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Role of silica-based porous cellulose nanocrystals in improving water absorption and mechanical properties

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Abstract: Epoxy resins are important thermosetting polymers. They are widely used in many applications i.e., adhesives, plastics, coatings, and sealers. Epoxy molding compounds have attained dominance among common materials due to their excellent mechanical properties. Here, the sol-gel simple method was applied to distinguish the impact on the colloidal time. The properties were obtained with silica-based fillers to enable their mechanical and thermal improvement. The work which we have done here on epoxy-based nanocomposites was successfully modified. The purpose of this research was to look into the effects of cellulose nanocrystals (CNCs) on various properties and applications. CNCs have recently attracted a lot of interest in a variety of industries due to their high aspect ratio, and low density which makes them perfect candidates. Adding different amounts of silica-based nanocomposites to the epoxy system. Analyzed with different techniques such as Fourier-transformed infrared spectroscope (FTIR) and thermogravimetric analysis (TGA), scanning electronic microscopic (SEM) to investigate the morphological properties of modified composites. The various %-age of silica composite was prepared in the epoxy system. The 20 % of silica was shown greater enhancement and improvement. They show a better result than D-400 epoxy. Increasing the silica, the transparency of the films decreased, because clustering appears. This shows that the broad use of CNCs in environmental engineering applications is possible, particularly for surface modification, which was evaluated for qualities such as absorption and chemical resistant behavior.

Keywords: Bisphenol epoxy; D-400 epoxy; thermal properties; silica; polymer.

1. Introduction

The most advanced technology, such as autos and electronics, are unable to match the unique qualities of the materials. Metals, ceramics, polymers, and alloys are examples (Mubashir et al., 2021). As a result of the enhancement of a number of features. It is necessary to create two composite phases (Mubashir et al., 2018). The matrix and the reinforcement phase (Allie et al., 2018; Aziz et al., 2020a; Jo et al., 2018). For the manufacturing of reinforcement polymers, many types of organic or inorganic fillers are commonly used (Ali et al., 2020). By this, the mechanical, thermal, electrical, and adhesive qualities have been enhanced (Ahmad and Al-Sagheer, 2014; Aziz et al., 2019c; Park and Yun, 2018). In the epoxy system, nanoparticles in a very small proportion are typically used for enhancement. Such modification methods have an impact on inferior reduction processes including curing, heat conduction, and mechanical supplies (Aziz et al., 2020c; Reig et al., 2018; Ullah et al., 2021a). Several factors influence the characteristics of the micro polymer (Ali et al., 2021a). Each component has fundamental qualities, such as shape, dimension, and the nature of its interfaces (Aziz et al., 2019a; Messersmith and Giannelis, 1994; Salahuddin, 2004). Only a modest amount of research on inorganic particles has been done in recent decades. The ability to manufacture composites containing nanofillers, i.e., nanocomposites or nanoparticles is the most significant (Aziz et al., 2020d; Zheng et al., 2021a). They're one of the most hotly debated nano-dielectric systems right now. The fillers are the reinforcing phases (Ali et al., 2021e; Aziz et al., 2019b; Tseng et al., 1999). Polymer-matrix composites are employed in a considerable amount due to their ease of processing (Aziz et al., 2020b; Li et al., 2018; Zhang et al., 2016). They are widely used in a variety of industries, including electrical, automotive (Chuah et al., 2022a; Chuah et al., 2022b), and aerospace (Ahmad and Guria, 2022). Polymer nanocomposites have received greater attention in recent years (Karim et al., 2022). It serves as a replacement for predictable polymer composites (Aziz et al.,

82   2021c; Jamil et al., 2021; Li et al., 2016). The number of nano-size molecules in a polymer

83   composition can significantly improve its mechanical properties (Abbasi et al., 2023; Arshad

84   et al., 2023; Munir et al., 2023). This is mostly due to the nanoparticle's exclusive holdings,

85   which result in effective development properties (Kim et al., 2013; Longmire et al., 2008;

86   Ullah et al., 2021b). Polymer nanocomposites are materials in which at least one dimension

87   of the matrix is strengthened by particles (Aziz et al., 2021a; Aziz et al., 2021d; Chen et al.,

88   2019a). As the reinforced portion, conservative polymer composites are used in the

89   micrometer range (Al Sheheri et al., 2019; Ali et al., 2021d; Chen et al., 2019b). The bulk

90   polymer has a close relationship with the minor particle filling proportion and the composite

91   quality. As a result, the developed filler filling ratio is often required to achieve significant

92   improvements (Alston et al., 2019; Aziz et al., 2021b; Hassanzadeh-Aghdam et al., 2019).

