Preparation and characterization of nanostructured biohybrid

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A R T I C L E   I N F O
Article history:
Received 1 April 2011
Received in revised form 6 May 2011
Accepted 10 June 2011

Keywords:
Biobybrid
Castor oil
Coating

A B S T R A C T
Recently, biohybrid materials have gained considerable interests worldwide. They consist of bioresource based derivative as organic matrix in combination with inorganic components with synergistic properties of both such as environment friendliness, biodegradability, flexibility of the former coupled with hardness, UV radiation stability, thermal stability and solvent resistance of the latter. In the present work, we have prepared DGEBA/Castor oil nanostructured biohybrid with a metal alkoxide as inorganic precursor for reinforcement of the matrix. The structure, morphology, thermal behavior and coating properties of the prepared biohybrid have been studied. Our studies revealed that the said biohybrid can be safely employed up to 180 °C as nanostructured protective coating.

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1. Introduction

Vegetable oils [VO] are considered as cost effective, abundant and benign alternative sources for polymers, e.g., polyesters, alkyds, polyeoxides, and polyurethanes. VO polymers have been widely used in adhesives, lubricants, packaging materials, coatings and paints. However, these polymers lack properties of rigidity and strength for applications as high performance materials [1–3]. Blending with commercially available resins such as epoxies, poly-methylmethacrylate, polystyrene has been a simple method to overcome the aforementioned drawbacks [4–7]. Besides this, by the inclusion of nanosized fillers (e.g., nanosilica, nanoclay, metal nanoparticles, and others) in small amounts, drastically improved performance of polymers may be achieved, encouraging their enhanced commercial applications [8–22]. In recent years, such modifications of VO polymers as well as organic–inorganic hybrids [OIH] therefrom have gained considerable attention. The preparation of VO based OIH has been carried out with VO polymers as organic matrices and metal alkoxides (Si, Ti, Zr), preformed nanoparticles, fumed silica, nanoclay, carbon nanotubes as inorganic precursors, respectively. VO based OIH show synergistic advantages of both the components, e.g., environment friendliness, biodegradation, flexibility, toughness, gas barrier properties, transparency, light weight characteristics, antimicrobial activity and others [1,2,5,8–10,23–28].

Castor oil [Ricinus communis] oil [CO] is a natural polyol with 90% ricinoleic acid. It is a non drying oil (iodine value = 85 g I₂/100 g, hydroxyl value = 160–168 mg KOH/g, acid value = 2.45 mg KOH/g) used in the preparation of elastomers, foams, adhesives, coatings and paints [24–28]. Efforts have been focussed on the preparation and characterization of organic–inorganic hybrids and composites from CO. Maria Augusta de Luca et al. have prepared transparent ceramer coatings from CO, epoxidized and hydroxylated CO and metal alkoxides through sol–gel process [25–28]. High performance epoxy/CO–polyurethane nanocomposites have shown improved mechanical and thermal properties [29,30]. DGEBA epoxy (diglycidyl ether of bisphenol A)/silica nanocomposites as reported by Fujiwara et al. have shown high thermal stability attributed to the interaction of hydroxyl groups of DGEBA with silica [31].

In the present manuscript, we have reported the preparation and characterization of DGEBA/CO epoxy blend (as organic precursor) based OIH with tetraethoxyorthosilane (TEOS) as inorganic precursor. The structure, morphology, thermal behavior and coating performance of DGEBA/CO OIH have been studied.

2. Experimental

2.1. Materials

CO was procured from local market. DGEBA (LY 556; Epoxide equivalent = 280, Ciba Specialty Chemicals Pvt Ltd, India), toluylene-2,4-diisocyanate [TDI] (Merck, Germany), TEOS (Merck, Germany), and triethylamine [TEA] (Merck, India) were used as received.
2.2. Preparation of DGEBA/CO blend based OIH

DGEBA epoxy and CO were mixed in a pre-determined ratio by weight [DGEBA/CO = 70/30]. DGEBA/CO was treated with 10% TEOS (prehydrolyzed) in a three-necked round bottomed flask fitted with nitrogen inlet tube, thermometer and condenser under continuous stirring at room temperature (28–30 °C). The reaction temperature was slowly raised to 55 °C and maintained at this temperature for 2 h [23]. Light yellow colored DGEBA/CO OIH was finally obtained.

2.3. Test methods

FT-IR spectrum of OIH was taken on Perkin-Elmer 1750, FTIR spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT) using NaCl cell. Thermogravimetric analysis [TGA] was performed using the Perkin-Elmer Diamond analyzer (Shelton, CT, USA) in nitrogen atmosphere at 10 °C/min heating rate. TEM micrograph of OIH (diluted) sample was taken onto a carbon-coated copper grid) on Morgagni 268-D TEM, FEI, USA. For the preparation of coating, DGEBA/CO OIH was mixed with TDI in presence of few drops of TEA, applied on mild steel strips and placed in an oven at 120 °C for 20 min.

