Castor oil based hyperbranched polyester/bitumen modified fly ash nanocomposite

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Abstract.   A low cost environmentally benign surface coating binder is highly desirable in the field of material science. In this report, castor oil based hyperbranched polyester/bitumen modified fly ash nanocomposites were fabricated to achieve the desired performance. The hyperbranched polyester resin was synthesized by a three-step one pot condensation reaction using monoglyceride of castor oil based carboxyl terminated pre-polymer and 2,2-bis (hydroxymethyl) propionic acid. Also, the bulk fly ash of paper industry waste was converted to hydrophilic nano fly ash by ultrasonication followed by transforming it to an organo-nano fly ash by the modification with bitumen. The synthesized polyester resin and its nanocomposites were characterized by different analytical and spectroscopic tools. The nanocomposite obtained in presence of 20 wt% styrene (with respect to polyester) was found to be more homogeneous and stable compared to nanocomposite without styrene. The performance in terms of tensile strength, impact resistance, scratch hardness, chemical resistance and thermal stability was found to be improved significantly after formation of nanocomposite compared to the pristine system after curing with bisphenol-A based epoxy and poly(amido amine). The overall results of transmission electron microscopic (TEM) analysis and performance showed good exfoliation of the nano fly ash in the polyester matrix. Thus the studied nanocomposites would open up a new avenue on development of low cost high performing surface coating materials.

Keywords: bio-based materials; hyperbranched polyesters; nano fly ash; nanocomposites; thermosets

1. Introduction

In recent time, environmentally friendly polymeric materials attracted enormous attention in fields of academic as well as in industrial research (Kržan 2009) Among the different sustainable polymers, renewable resources such as vegetable oil based polymers are scored tremendous interest due to its easy availability, biodegradability, sustainability, non-toxic nature and cost effectiveness. Different vegetable oils such as coconut, sunflower, castor, palm oil and so forth are extensively used to synthesize different types of polymers (Madbouly *et al.* 2015, Petrovic *et al.* 2008, Karak 2012). Amongst them, castor oil carves a distinct niche owing to its unique fatty acid composition (92-95% ricinoleic acid) (Thakur and Karak 2013, Ogunniyi 2006). Different types of industrial polymers like polyamides, polyurethanes, poly(ester amide), polyester etc. are reported

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from castor oil (Karak 2012, Thakur and Karak 2013). In this context, castor oil based polyester resin is one of the most economically feasible polymers (Kunduru *et al.* 2015). Polyester resins possess many advantages over other industrially used resins for different applications and oil modified polyester resins is widely used in surface coating industry for a long time (Malshe and Sikchi 2004). The thermosets produced by alcoholysis of castor oil with various polyols, such as glycerol, pentaerythritol, bisphenol A propoxylate, etc. and their subsequent reaction with saturated and unsaturated anhydrides manifested properties comparable to those of high performance unsaturated polyester thermosets. Thus, such bio-based polyesters depicted promise as replacement for petroleum-based materials (Can *et al.* 2006). In this context, it is pertinent to mention that the hyperbranched polyesters show tremendous potential over the last two decades for their favorable properties like low viscosity, high solubility, high reactivity, high compatibility etc. (Karak and Maiti 2008). Even though, such hyperbranched polyesters resin possesses many advantageous properties but they also suffer from less resistant to alkali due to the presence of hydrolysable ester bond in the main chain. Their mechanical properties are also not high enough to be used for commercial purpose (Umare and Chandure 2008). Thus modification of such polyester by commercially available bisphenol-A based epoxy is reported in literature, as epoxy possesses good mechanical, thermal and chemical etc. properties. Further, epoxy in presence amine like poly(amido amine) can effectively crosslinked polyester resin to obtain desired thermoset.