93   Soft rubber particles and silica particles are examples of small collective particles. However,

94   polymer nanocomposites have received more attention than traditional polymers (Ali et al.,

95   2021c).

96   This remarkable enhancement began to be associated with the high surface range (Ahmad et

97   al., 2022). Between nanofillers and the polymer matrix, the volume proportion of

98   nanoparticles sets a substantial limit (Klonos et al., 2019; Li et al., 2018). Researchers have

99   also discovered that nanometer-scale fillers have greater active reinforcing characteristics

100   than micrometer-scale fillers (Ali et al., 2021b; Pan et al., 2019; Terzic et al., 2019). For these

101   active reinforcing effects, high definite surface area is largely responsible. As a result, the

102   area of interface with the polymer matrix affects efficient transmission of load from the

103   outside (Xie et al., 2018; Zotti et al., 2019a; Zotti et al., 2019b). Nanoparticles surface of

104   various materials makes them more valuable is one of the basic aspects of nanotechnology.

105   Geometry, filler kind, crystallinity, surface treatment, and degree of dispersion all influence

106   attributes of nanocomposites. The use of several types of fillers to agglomerate polymeric

materials improves their characteristics. The polymerization technique was used to modify the surface of silica for epoxy molding compounds (EMC), such treatment was explored comprehensively in this work (Ahmad et al., 2023). The current research focuses on epoxy-based nanocomposites. The use of a Fourier transformed infrared spectroscope (FTIR) and thermogravimetric measurements proved that the particles surfaces had been successfully modified. To check and confirm the structural qualities of nanoparticles and nanocomposites, several analysis and techniques were used.

Cellulose nanocrystals are nano-sized components that are biodegradable, biocompatible, and renewable. It offers mechanical strength and stability. Environmental contamination is reduced by employing various bioremediation techniques. The mechanism happening between the contaminant and CNCs adsorbent should be developed in effective new bioremediation strategies. CNCs structural functionalization helps to modify the nanocellulose structure based on which it can be utilized for specific functions. Exploring the mechanisms that contribute to the implementation of CNCs helps further developments and advancement in biomedical applications.

Nanocellulose has drawn a lot of investigation over the last decade since. It is a plentiful natural nanomaterial with a lot of potential. They are formed into multiphase order after dispersing in a polar solvent, resulting in excellent optical and structural characteristics. Significant progress has been made in addressing multi-dimensional qualities and a wide range of high-tech applications of cellulose nanocrystals (CNCs) in many domains, according to the report. In the long run, these qualities have an impact on the composite's overall performance. Cellulose is a polysaccharide macromolecule with a linear structure. Through Vander wall contacts and hydrogen bonds, these macromolecules combine and form microfibers that are aligned and stabilized horizontally, resulting in crystal and non-crystalline areas. As a result, CNCs in all walks of life play a vital role in numerous industrial

applications to provide a complicated approach in the future, as shown in this preliminary study. We present native cellulose nanocrystals that have undergone surface modification through the use of a silane coupling agent as shown in Figure 1.

2. Experimental work

2.1. Materials and methods

Bisphenol epoxy or E-51 (DGEBA) commercially available epoxy.

Diamine D-400 also commercially available epoxy,

3-aminophenyltetraethylorthosilicate (APTES) were supplied from (Thermo scientific) employed as a cross-linker were used in this experiment.

The Aladdin Shanghai industry in China provided the highly pure analytical ethanol absolute (purity 99.7%).

