Research Article

Investigations on the Structural and Mechanical Properties of Polyurethane Resins Based on Cu(II)phthalocyanines

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This work report was reported on the effect of the addition of organic filler, that is, 2(3),9(10),16(17),23(24)-octahydroxycopper(II)phthalocyanine [(OH)₈CuPc] (3), on the thermal, tensile, and morphological properties of a polyurethane matrix. The mechanical and dynamic mechanical thermal tests together with microstructural characterization of CuPc/PU composites were performed. The three PU composite films containing up to 1, 15, and 30 wt% of CuPc have different behaviors in terms of their morphological issues, thermal properties, and tensile behavior in comparison with the PU film as the reference material. Very high elongations at break from 910% to 1230%, as well as high tensile strengths, illustrate excellent ultimate tensile properties of the prepared samples. The best mechanical and thermomechanical properties were found for the sample filled with 30 wt% of CuPc.

1. Introduction

Polyurethane (PU) is widely used polymeric material as a kind of coating for different daily life applications, such as fiber, automobile, construction, and biomaterials [1]. It improves the appearance and lifespan for many different materials. On automobiles, PU coatings give improved color retention, high gloss, corrosion resistance, and improved scratch [2]. Different types of PU coatings are used in building floors, concrete supports, and steel trusses which are spray coated. They were used against environmental deterioration [3].

There are six different groups of PU coating types assigned by ASTM. Most of them are high solids and solventless PU coatings [4]. PU are family of engineering thermoplastic elastomers.

It possess a good cost/performance ratio. Different kinds of polyurethane based coatings have been developed and used in different industries due to their superior properties, such as flexibility at low temperature, high abrasion resistance, high impact and tensile strength, high transparency, excellent gloss, color retention, corrosion protection properties, and

good weathering resistance [5, 6]. However, polyurethane has some disadvantages, that is, low thermal resistance, low adhesion, and low mechanical and anticorrosive properties [7].

In recent years, researchers have tried to conquest these disadvantages through different ways. Addition of pigments to the coatings has been introduced as an effective way to obtain polyurethane based coatings with enhanced mechanical and anticorrosion properties [8, 9]. In this regard, the use of fillers in polymer matrix allows for further improving of mechanical behavior. The resulted composites have properties different than the properties of the bulk polymer matrix itself [10–12].

There are a large number of reports in the literature indicating that the mechanical properties of the polyurethane based coatings can be significantly improved through improving tensile strength and Young's modulus of the coating [13].

The chemical structure and properties of polyurethane are influenced by using the metal complex systems based on transition metal for their synthesis, where metal complexes have the ability to order the chains, as well as have an effect

on the chemical properties, and can improve the mechanical and anticorrosion properties of the coatings of polyurethanes [14].

They understood that the procedure of composite preparation is so important which can affect the filler dispersibility in the resin. It was shown that there is a logical relationship between the glass transition temperature (T_g) of the coating and the amount of resin chemically bonded to the filler surface. Fillers could increase the T_g of the coating when the resin segment chemically linked to the surface of particles. Depending on the surface nature of the filler, they could migrate to the surface of the coating or remain in the bulk [15, 16].

Metallophthalocyanines are interesting classes of organic fillers; they have been used as a new brand of materials to reach this target, due to their high specific surface area and thermal and chemical stability [17].

The contribution of our group to this field of research has been quite remarkable and described in detail in [18, 19].

As reported in literature, a considerable academic research efforts have described some metallophthalocyanine derivatives modified coatings for improving the mechanical and anticorrosion properties of the coatings. Yagi et al. [20] used cobalt(II)phthalocyanine as filler linked to a thermoplastic polyurethane resin.

In addition, copper phthalocyanine was used as a filler in a PU matrix to enhance its dielectric properties [21]. The mechanical and dynamic mechanical properties of Fe-octacarboxyl acid phthalocyanine (Fe-OCAP)/PU was evaluated by tensile tests and dynamic mechanical analysis. The results indicated that the incorporation of Fe-OCAP significantly improved the tensile strength, elongation at break, and thermal deformation property of PU matrix [22].