Aagin, nanotechnology is a promising route to fabricate polymeric dispersions with extraordinary properties that can lead to advanced materials (Diaconu *et al.* 2008). With the development of nanotechnology, nanostructured hybrid organic-inorganic nanocomposites based on organic polymer and inorganic nanomaterials have attracted much interest to both industry and academia (Leszczynska *et al.* 2007, Kornmann *et al.* 2002). This is due to their unique functions and specific properties such as improved mechanical, thermal, optical or chemical properties relating to pure organic or pure inorganic materials (Leszczynska *et al.* 2007, Kornmann *et al.* 2002, Chun *et al.* 2006, Kornmann *et al.* 2001, Krook *et al.* 2002). In this regard, fly ash obtained as waste material from thermal power stations, combustion processes etc. It mainly comprises SiO_2 and Al_2O_3 and can be converted to nano fly ash which is a value added product (Criado *et al.* 2007, Cioffi *et al.* 1994). This will also address the disposal related problem as fly ash is a very fine powder and tends to travel a long distance through air (Belardi *et al.* 1998). Functionalized fly ash was used for enhancement of properties of pristine polymeric system by different researchers (Pandian and Krishna 2003, Khan *et al.* 2013, Gaohui *et al.* 2007, Satapathy *et al.* 2013). Chemical modification of fly ash was necessitated to convert its hydrophilic nature into organophilic for providing adequate interactions with the polymer matrix. For this purpose, bitumen is a good choice and can be used as a modifying agent. It consists carboxylic, anhydride, sulfoxide groups (Ramos *et al.* 2005). These groups can interact with the free hydroxyl groups present in the fly ash particles. Ultrasonication was generally used to reduce the dimension of the fly ash particles to a level of nano dimension (Cao *et al.* 2008a, 2008b). So in the present investigation, castor oil based hyperbranched polyester resin and bitumen modified nano fly ash based nanocomposite was used as an environ-friendly low cost surface coating material.

2. Experimental

2.1 Materials

The Fly ash was received from Hindustan Paper Corporation Limited, Assam, India. Castor oil (*Ricinus communis*, BD Pharmaceutical Works Pvt. Ltd., Kolkata, India, acid value 3.7 mg KOH/g, hydroxyl value 157 mg KOH/g) and glycerol (Merck, India) were used after vacuum drying. Phthalic anhydride, maleic anhydride, styrene, 2,2-bis (hydroxymethyl propionic acid) (bis-MPA), benzoyl peroxide (BPO) and calcium monoxide were procured from Merck, India and used without further purification. Poly (amido amine) hardener (Aradure 140, Petro Araldite Pvt. Ltd., Chennai, India) and commercial diglycidyl ether of bisphenol A-based epoxy (Araldite GY 257 IN, Petro Araldite Pvt. Ltd., Chennai, India) were used as received without any further purification. Castor oil and styrene were dried using molecular sieves for about two weeks before use. All other reagents used in the present investigation were of reagent grade.

2.2 Preparation of monoglyceride of castor oil

Monoglyceride from the oil was prepared by the standard procedure as reported elsewhere (Thakur and Karak 2013). A three necked round bottom flask equipped with a mechanical stirrer, a thermometer and a nitrogen inlet was charged with 20 g (0.0217mol) of castor oil, 4 g (0.043mol) of glycerol and 0.01 g (0.05 wt. % with respect to the oil) of calcium monoxide under continuous stirring. The mixture was then heated up to $(225\pm5)\,°C$ for about 1.5-2 h with vigorous stirring until it formed the monoglyceride, which was confirmed by its solubility in methanol (monoglyceride: methanol-1: 3 v/v) at room temperature.

2.3 Synthesis of the hyperbranched polyester

An amount of 14.72 g (0.04 mol) of this monoglyceride was taken in the three necked round bottom flask and heated to $100\,°C$. An amount of 2.09 g of maleic anhydride (0.021 mol) and 4.74 g of phthalic anhydride (0.032 mol) was added into the above reactant, with the same setup as described above. This was then heated to $(225-230)\,°C$ for 1 h with vigorous stirring using xylene as a solvent to avoid gelation. The product obtained was taken as the pre-polymer.