3. Results and discussion

3.1. Synthesis

The methodology for the preparation of DGEBA/CO OIH has been depicted in Fig. 1. DGEBA/CO OIH was prepared by hydrolysis–condensation reaction with DGEBA/CO as organic and TEOS as inorganic precursor, respectively. The first step involves hydrolysis of TEOS, followed by condensation with hydroxyl groups located in DGEBA/CO resulting in the introduction of –O–Si–O– in their backbone, respectively [31].

3.2. Spectral analysis

FTIR spectrum of CO shows the characteristic absorption bands as given below:

FTIR (cm⁻¹): 3007.1 (–C–H str), 2915.0 (–CH₂–, –CH₃ sym str), 2853.0 (–CH₂–, –CH₃ asym str), 1739.0 (–C=O ester), 1240.0, 1168.0 (–C–O–O–) str), 1095.0 (–O–C–C str(ester), 1650.0 (–C=C–), 3408.0 (–OH).

FTIR spectrum of DGEBA/CO shows the following characteristic absorption bands:

FTIR (cm⁻¹): 1291.0–1183.8 (C–O–C, aryl alkyl ether, asym str), 1073.9 (aryl alkyl ether, sym str), 2963.9 (–CH₃ of quaternary carbon), 3056.0, 1581.4, 746.3 (aromatic rings str), 2927.4 (–CH₂ sym str), 2855.3 (–CH₂, asym str), 976.0–914.8 (oxirane ring), 1363.5 (CH₃)₂C), 3506.2 (–OH), 3007.0 (–C–H str) [4].
FTIR spectrum of DGEBA/CO OIH shows additional bands typical for –O–Si–O– at 800 cm\(^{-1}\) and 1100 cm\(^{-1}\) [8,31], which confirm the formation of biohybrid.

3.3. Morphology

TEM micrograph of DGEBA/CO OIH (Fig. 2) shows the presence of silica nanoparticles of size 80–200 nm, respectively. These exist as spherical particles with distinct boundaries, which are chemically bonded to hydroxyl groups of CO or DGEBA in OIH [31].

3.4. Coating properties

DGEBA/CO OIH produced transparent and glossy coating with good scratch hardness (>6 kg), impact resistance (250 lb/in.) and flexibility (1/4 in.). Such good performance may be attributed to good adhesion of coating conferred by electrostatic interactions between the functional groups of the coating material and the substrate. Reportedly, hybrid coatings produced earlier were found to be breakable [27]. However, the biohybrid coating in discussion showed good mechanical strength attributed to the excellent combination of DGEBA epoxy, CO and inorganic reinforcement (TEOS), which produced hard, homogenous and transparent coating. The photograph of virgin DGEBA/CO coating [PG1] shows visible damage on testing for scratch hardness, while DGEBA/CO OIH coating was found to be scratch resistant [PG2], impact resistant [PG3] (Fig. 3) and showed good flexibility retention characteristic. It is evident that the inorganic reinforcement in the organic matrix has profound influence on coating performance of OIH.

3.5. Thermal analysis

TGA thermogram of DGEBA/CO OIH (Fig. 4) showed the onset of degradation at 180 °C, which can be considered as the maximum temperature for its safe usage. 10 wt% loss was observed at 260 °C and 50 wt% loss occurred at 400 °C. DTG showed three-step degradation pattern, with highest degradation temperature (approximately) 400 °C. The percent residue obtained matched (in close approximation) with –O–Si–O– content in DGEBA/CO OIH [28].

4. Conclusion

DGEBA/CO OIH was obtained by hydrolysis–condensation reaction with TEOS as inorganic precursor. DGEBA/CO OIH formed transparent, glossy and hard coating on mild steel substrate due to the synergistic effect conferred by DGEBA, –O–Si–O– and CO. It may be employed as easy to handle, solventless, “environment friendly” protective coating in an attempt to partially replace commercial resins with VO polymers, bearing the advantages of environment friendliness, cost effectiveness and good performance characteristics. DGEBA/CO OIH shows less time consuming preparation method and curing route, simple cure schedule and easy operational process.

The effect of the amount of inorganic reinforcement and CO on the structure, morphology, thermal stability and physico-mechanical performance of the said biohybrid will be discussed in a follow up communication soon.

Acknowledgements

Dr. Eram Sharmin is thankful to CSIR, New Delhi, India for Research Associateship against Grant No. 9/466(0102) 2K8-EMR-1.
for carrying out this work. She also acknowledges CSIR, New Delhi, India for Senior Research Associateship against Grant No. 13/8464-A/2011-Pool (Scientists’ Pool Scheme, CSIR, India), joined in the Dept of Chemistry, Jamia Millia Islamia, New Delhi, in the forenoon of 1st April 2011. Dr. Fahmina Zafar (Pool Officer) acknowledges CSIR, New Delhi, India for Senior Research Associateship against Grant No. 13/8385-A/Pool/2010. Dr. Deewan Akram is thankful to CSIR (New Delhi, India) for Senior Research Fellowship against Grant No. 9/466(0122) 2K10-EMR-I. They also thank the Head, Dept of Chemistry, Jamia Millia Islamia, for providing facilities to carry out the research work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.porgcoat.2011.06.004.

References