Therefore, the improvements of the mechanical properties of polyurethane as mentioned above are essential for its industrial, technical requirements for several applications and help to create high performance PU coatings [23]. In light of the above considerations, this work reports how the presence of CuPc as filler can influence the mechanical behavior of polyurethane coating in composite forms based on bonding between CuPc and PU chains (referred to as CuPc/PU here).

2. Materials and Methods

2.1. Materials. PU coating sample (Nitocoat UR512) was developed by Fosam Company Limited (Saudi Fosroc), Industrial Zone, Jeddah, KSA.

The octahydroxycopper(II)phthalocyanine (**3**) was synthesized as reported in our previous work [24]. Analytical grade dimethylformamide (DMF) was dried with CaH_2 , distilled in vacuo, and stored under dry nitrogen. The other reagents, such as organic solvents and bases, were analytical grade. Dimethylacetamide (DMAC) was purchased from Sigma Aldrich and used as received.

2.2. Apparatus. Microwave oven utilized for heating was used: Discover Lab Mate single mode microwave cavity from

CEM Corporation. The reactions were conducted in a 25 mL Schlenk tube, with a maximum operating temperature of 180°C and a maximum operating pressure of 8 bar.

2.3. Synthesis of 2(3),9(10),16(17),23(24)-Octahydroxycopper(II)phthalocyanine $[(\text{OH})_8\text{CuPc}]$ (3**).** A solution of **2** was suspended in dichloromethane (80 mL) and BBr_3 (20 mL, 240 mmol) was added under N_2 . The mixture was stirred for 2 days at room temperature, then methanol was added slowly, and dark green suspensions were formed. The suspended solution was centrifuged. The precipitated solids were filtered off, washed with methanol, and dried under vacuum, to yield 80% of **3**, respectively, as black blue powder (Scheme 1).

IR (KBr) $\text{m}(\text{cm}^{-1})$: 3308 (br, OH), 2953, 2925, 2851, 1660, 1542 (s), 1469 (s), 1440 (m), 1322 (m), 1274 (m), 1144 (s), 1130, 920 (s), 880 (m), and 753 (m). UV-Vis (DMF), λ_{max} (nm): 679, 610, and 353. MS (FD): m/z 704.07 (M^+).

2.4. Preparation of Copper Phthalocyanine/Polyurethane Composites. A solution-cast method was used to fabricate the CuPc/PU composite films. A calculated amount of CuPc was added to a solution of PU in DMAC. The Ultra-Turrax T25 digital Homogenizer was used to complete blending the CuPc with the polyurethane/DMAC solution at high speed rotation 24,000 rpm for 15 minutes. The mixture was then ultrasonically stirred for approximately 2 h to obtain a homogeneous solution. Afterwards, the mixture was casted on either glass or cement substrates at different wet thicknesses. The CuPc/PU films were left for 6 hours at room temperature, allowing for evaporation of the solvent. The schematic of possible dispersions of CuPc in PU was presented in Scheme 2. In this manner, three samples with CuPc content of 1, 15, and 30 wt% were prepared. The resulting composites were labeled CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU, respectively.

2.5. Preparation of Test Specimens. Polymer specimens of PU or polymer composites of CuPc/PU ca. 2 mm thickness were obtained by pouring the above mixture into the bone-shaped molds. The molds were left at room temperature for 6 hours. After evaporation of the solvent. The resulting polymer composite specimens were then easily removed from the bone-shaped molds. They were stored under vacuum at room temperature until needed for testing.