This pre-polymer was then cooled to room temperature and 3.48 g (0.026 mol) bis-MPA in minimum amount of *N, N*-Dimethylformamide (DMF) was added with the same arrangements as described above under nitrogen atmosphere with constant stirring. The mixture was heated for 3 h at $(180-220)\,°C$ followed by increasing the temperature up to $220\,°C$. This facilitates to complete the condensation and removal of the solvent. The formation of the resin was monitored by the acid value determination at different intervals of time. When the acid value reached below 15, it was assumed that the reaction was completed.

2.4 Preparation and modification of nano fly ash

The fly ash was first sieved through a fine sieve to remove any bulk impurities and to get uniformity in size. Then a solution of the fly ash was made in water with 5% poly (ethylene glycol) (PEG) solution. PEG was added to prevent agglomeration of the fly ash. This was then magnetically stirred for 3-4 h followed by ultrasonication for 3 h at room temperature. Then centrifugation was done to separate out the denser particles from the slurry. The process was repeated until the decanted water was almost clear. Then the particles were taken in tetrahydrofuran (THF) to get a dispersion of the fly ash nano particles in an organic solvent through centrifugation. This was done for three times to ensure complete removal of water.

Chemical modification of the fly ash was done with bitumen to enhance its hydrophobicity. In a round bottom flask fitted with a condenser the THF-dispersed nano fly ash was taken with bitumen at weight ratio of 1:5. Then a little amount of xylene was taken to facilitate the mixing of the components. The mixture was heated to (120-150)℃ for 5 h under constant stirring. Finally the product obtained was taken as bitumen modified nano fly ash.

2.5 Preparation of polyester/fly ash nanocomposites and curing

For the fabrication of the nanocomposites, the prepared polyester resin with desired amount of modified nano fly ash and styrene monomer (20 wt% with respect to polyester) and a pinch of BPO initiator was charged into a round bottom flask equipped with a condenser under constant stirring. A minimum amount of xylene was added into the mixture to facilitate the dispersion. The mixture was heated slowly up to a temperature of (170-180)℃ to obtain the desired nanocomposite. It was then allowed to cool to room temperature followed by ultrasonication for 10 min. The nanocomposites with 1, 5 and 10 wt% bitumen modified nano fly ash were coded as PENC1, PENC5 and PENC10 respectively. The hyperbranched polyester without nano fly ash was coded as PENC0.

