between the hard segments and soft segments. Among the other factors, e.g. size and shape, concentration of the hard segment within the PU matrix controls the tensile behavior of WPUDCO matrix. The elasticity, toughness and other physical properties of these materials were determined largely by the degree of phase separation, interconnectivity of the hard segment, i.e. hard segment cohesion, as well as the nature of the segment interface and the mixing of the hard segment in the soft segment [9–12, 17, 29–31]. The mechanical performances, like tensile strengths, Young’s modulus and percentage of elongation at break of the CO based PU-prepolymer, are summarized in Table 4, and the data depict that Young’s modulus was increased to 33.8 MPa from 13.2 MPa and tensile strength was escalated to 12.3 MPa from 9.3 MPa due to the increment in the hard segment content from WPUDCO-1 to WPUDCO-2 [9, 29]. The WPUDCO-1 has a higher tensile strength which may be due to strong intermolecular hydrogen bonding content and improved cross linking density in the matrix.

Table 4: Mechanical and coating properties of polyurethane (PU)-prepolymer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mechanical properties</th>
<th>Coating properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(σb MPa)</td>
<td>E’(MPa)</td>
</tr>
<tr>
<td>WPUDCO-1</td>
<td>13.2</td>
<td>9.3</td>
</tr>
<tr>
<td>WPUDCO-2</td>
<td>33.8</td>
<td>12.3</td>
</tr>
</tbody>
</table>

4.5 Coating properties of prepolymer film

4.5.1 Abrasion resistance

Abrasion is the ability to resist the surface wear and tear of the film when rubbed with another flat material. Protection to external wear and friction to the coating films can be judged from its good abrasion resistance property [3, 4, 31]. Weight loss in response to the abrasion test of the CO based WPUD prepolymer film is presented in Table 4. Since the thickness of the coating material was fixed, a specified number of revolutions was performed (1000 cycles) with all coated samples. From Table 4, it can be observed that weight loss for WPUDCO-1 and WPUDCO-2 films was about 9 mg and 6 mg, respectively. This draws a conclusion that a compact film with a stronger surface interaction was obtained with increasing molar ratio [31]. This is mainly due to a strong hydrogen bonding ability within the PU macromolecule which is in good agreement with our FT-IR studies. Figure 10A and B show the SEM micrographs of abraded CO based WPUD prepolymer films. It can be observed from the images that the emulsion

Table 5: Chemical resistance properties of polyurethane (PU)-prepolymer.

<table>
<thead>
<tr>
<th>Samples</th>
<th>10% aq. NaOH</th>
<th>10% aq. EtOH</th>
<th>5% aq. HCl</th>
<th>Water</th>
<th>Detergent</th>
</tr>
</thead>
<tbody>
<tr>
<td>WPUDCO-1</td>
<td>–</td>
<td>MS</td>
<td>–</td>
<td>MS</td>
<td>N</td>
</tr>
<tr>
<td>WPUDCO-2</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

MIBK, Methyl isobutyl ketone; MS, mild swelling; N, no swelling.
system with WPUDCO-2 shows less distorted surface morphology with 1000 cycles of abrasion and the weight loss was recorded as about 6 mg. This concludes the ability of CO based PU prepolymer as a good coating material.

4.5.2 Chemical resistance and gloss

When tested under the experimental chemical environments of 10% aqueous NaOH (w/v), 10% aqueous ethanol (v/v) and 5% aqueous HCl (v/v) solutions, all of the prepolymer films responded well to alkali, solvent and acid environment. No weight loss was recorded in water. The swelling conditions after 21 days of testing are provided in Table 5. From the data shown in Table 5, it is observed that no significant difference in terms of weight loss was noticed for any of the CO based WPU prepolymer dispersions. This may be due to compact structure with strong chemical bonding within the networking structure in the system [9]. Among the other reasons are formation of good cross linking between the three dimensional network with increase in the hard segment in the PU matrix and strong interfacial bonding within the polymer matrix in the WPUD structure. However, under acidic conditions, the films countered weakly, which may be due to rapture of crosslinks in acidic conditions [33]. Table 5 shows that the gloss of the film decreases with increase in the molar ratio, which may be due to increase in the cross linking in the macromolecules by covalent bonding [29].

4.5.3 Pencil hardness

The results of the pencil hardness test carried out for WPUDCO prepolymer films for different -NCO/OH are given in Table 4. According to García-Pacios et al. [32], the scale of the pencil hardness of the coatings follows in order as below:

\[
\text{Soft} \leftarrow 6B \rightarrow 5B \rightarrow 4B \rightarrow 3B \rightarrow B \rightarrow HB \rightarrow F \\
\rightarrow H \rightarrow 2H \rightarrow 3H \rightarrow 4H \rightarrow 5H \rightarrow 6H \rightarrow \text{Hard}
\]

Pencil hardness values were found to be 3B for both of the films. This suggests that with increase in the NCO/OH ratio, the physical hardness of the films was the same. Increasing of pencil hardness for the films can be attributed to the extent of cross-linking of the PU prepolymer derived from CO. The extent of pencil hardness depends upon the crosslink density, molecular weight of chain extender, hard and soft segment ratio, etc. This inference of increasing in the hardness is also supported from mechanical results as obtained for films [3, 31].

4.5.4 Contact angle (θ)

The behavior of films towards the water was evaluated considering the contact angle measurement. The data regarding the contact angle measurement for the PU-prepolymer is provided in Table 4. The study suggests that the contact angle decreases with increase in -NCO/OH ratio for the CO based prepolymer. The data obtained from Table 4 indicates that the contact angle for WPUDCO-1 is about 76.6°, whereas it decreases to the value of 74.5° for the WPUDCO-2 prepolymer. This decrease in contact angle is mainly due to the presence of more polar hydroxyl groups on the surface of the higher -NCO/OH ratio in the film [9, 29]. Thus, increase of -NCO/OH ratio of the WPUDCO prepolymer matrix helped to improve the wettability and reduced the θ value.
5 Conclusions

This investigation describes how CO based aqueous PU prepolymer dispersion was synthesized in an environmentally friendly process employing using CO, IPDI and DMPA in varying NCO/OH ratios of 1:3 and 1:5. The influence of molar ratio on the film properties was noted during the study. The FT-IR study suggests that the -C=O and N-H stretching vibration study confirms the formation of higher hydrogen bonding with increasing molar ratio. Moreover, the morphological images obtained from SEM and TEM provided inferences similar to the FT-IR results. The mechanical properties showed improvement in strength with increasing hard segment content to the macromolecule. The coating properties, like gloss and contact angle, are in good agreement with our results obtained by FT-IR and SEM. Improvement in the abrasion resistance properties shows the compactness of the film increasing with the molar ratio, which is further confirmed from our SEM images. By the above obtained results, we can further conclude that replacement of petroleum based polyol with a bio-renewable CO provides us similar properties and is helpful in obtaining nanocomposite coatings and other useful alternate green products.

References


Bionotes

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Siva Sankar Panda completed his MTech degree in surface science and engineering and is presently pursuing his research work in the field of synthesis and characterization of thermosetting polyurethane systems including elastomers and foams, particularly utilizing bio-based materials.

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Sanjay K. Nayak

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