2.6. Characterization Techniques. FT-IR spectra were recorded on a Bruker tensor 27 FT-IR spectrophotometer utilizing a Spectra-Tech ATR attachment model 0012-405 using a horizontal ZnSe crystal. Spectra were analyzed using Opus 6.0 software. The parameters used for the determination of each spectrum were the following: Mirror velocity: 0.4 cm/s Spectral range: 400–4000 cm^{-1} . Resolution: 8 cm^{-1} Number of scans: 512. The Ultraviolet-Visible Spectroscopy (UV-Vis) spectra of the fresh and produced CuPc were taken in *N,N*-dimethylformamide (DMF) using a Shimadzu UV-1800 spectrophotometer. FD mass spectra measurements were carried out with a Varian MAT 711 A spectrometer and

SCHEME 1: Preparation of octahydroxycopper(II)phthalocyanine **3**.

reported as mass/charge (m/z). Elementary analyses were performed on a Carlo Erba Elemental Analyzer 1104, 1106.

XRD was performed on an INEL CPS 180 powder diffractometer EQUINOX 1000 system (filtered Cu K α 1 radiation, 30 KV 30 mA, spinning sample holder). The powder pattern analysis was processed by using Match software for phase identification with both COD and ICDD database, IMAD-INEL data processing software for graphical illustrations, MAUD software for Rietveld analysis method, and Fityk software for FWHM estimations.

Scanning electronic microscope (SEM) was used for investigating the surface morphology of CuPc, PU, and CuPc/PU. They were examined with a scanning electron microscope (JSM-6360LA, JEOL, Tokyo, Japan).

The abrasion resistance test of the films was measured using a Taber Abrasion Tester Model 5150. The pull-off test of the films was measured using an Elcometer adhesion tester. The test is done by securing loading fixtures (dollies) perpendicular to the surface of a coating with an adhesive.

The stress-strain behavior of the films was measured using an Instron Model 4400 Universal Testing System controlled by Series IX software. This type of machine has two

crossheads; one is adjusted for the length of the specimen and the other is driven to apply tension to the test specimen.

Dynamic mechanical analyses were performed with a TA Q800 dynamic mechanical analyzer. The size of samples was about 11.0 mm $\times$ 7.0 mm $\times$ 0.30 mm. A temperature scan mode was used and the temperature was ramped at a rate of 3°C/min from -50 to 250°C under a nitrogen atmosphere with the frequency of 30 Hz and amplitude dynamic control of 15 μ m with dynamic forces of 100 mN. The parameters such as storage modulus, $\tan \delta$, and displacement as a function of temperature (which corresponded to the irreversible deformation) of the samples were obtained.

3. Results and Discussion

3.1. Characterization of Octahydroxycopper(II)phthalocyanine [(OH)₈CuPc] (3**).** The first main task for this work was the synthetic route to novel peripherally octasubstituted copper(II)phthalocyanine **3**, Scheme 1. It was synthesized as reported in our previous work [24]. The new copper phthalocyanine **3** was purified.

SCHEME 2: The schematic of possible dispersions of CuPc in PU skeleton.

It was characterized by spectral data (IR, UV-Visible spectroscopy, mass spectral data, and elemental analysis). The characterization data of the new compound were consistent with the assigned formula. In the IR spectra of octahydroxyphthalocyanine $[(OH)_8CuPc]$ (**3**), the appearance of OH stretched at $\nu = 3228\text{--}3210\text{ cm}^{-1}$ was observed.

In the mass spectrum of **3**, the presence of molecular ion peaks at m/z 704.07 (M^+) confirmed the proposed structure. The result of elemental analysis also confirmed the structure of complex **3**. The electronic absorption spectra of **3** were carried out in DMF at room temperature. The split Q bands appeared at 679 and 610 nm, while the split B band remained at 353 nm. The CuPc/PU composites were prepared by solution-cast method.