Finally, the product was mixed with bisphenol-A based epoxy resin at 60:40 weight ratio with minimum amount of xylene and 25 wt% poly(amido amine) hardener (with respect to epoxy resin). The mixture was then cast on mild steel plates (150 mm×50 mm×1.60 mm) and glass plates (75 mm×25 mm×1.75 mm). The sample plates were then degassed under a vacuum desiccator overnight and then they were allowed to cure at 120°C for specified period of time. The curing time is estimated based on the hard drying time of the cast film of resin or nanocomposites on glass plates. The curing time is the time taken by the film to achieve the swelling value of 20-30%. The average film thickness was 0.7-1.0 mm.
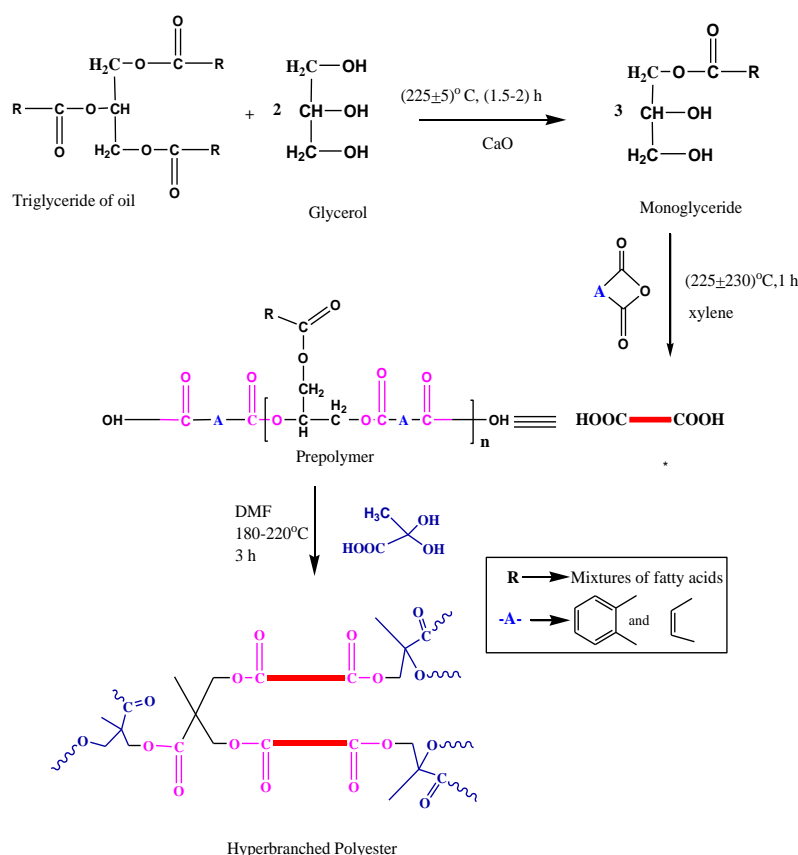
2.6 Characterization

For converting the fly ash particles into nano size an ultrasonicator (Sonics Vibra Cell ^{TM}, Sonics and Materials Inc. United States) was used. For dispersion of the nano fly ash in the polymer an ultrasonicator (UP200S, Hielscher, Germany) was used at 60 amplitude and in 0.5 continuous cycle. The Fourier transformed infrared (FTIR) spectra of the pristine hyperbranched polyester and the nanocomposites were obtained with a Nicolet FTIR Impact 410 spectroscope (Madison, USA) with KBr pellets. The ^{1}H NMR and ^{13}C NMR spectra of the resins were recorded by a 400 MHz JEOL FT-NMR spectrometer by using TMS as the internal standard and $CDCl_3$ as the solvent. *X*-ray diffraction (XRD) was carried out with a Rigaku *X*-ray diffractometer (Miniflex, Tokyo, Japan) at a scanning rate of 2°/min using generator mode in the angular range (2θ) of 10-80°. Thermogravimetric analyses (TGA) of the cured polyester and nanocomposites were carried out with a Shimadzu thermal analyzer (TGA 50, Japan) under a heating rate of 10°C/min and a nitrogen flow rate of 30 mL/min. The polyester/epoxy blends and nanocomposites were applied on commercially available standard-size mild steel strips (150×50×1.60 mm^3) and glass plates (75×25 ×1.75 mm^3) for the determination of scratch hardness by a scratch hardness tester (Sheen Instrument, Ltd., Surrey, United Kingdom), gloss at 60° by a digital mini gloss meter (Sheen Instrument, Ltd., United Kingdom), impact resistance by a falling weight impact tester (SC Dey, India), and chemical resistance by the ASTM D 593-67 (in brine, water, acid, alchohol and alkali) performance of coated cured panels. The surface morphology of the cured hyperbranched

polyester and the nanocomposites films were observed with a JSM-6390LV scanning electron microscope (JEOL, Japan). The size and distribution of the nano fly ash particles in the nanocomposites were studied with a JEOL JEMCXII transmission electron microscope at an operating voltage of 200 kV. For the determination of the tensile strength, the cured nanocomposites films were cut to a uniform thickness of 0.67 mm, a width of 10 mm, and a length of 6.5 cm. The tensile strength of the nanocomposite films was measured with a Jinan universal testing machine (Jinan, China) with a 500N load cell and at jaw separation speed of 50 mm/min under ambient conditions. Swelling (percentage) was measured by taking the difference in the weights between the swollen film of the nanocomposites/ hyperbranched polymer and the dried film using THF as the solvent. The weight of the swollen film was measured after a constant weight was obtained. The swollen films were blotted between sheets of blotting paper to dry them before the weight was measured.