Petri dishes, hot air oven, distilled water,

Silica powder from DINGLONG QUARTZ, China, purity of 99.3%.

During the entire experiment, distilled water was used, as well as other lab equipment. The E-51 epoxy was made by reacting an equimolar quantity with diamine at a 4:2 ratio. In the round bottom flask, 4g of E-51 epoxy and 2g of diamine were combined for this reason. The mixture was then swirled for 3 hours at normal temperature. After forming a clear and transparent solution, it was poured into 2-3 clean containers Petri dishes. These containers were then carefully placed and baked for 120 minutes at 100°C in a hot air oven. After curing, another 45 minutes at 60 °C were put in vacuum oven. A flexible thin film with a consistent of 1cm was cast. FTIR, TGA and Raman techniques were characterized on the same day. Two different types of composite systems were created, with a different quantity of silica. Each system was given a distinctive abbreviation. The measured phase separation and the percentage of silica are given in Table 1.

2.2. Epoxy-silica composite material and casting thin films

Silica composite films were obtained with varying %-ages using hydrolysis methods. The separation of silica was found to be 20 percent. As the silica content increased the transparency of the films reduced. Epoxy-silica composite film was found with consistent thickness. Epoxy-silica systems were created by pouring them into petri dishes with a flat surface.

2.3. Epoxy-silica composite coupled and uncoupled synthesis

In a separate beaker, the uncoupled epoxy-silica composites were carefully weighed. The E-51 epoxies and tetramethylorthosilicate (TMOS) were added. Stirred for an hour at normal room temperature with an anhydrous state. After obtaining a clear mixture, a stoichiometric amount of water was added and swirled at room temperature for another 2 hours. The temperature was increased up to 80 °C and swirled it for another 8 hours. After that, diamines were added to the epoxy system as a curing agent and mixed for 1 hour. The mixture was then poured and baked at 100°C for 90 minutes into petri dishes for curing process completion. The flexible films were obtained with a uniform thickness of 1cm (Ali et al., 2021b; Zheng et al., 2021b). APTES was combined with TMOS to chemically connect the inorganic phase. On one side, the APTES combined with silica, while on the other, it reacted with the secondary amino group of the epoxy. As a result, chemical linkages were formed between two phases in APTES (Ahmed et al., 2019; Ahmed et al., 2021). This improved system, which is presented in Table 2 was used to make composites with varied percentages of silica, just like an uncoupled system. E-51 epoxy system, 3-APTES, and epoxy-silica linked was also carefully weighed. This mixture was added and stirred for one hour continually to form a solution in glass plates. Tetraethylorthosilicate and distilled water was added drop by drop and stirred the mixture for the next 5 hours continually at temp; 60 °C to

182   maintained the solution. Diamine was added to the mixture at a calculated amount, which was

183   then agitated for 60 mints until it became homogeneous. To eliminate the contaminants, the

184   mixture was poured onto Petri plates and baked at 100 degrees Celsius. At 110°C, films were

185   then cured for 1 hour. A constant thickness of 1cm was used to make the solid films.

186   Different techniques, including as FTIR, Raman, and TGA, were used to characterize the

187   films.

188

189   2.4.   Characterization of the material

190   Various analytical approaches were used to characterize epoxy-based silica nanocomposites

191   systems with varying %-ages. The morphology of polymer nanocomposites with and without

192   the influence of APTES was investigated. It provides qualitative information regarding

193   conversion of monomer-to-polymer. Fourier transform infrared spectroscopy (FTIR) Nicolet-

194   5700 spectrophotometer by the KBr-pellet method and scanned from 4000-500 cm^{-1} with a

195   resolution superior to 0.5 cm^{-1}. Exciting light of 532 or 633 nm is used to perform. Raman

196   spectroscopy measurements are performed at room temperature, using exciting radiation of

197   532 or 633 nm, with an incident power included between 0.04 and 5 mW. Raman spectrum of

198   polymer nanocomposites is characterized by three typical bands, namely at 1350 cm^{-1} the D

199   band, at 1580 cm^{-1} the G band, and the 2D band at a frequency at 2700 cm^{-1}. The D band is