3.2. Characterization of CuPc/PU Composite Films

3.2.1. Structural Properties of Cured Coatings

Fourier-Transform Infrared Spectroscopy. In the polyurethane N=H and C=O are the significant bonds, which represent the urethane and the carbonyl linkages. The carbonyl in the amide group ($-NHCO-$) appeared at $\nu = 1643\text{ cm}^{-1}$. The N-H stretching vibration overlapped with the vibration of the O-H of the carboxyl group in CuPc appeared approximately at $\nu = 3404\text{--}3435\text{ cm}^{-1}$. The C=O stretching vibration (free urethane C=O) appeared at $\nu = 1722\text{ cm}^{-1}$ and the absorption bands in the range of $925\text{--}933\text{ cm}^{-1}$ were attributed to the stretching vibration of $-C-O-C-$.

X-Ray Diffraction (XRD). The X-ray diffraction (XRD) patterns of pure PU, 1 wt%, 15 wt%, and 30 wt% of CuPc/PU were performed. The hard segments in the PU appeared at the diffraction peak near $2\theta = 20.26^\circ$, and the sharp peak were seen at 2θ value of 110.20° indicative of metallic copper. The intensity of the peak at $2\theta = 73^\circ$ for CuPc(30%)/PU was much stronger in comparison with that of CuPc(1%)/PU.

Energy-Dispersive X-Ray Spectroscopy (EDAX). The EDAX copper mapping for PU, 1 wt%, 15 wt%, and 30 wt% of CuPc/PU samples, respectively are shown in Figure 1. The pure PU clearly described a surface with no Cu, whereas the other three surfaces contained a certain percentage of Cu. The 1 wt% CuPc/PU composite sample showed an absorbance at 8.10 keV, but the 15 wt% CuPc/PU and 30 wt% CuPc/PU composite samples showed much larger absorbance's counts.

3.2.2. Optical and Imaging Properties of Cured Coatings. In order to examine the microstructure of the polyurethane composite coating samples, SEM analysis was conducted. Figures 2(a)–2(d) showed the SEM micrographs of the agglomerated crystal structure of PU and CuPc/PU composites.

SEM micrographs of PU, CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU, respectively, were illustrated in Figure 2. It indicated the full dispersion of CuPc into PU chains. It was found that CuPc molecules aggregated into nearly spherical particles in the PU matrix for CuPc(1%)/PU, due to insufficient addition of CuPc amount; see Figure 2(b). This behavior was due to the planar shape and aromatic nature of CuPc.

FIGURE 1: EDAX for PU (a), CuPc(1%)/PU (b), CuPc(15%)/PU (c), and CuPc(30%)/PU (d), respectively.

FIGURE 2: SEM Images of PU (a), CuPc(1%)/PU (b), CuPc(15%)/PU (c), and CuPc(30%)/PU (d), respectively.

TABLE 1: Abrasion test results for CuPc/PU composites.

Number of cycles	PU	CuPc(1%)/PU	CuPc(15%)/PU	CuPc(30%)/PU
100 cycles	0.08	0.05	0.04	0.03
200 cycles	0.03	0.01	0.01	0.01
300 cycles	0.03	0.01	0.02	0.02
400 cycles	0.04	0.03	0.02	0.02
500 cycles	0.03	0.02	0.02	0.02
Total weight loss in gm	0.21	0.12	0.11	0.10

FIGURE 3: Adhesion test of PU (a), CuPc(1%)/PU (b), CuPc(15%)/PU (c), and CuPc(30%)/PU (d), respectively.

The aggregation behavior was smaller than in the case of the particles in CuPc(15%)/PU sample; confer Figure 2(c). It can be observed that the mobility of the bonded CuPc was hindered by the PU chains and the growth of CuPc crystals was limited. Actually, the aggregation of CuPc readily occurred in CuPc(1%)/PU. The shapes of the CuPc particulates change into irregular shape. It showed improved separation and decreased agglomeration compared to that of PU sample.