The swelling value can be found using the following formula:

$$\text{Swelling}\,(\%) = (\text{final weight -initial weight}) / \text{initial weight} \times 100$$

The swelling percentage should be in the range from 20-30%, i.e., 70-80% crosslinked or gel percentage.

Scheme 1 Reaction scheme for synthesis of the hyperbranched polyester resin

3. Results and discussion

3.1 Synthesis and characterization of the hyperbranched polyester resin

Castor oil based polyester resin (Scheme 1) was prepared by alcoholysis followed by polycondensation reaction in a three step single pot reaction. In the first step, monoglyceride was synthesized by alcoholysis of castor oil after which it was treated with excess amount of maleic and phthalic anhydride to form a carboxyl terminated pre-polyester. In the third step, this pre-polyester was treated with bis-MPA in DMF as a solvent to avoid gelation during reaction. The -OH groups of bis-MPA reacts with the -COOH groups of the pre-polymer during the polycondensation reaction to form desired hyperbranched polyester. Bis-MPA may also undergo self-condensational reaction. The resultant hyperbranched polyester was soluble in most of the common organic solvents, like methanol, ethanol, acetone, DMF, THF, DMAc, DMSO, CHCl$_3$, toluene, xylene, etc., supporting its hyperbranched nature. The solubility in hydrocarbon solvents like toluene and xylene supports the presence of a hydrophobic fatty acid chain in the hyperbranched structure.

The structure of the hyperbranched polyester was confirmed by ^{1}H NMR (Fig. 1) studies. From ^{1}H NMR spectrum of the prepared hyperbranched polyester resin the presence of following protons were confirmed. Chemical shifts at δH=0.87 ppm were for terminal methyl group (-CH$_3$ moiety) of the fatty acid chains, at δH=1.29-1.33 ppm for fatty acid chain protons (internal -CH$_2$- moiety), at δH=1.44 ppm for proton in -CH$_2$- moiety attached to -OH group in fatty acid chain, at δH=2.01 ppm for proton in -OH moiety in fatty acid chain, at δH=2.27 ppm for proton in -CH$_2$- moiety adjacent to carbonyl group in fatty acid chain, at δH=5.47-5.48 ppm for protons in -CH=CH- moiety, at δH=7.55-8.08 ppm for aromatic protons and δH=5.102 ppm for proton in central -CH- moiety of monoglyceride were evident (De *et al.* 2014).

In the ^{13}C NMR (Fig. 1), chemical shifts at δC=173.1 ppm for carbonyl carbon, δC= 14.1 ppm for -CH$_3$ moiety of bis-MPA unit, δC=22-31 ppm for fatty acid chain carbons, δC=62-65 ppm for monosubstituted, disubstituted and trisubstituted central carbon of bis-MPA unit, δC=72 ppm for -CH$_2$- attached with -OH, δC=166-173.2 ppm for carbon in carbonyl group and δC=73 ppm for -CH- attached with -OH were observed in the spectra (Konwar *et al.* 2009).
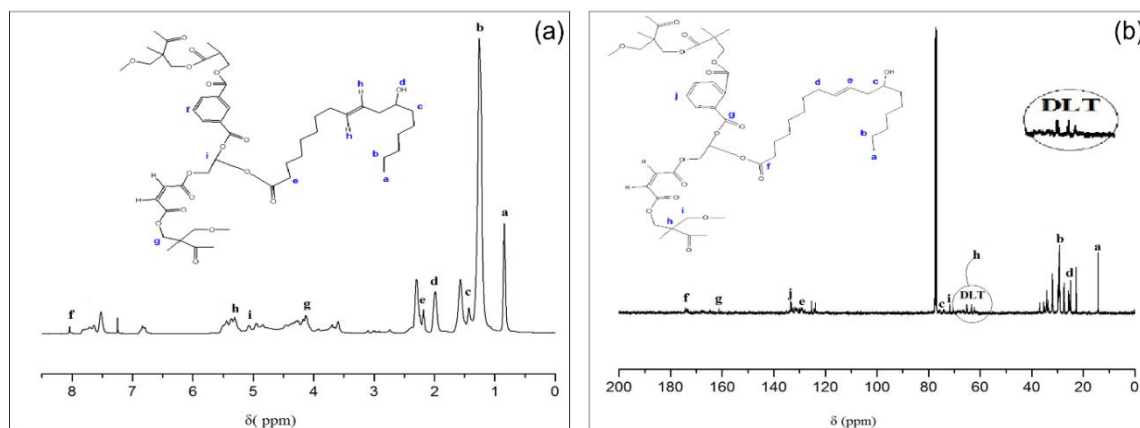