200   related to the breathing mode of carbon atoms on the aromatic ring and is not always visible;

201   the G peak is determined by in-plane optical vibrations of the sp_2-bonded carbon atoms,

202   whereas the 2D peak is approximately double the frequency of the D band as well as arises

203   from second-order Raman dispersion process. Thermal gravimetric analyses (TGA) TA,

204   Q200 were used. For stirring Magnetic stirrer 85-1 type Zhi Wei Shanghai was used. (Cence

205   TG16-WS) Hunan Xiangyi Laboratory Instrumental Development Co. Ltd was used as

206   centrifuged for centrifugation. The thermal stability of the polymer films in these

207 nanocomposites added the creation of an inorganic network according to the findings. As the

208 amount of silica in the system increased. The deterioration process has slowed as the TMOS

209 content has increased.

210

3. Results and discussion

3.1. FTIR spectra of cured systems

213 FTIR spectrum nanocomposites system in Figure 2, reveals a variety of peaks, revealing vital

214 information about SiO_2-epoxy. The removal of specific epoxide and amino functional group

215 confirmed the creation peaks of the epoxy network. O-H (str) at 3741 cm^{-1} and N-H (str) at

216 3642 cm^{-1} functional groups, respectively (Zhang et al., 2021).

217 At 2968 cm^{-1} a peak develops while C-H with extending vibration. The C-H stretch at 925

218 cm^{-1}, confirms the successful formation. In the functional group regions, cured

219 nanocomposites systems show some comparable peaks. The asymmetric stretching vibration

220 peak of C-H is located at 2966 cm^{-1}, as can be seen in Figure 3. The band appeared at 1452

221 cm^{-1} corresponding to CH_2 in epoxide moiety. The band generated at 1775 cm^{-1} attributed to

222 the carbonyl group (C=O) in epoxide network. Similarly, the band for Si-O-Si symmetric

223 vibrations was appeared at 129 cm^{-1}.

224

3.2. Raman spectra of nanocomposites system

226 To examine the chemical groups in the nanocomposites system, Raman spectra were also

227 study. Several Raman spectra bands conforming the epoxide vibration in the 1230cm^{-1} to

228 1280 cm^{-1} region. At 1250 cm^{-1}. The epoxide groups absorption in the epoxy resin mixture

229 determines the intensity of this peak. The epoxide ring deformation appears to be weaker at

230 912 cm^{-1}. At 1118 cm^{-1}, the other Raman peaks show epoxy resin backing vibrations.

231 Throughout the curing process, they maintain the same intensity. The oxirane ring was

232 designated at 3070 cm^{-1} of C-H stretching peak are shown in Figure 4.

233

3.3 Thermal stability of composites and nanocomposites system

235 The polymer composite shows thermal deterioration with a maximum temperature (T_{max}) of

236 539 °C. There was no evidence of silica content. The thermogravimetric analysis curve

237 begins at 220 °C and gradually decreases in weight until it reaches 427 °C due to TMOS

238 moisture condensation reaction absorption. Because open-chain carbon has a lower energy of

239 degradation than closed-chain carbon (Chuah et al., 2022c; Hii et al., 2009; Cheah et al.,

240 2016; Chuah et al., 2021). Figure 5 shows the curve of weight loss abrupt fall from 500 °C to

241 519 °C, indicating that open chain carbon combustion begins about 450 °C. For silica-based

242 epoxy, a two-step degrading mechanism was investigated. The neat epoxy composite

243 polymer degradation temperature was raised. With the enormous weight loss compared to

244 silica loadings, the thermal degradation temp; increased at 15% of silica. This research

245 increased the thermal stability and organization of nanocomposites at high temperatures. All

246 uncoupled silica-epoxy systems experience a reduction due to the presence of a silica

247 network. Thermal breakdown of macromolecular chains is further slowed by the reaction of

248 the thermograms of the uncoupled nanocomposites system as shown in Figure 6.