3.2.3. Mechanical Properties

Abrasion Test. Resistance to abrasion of the surface of PU composite samples was established by differential weighing of

the specimen through a specific number of test cycles. Poor abrasion was denoted by higher weight loss as in pure PU samples, while good abrasion was denoted by less weight loss as in CuPc/PU composite samples as shown in Table 1.

Adhesion Test. The adherent strength of the PU sample and cured films of CuPc/PU were shown in Figure 3. All CuPc/PU composite film samples exhibited good adhesion to mild concrete substrates; it was quite flexible, good impact resistance and hardness, except pure PU sample failed in impacting resistance and flexibility, where the record value of adhesion for PU was 1.73 MPa and was raised to 3.00 MPa for CuPc/PU samples.

FIGURE 4: Stress-Strain behavior for PU and CuPc/PU composites.

Stress-Strain Analysis. The stress-strain tests for CuPc/PU composite films were carried out to understand the effect of CuPc reinforcement on the physical and mechanical properties of the PU composite films, when a load transfers from PU to CuPc.

The stress-strain curves of pure PU and the CuPc/PU composite films with different ratio contents of CuPc are shown in Figure 4. The tensile strength of the samples increased from 31.1 to 58.3 MPa; also the elongation at break of the samples increased from 910% to 1230% due to the increasing of CuPc content from 1 to 30%. The rapid increase in tensile strength and the elongation of the uncrosslinked polyurethane phase happened through the stress-strain relationship. In addition, the CuPc/PU composite film showed a uniform change, as evidence for a more bounded network. This behavior was close to the ideal (theoretical) stress-strain curve as shown in Figure 4.

The elastomeric behavior of CuPc/PU composites was observed; the values of Young's modulus, tensile strength, and elongation at the break point of the CuPc/PU composite films were different than values of PU matrix.

The mechanical properties of CuPc/PU composite films were more excellent than those of pure PU, due to the highly homogeneously dispersion of CuPc within the PU chains. Table 2 showed the corresponding tensile strength and the elongation at break of the samples.

3.2.4. Dynamic Mechanical Thermal Properties. The dynamic mechanical thermal analysis (DMTA) investigations for PU sample showed poor mechanical properties due to its more uniformly cross-linking for CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU samples exhibited different dynamic mechanical properties, and they have the best mechanical properties.

Similarly, DMTA can reveal significant details about the structure property relationships of PU films. Viscoelastic properties such as storage modulus, loss modulus, and $\tan \delta$

TABLE 2: Mechanical properties of PU and CuPc/PU composites.

Sample	Tensile strength (MPa)	Elongation at break (%)
PU	31.1	910
CuPc(1%)/PU	32.4	982
CuPc(15%)/PU	40.8	990
CuPc(30%)/PU	58.3	1230

FIGURE 5: Temperature dependence of loss tangent ($\tan \delta$) for the PU, CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU samples.

were obtained as functions of time, frequency, and temperature. The DMTA experiments were done for our PU film samples to know the variation of the mechanical dynamic properties between them.

The curves of $\tan \delta$ as a function of temperature for PU and CuPc/PU composite films showed a loss peak around -25°C , which corresponds to the T_g of soft segments in PU as shown in Figure 5. At the temperature above 50°C , the $\tan \delta$ values of the samples increased corresponding to the T_g of hard segments. However, a clear irreversible deformation of samples was developed in the temperature range.

The logarithm of the storage modulus ($\bar{E}$) versus temperature for the pure PU, CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU was shown in Figure 6. The values of $\bar{E}$ of the composite samples were below -50°C . When the temperature was above -50°C , the values of $\bar{E}$ increased with the increase of filler CuPc content, because the samples were in the glassy state below temperature of -50°C , which reduce the molecular motion of both hard and soft segments. At temperature above the T_g of soft segments, a broad plateau modulus appeared.

It can be seen from Figure 6 that the value of $\bar{E}$ of PU decreased quickly with increasing of temperature, while it decreased in the case of the CuPc/PU composites. This result approved that the addition of filler CuPc enhanced the physical cross-links in PU matrix and improved the mechanical properties of composites.