Fig. 1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra for hyperbranched polyester

The NMR spectroscopy is an important assessment for the characterization degree of branching (DB) of a hyperbranched polymer. The polymerization mechanism of the hyperbranched polymer dictates that the resulting polymer should contain a dendritic unit (D), linear unit (L), and terminal unit (T). The DB is the ratio of the sum of integration of dendritic and terminal units to the sum of integration of dendritic, linear and terminal units, i.e., DB = (D + T)/(D + L + T) (Karak 2009). From the ^{13}C NMR spectrum of the hyperbranched polyester (Fig. 1), the monosubstituted (T), disubstituted (L) and trisubstituted (D) central carbon of bis-MPA was observed at δC=62, 63.5 and 65 ppm, respectively. From the intensity values of these peaks, the degree of branching (DB) of the hyperbranched polyester was calculated and found to be 0.67. The presence of important linkages such as ester group, olefinic double bond etc. of resin was confirmed by FTIR analysis, which indicates polycondensation esterification reaction. The characteristic absorbance bands appeared in FTIR spectrum at v_{max}/cm^{-1} 3446(O−H), 2930 (C−H), 1725 (C=O), 1640 (maleic anhydride moiety) and 706 (aromatic phthalic anhydride moiety) (Konwar *et al.* 2009).

3.2 Preparation of nanocomposite

The polymer matrix helped in dispersion of the nano fly ash particles by molecular interactions. The carboxyl groups of the polyester could easily interact with hydroxyl groups of nano fly ash as well as the bitumen through H-bonding or other polar-polar interaction which resulted in a stable and well dispersed nanocomposites. The nano fly ash particles were not perfectly spherical as confirmed by TEM study, hence this helps in increase of the surface area of the nanoparticles and also ensures a rough surface morphology of the nanoparticles. This further led to the increase in the physical interaction between the polymer and the dispersed particles. For better dispersion of the nano fly ash particles mechanical agitation with high shear force and ultrasonication were employed. This resulted in good dispersion of the nano fly ash particles in the polyester matrix as confirmed by XRD and TEM studies. Again the confined geometry of highly branched polymer helped in stabilization of the dispersed nanoparticles in the matrix.

3.3 Characterization of nanocomposites

3.3.1 FTIR study

FTIR spectra of the nanocomposites (Fig. 2) revealed that, some changes took place around the different moieties due to the interactions with the bitumen modified nanofly ash. The -C=O- band of the hyperbranched resin shifted from 1725 cm^{-1} to (1728-1729) cm^{-1} suggesting that polyester segments (-COOH and -OH) interact with the -OH groups of the bitumen (which was used as a modifying agent for the fly ash particles) and fly ash through H-bonding or other polar-polar interactions. There may have some chemical bond formation like ester ether with the nanofly ash and bitumen. Also, the -OH band of the hyperbranched resin shifted from a higher value of 3446 cm^{-1} to (3430-3438) cm^{-1} in case of the nanocomposites (Konwar *et al.* 2009).