249

3.4   CNCs modification

251 Round bottom flask of 150 mL with 100 mL distilled water and 5 mL (KH-560) were added.

252 For adjust the pH to 4, acetic acid was added to the mixture and stirred for 60 mints. 0.3 g of

253 CNCs were added to the mixture and sonicated for thirty minutes were used for dispersion.

254 The mixture was then agitated for 150 minutes at room temp; To remove excess silane, it was

255 washed twice by centrifugation techniques with ethanol and once with distilled water. It was

256 then dried for 6 hours at 80°C in an oven. The crystals were identified as MCNCs and

257 preserved in a glass vial for further use.

258 One of the simple ways to obtain materials with the appropriate qualities is to purchase

259 surface changes from various natural and synthetic resources through various treatments

260 (Dhakal et al., 2012). The effects of monomers on particle size have been studied in the past

261 (Jiménez Saelices et al., 2019). However, research on the effects of KH-560 treatment on the

262 physical and chemical properties of CNCs is limited (Javanbakht et al., 2016a; Javanbakht et

263 al., 2016b). As a result, the effects of KH-560 treatment on physical and chemical

264 parameters, such as CNC water absorption, were investigated in this study. The CNCs' OH

265 group was discovered to be responsible for water/moisture absorption. These functional

266 groups, which consist of a linear polymer lacking water units joined by the glycosides bond,

267 playing a crucial role in the surface modification of CNCs (Sun et al., 2005; Thakur et al.,

268 2013). Mercerization is the most effective method for removing contaminants from natural

269 cellulose's surface. The CNCs function group is started utilizing the standard manner

270 described in the literature in this study. After that, the CNCs are changed with a silane

271 coupling agent.

272

273 3.5 CNCs with coupling agent

274 Figure 7 depicts the KH-560 modified with CNCs. OH, groups are present on the surface

275 prior to modification. The peak of the Si-O-C bond appeared at 1028 cm^{-1}. The existence of

276 the silane functional groups was clearly demonstrated by the peaks at 1575 cm^{-1}. It signifies

277 that the surface of CNCs was successfully changed with KH-560 silane (Abraham et al.,

278 2016; Xu et al., 2013).

279

3.6 Thermal properties

The cellulose nanocrystals (native and modified) are a dynamic approach to investigating the response to temperature change. Native cellulose nanocrystals have a different thermal behavior than modified cellulose nanocrystals (Li et al., 2011; Ma et al., 2017). Figure 8 demonstrates that thermal deterioration occurs at a higher temp; range in CNCs, owing to its size, excellent thermal stability, and a considerable drop in molecular weight degradation in the high amorphous regions. The disintegration of the CNCs follows a usual pattern, with temperatures ranging from little above 340-460°C, with a minor quantity of ash remaining at 600°C. The insertion of sulfate groups by hydrolysis found considerably lower the activation energy of CNCs breakdown (Feng et al., 2017; Lu and Hsieh, 2010). Furthermore, the disintegration of CNCs at low temp; 370°C implies have a quicker heat transmission rate. The thermal conductivity of the (NCNCs and MCNCs) mixtures is nearly identical, while the modified mixture's thermal conductivity is lower than that of the native ones (Fortunati et al., 2012; Kumar et al., 2014).

3.7 Scanning electron microscopy

CNCs particularly unaltered are brittle and easily shattered. The SEM image shows a broken cross-section surface of the CNCs. The surface layers are apparent in which the orientation of the nanocrystals is clearly seen exhibit reasonable homogeneous mixture as shown in Figure 9A. Agglomeration happens when more cellulose nanocrystals are added (MCNCs) as illustrated in Figure 9B. Dispersion of modified cellulose nanocrystals also appear on the surface. A micro-sized interfacial interaction between MCNCs and epoxy system could be visible (Espino-Perez et al., 2016; Majoinen et al., 2012; Peng et al., 2017). It indicates that the rough surface layer on the surface of modified CNCs materials treated with KH-560

exhibits a significant improvement. The elimination of contaminants is responsible for morphological alterations.