FIGURE 6: Storage modulus (E') for the PU, CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU samples.

The irreversible deformation of the PU and CuPc/PU composite samples as a function of temperature was shown in Figure 7. The temperatures of deformation of PU, CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU were 170°C, 175°C, 180°C, and 190°C, respectively. The thermal deformation was improved with increasing of the content of filler CuPc.

3.2.5. Chemical Properties of Cured Coatings

UV Weathering Resistant. Coatings are chemically degraded by the effect of UV radiation depending on duration and intensity. In the case of pure PU, a surface embrittlement was formed, followed by a slightly yellowing in the color of the sample.

Addition of filler may improve UV resistance and prevent the deep penetration of UV rays and mechanical destruction. The modified PU with CuPc showed an improvement in the UV resistance. The CuPc/PU samples clearly indicate no degradation or surface discoloration of composite coated samples when exposed to UV radiation.

The surface micrographs of UV exposed for PU and CuPc/PU samples after 1000 hours were shown in Figure 8.

Chemical Resistance Properties. The chemical resistance of PU and CuPc/PU coating series in acid and base solutions was performed for the cured films. No changes were observed for the PU coating modified with 1%, 15%, and 30% CuPc. No appearance of blue color of Cu/PU composites impressed in the acid or alkaline solutions was clearly observed. The acid solutions colors were still transparent until thirty days of the experiment, whereas slightly blue color appeared in basic solutions from the thirty day; it may be due to the action of alkali on urea bonds in PU. This suggests that there is no chemical degradation of Cu/PU composites and the performance of the coating was strong.

It was known that the chemical resistance depends on several factors like the concentration, the period of exposure, the temperature, and the quantity.

Contact of composite coating samples with saturated hydrocarbons, such as kerosene, results in a limited swelling.

FIGURE 7: Irreversible deformation of PU, CuPc(1%)/PU, CuPc(15%)/PU, and CuPc(30%)/PU samples.

Contact of composite coating samples, such as toluene and benzene, afforded a considerable swelling even at room temperature. As ethanol, swelling of composite coating samples caused and lead to a loss of tensile strength.

Ketones such as acetone are partial solvents for thermo-plastic polyurethane elastomers. Solvents like ethyl acetate cause swelling of composite coating samples. Solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) dissolve all polyurethane coating samples.

4. Conclusions

Finally, we wish to comment on the state of our CuPc filler dye. Our results indicated a considerable improvements in mechanical and thermomechanical properties of PU.

As already mentioned above, in the formed composites, the size of the filler CuPc particles dispersed in the PU matrix has enhancement of the mechanical response of the formed composites.

On the other hand, the values of Young's and storage moduli increased with the increase of CuPc filler content, indicating good rigidity (storage and Young moduli) of the samples, high values of the mechanical parameters, and greater thermal stability, and could prove to be a very valuable industrially.

All CuPc/PU samples exhibited good adhesion to mild concrete substrates; it was quite flexible, good impact resistance and hardness, and the record value of adhesion for PU was 1.73 MPa and raised to 3.00 MPa for CuPc/PU samples.

Poor abrasion was denoted by higher weight loss as in PU sample, while good abrasion was denoted by less weight loss as in CuPc/PU sample. The weight loss of the PU specimen after 500 cycles was 0.21 g but for CuPc/PU specimen was 0.10 g only.

The stress-strain curves of PU and the composites with different ratio contents of CuPc showed an increase in the tensile strength of 31.1 MPa (PU) to 58.3 MPa (CuPc/PU) and the elongation at break of the samples increased from 910% to 1230% for the PU and CuPc/PU composite samples, respectively.

FIGURE 8: Samples of PU (a), CuPc(1%)/PU (b), CuPc(15%)/PU (c), and CuPc(30%)/PU (d) before and after being exposed to UV.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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