The peaks at 2930 cm^{-1}, 2857 cm^{-1} and 1286 cm^{-1} for aliphatic C-H symmetric stretching, aliphatic C-H asymmetric stretching and C-O-C stretching vibration attached with aromatic moiety shifted to 2928 cm^{-1}, 2856 cm^{-1} and 1283-1284 cm^{-1} in case of the nanocomposites. Also, peaks at 1645 cm^{-1} and 1457 cm^{-1} due to unsaturation of -CH=CH- maleic anhydride and -C=C- aliphatic moiety were shifted to (1623-1624) cm^{-1} and (1456-1460) cm^{-1} respectively (Konwar *et al.* 2009). This might be because, styrene monomer was also used in the nanocomposites synthesis, and styrene formed bridges at the points of unsaturation in the chain. Due to incorporation of bitumen
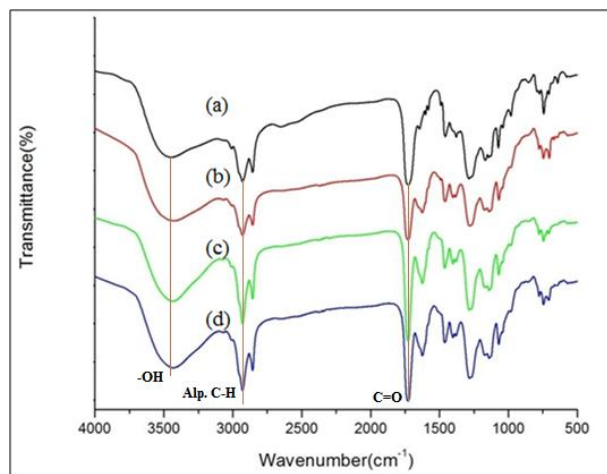
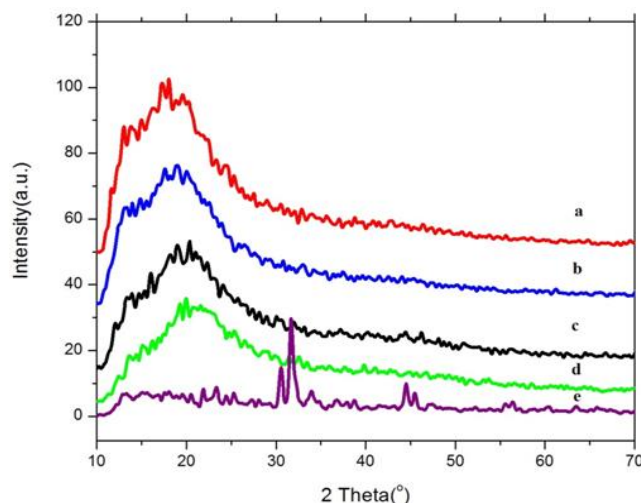Fig. 2 FTIR spectra of (a) PENC0 (b) PENC1 (c) PENC5 and (d) PENC10

Fig. 3 XRD patterns for (a) PENC0, (b) PENC1, (c) PENC5, (d) PENC10, and (e) Fly ash

as a modifying agent, some moieties present in the bitumen were also observed in the nanocomposites. Peaks (cm^{-1}) at 1380, 700-800, 1140 and 1580-1596 were evident due to the sulfone, sulfoxides, alkyl halides and primary amines present in bitumen (Borrego *et al*. 1996).