3.8 Water absorption study

The water absorption of epoxy materials has been a research topic in many studies (Chow, 2007; Takeshita et al., 2014). The improved performance of epoxy materials can be considerably influenced by the amount of water absorbed; its structural applications are limited. Combining natural hydrophilic elements as enhancers, such as CNCs, may exacerbate moisture absorption and have a negative impact on nanocomposites' characteristics. Grafting boosted the water uptake capacity, according to reports (Cankaya and Temuz, 2015; Kumar et al., 2019; Mekonnen et al., 2013). CNCs hydrophobic transformation has the ability to alleviate this fundamental issue. This research looked at how adding native and enhanced CNCs to epoxy composites influences water ingress. Within seven days, the water absorption mode of native and modified CNCs is incorporated into clean epoxy resin and nanocomposite materials. Different CNCs are processed with the KH-560 in accordance with the approach described in the experimental section as shown in Figure 10. CNCs surface functionalization using the KH-560 is a simple approach to modify the surface properties. Because hydrophobic polymers are grafted to CNCs, it is not as successful as transplant copolymer technique. Hydrolysis, condensation, and bond formation are all functions of the KH-560 CNCs. One of the most practical ways to produce materials with the desired qualities is to modify the surface of materials purchased from various natural and manmade resources using various treatments. The effects of KH-560 treatment on the physical and chemical properties of CNCs have been examined, as well as the impacts of KH-560 treatment on the mechanical properties of polymer composites. As a result, here investigated the impacts of KH-560 treatment on physical and chemical parameters, such as

329 CNCs water intake. Moisture absorption was discovered to be caused by hydroxyl groups

330 contained in the backbone of CNCs. Because such substrates are made up of linear with

331 repeating glucopyranose units. These functional groups are also important in surface

332 modification. The function group of CNCs is launched in this work utilizing the standard

333 approach and the reinforcement method of various concentrations. After that, silane couplers

334 are used to surface-functionalize the modified CNCs.

335 On CNCs, the KH-560 coupler was found to be the most efficient. Chemical resistance is

336 another feature of these functional CNCs. The functionalization of silane improves the

337 chemical resistance of CNCs. On CNCs that are vulnerable to chemical attacks, this behavior

338 is likewise attributed to the blockage of the active function group. Water is dependent on the

339 existence of the polymer matrix's midstream. (Becker et al., 2004; Jahan et al., 2018). By

340 taking up available space, nanoparticles can usually restrict their acceptance. The kind,

341 concentration, and function of nanoparticles, on the other hand, are critical in preventing

342 moisture absorption. The absorption was higher when primary CNCs and modified ones were

343 used instead of the neat epoxy matrix concentration range. Higher grafted modified CNCs,

344 considerably enhanced water absorption relative to unmodified CNCs, while unmodified

345 CNCs' moisture absorption reduced. Nanocomposites have a much lower moisture absorption

346 rate than native CNCs, and their load is just 1% of that of modified CNCs. It becomes

347 hydrophobic when the OH function is replaced by hydrophobicity. It appears that the

348 modified CNCs' hydrophobic qualities are transmitted to epoxy nanocomposites, resulting in

349 a reduction in water absorption.

350

4. Conclusion

352 Hydrolysis is a critical method. Different silica-based epoxy nanocomposites were used in

353 this study. The CNCs function group is started utilizing the standard manner described in the

354 literature in this study. After that, the CNCs are changed with a silane coupling agent. The

355 existence of the silane functional groups was clearly demonstrated by the peaks at 1575 cm^{-1}.

356 The thermal characteristics of the modified nanocomposites have been significantly

357 improved. The surface layers are apparent in which the orientation of the nanocrystals is

358 clearly seen exhibit reasonable homogeneous mixture. CNCs, with KH-560 coupler was

359 found to be the most efficient. The functionalization of silane improves the chemical

360 resistance of CNCs. The epoxy properties are developed by using an APTES coupling agent

361 with silica. The interfacial contact was improved by using silica-based nanocomposites. The

362 20 % of silica was shown greater enhancement and improvement. They show a better result

363 than D-400 epoxy. The temperature has a significant effect on changed silica over the course

364 of the experiment. The rate of hydrolysis rises with time, as does the alteration of silica.

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