3.3.2 XRD analysis

The XRD diffractograms of the nanocomposites containing different proportions of bitumen modified nano fly ash are displayed in Fig. 3. Peaks at $2\theta=25.3^{o}$, 31.7^{o} and 44.55^{o} indicated the presence of quartz crystals, while peaks at 18.05^{o}, 23.4^{o} and 33.9^{o} showed the presence of mullite in the fly ash sample (Criado *et al.* 2007). Peaks at 30.45^{o} and 38.8^{o} showed the presence of aragonite while peaks at 36.7^{o} and 55.55^{o} indicated presence of haematite. Further the peak at 56.5^{o} confirmed the presence of magnetite in the fly ash (Kusuma *et al.* 2012). Thus the XRD spectrum of the fly ash supported the presence of mullite ($3Al_2O_3.2SiO_2$), quartz (SiO_2), aragonite ($CaCO_3$),
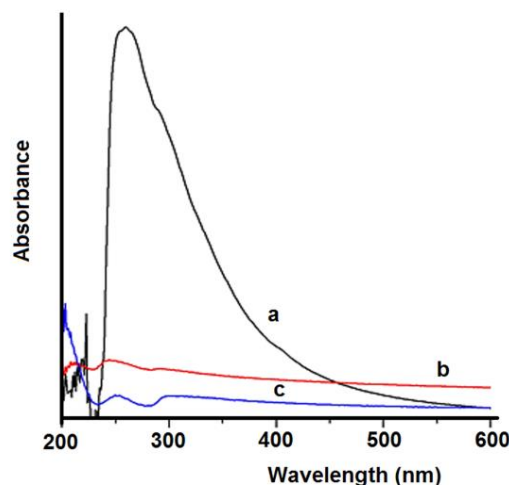
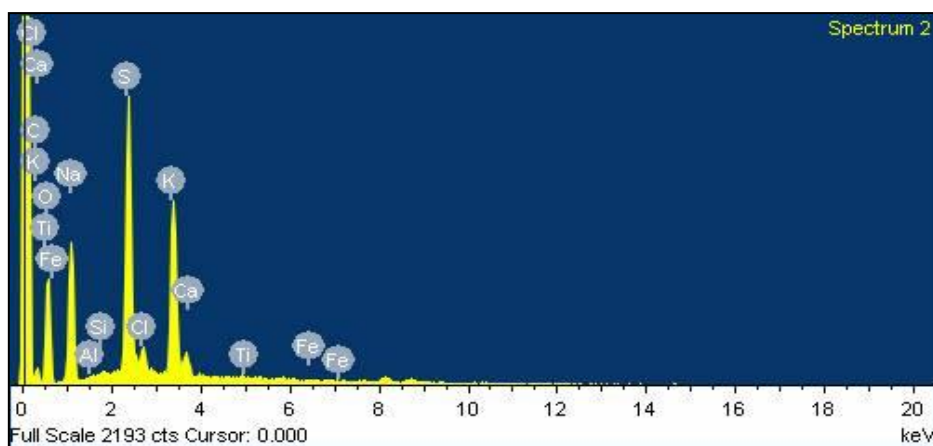Fig. 4 UV spectra of (a) bitumen modified nano fly ash in THF, (b) bulk fly ash in water and (c) nano fly ash in water

Fig. 5 EDX spectrum of the fly ash

magnetite (Fe_3O_4), hematite (Fe_2O_3), albite ($NaAlSi_3O_8$), FeS_2, KCl and Ti. This is further supported by EDX analysis as discussed later. A broad peak in the XRD spectra was observed for PENCO, PENC1, PENC5 and PENC10 at around $15\text{-}25^o$ (2 theta), which appeared due to the amorphous nature of the polyester. The disappearance of the crystallite peaks of fly ash in the nanocomposites indicated the random dispersion of the fly ash particles took place in the polyester matrix. This indirectly indicates uniform distribution of the nanoparticles in the nanocomposite which is supported by the TEM analysis as discussed later.

3.3.3 UV study

The bitumen modified fly ash nanoparticles showed an UV-visible absorption sharp peak at 260 nm though no distinct absorption peak was evident in the spectrum for the bulk fly ash particles as shown in Fig. 4. However, after the reduction in size by ultrasonication a small absorption peak at

about 251 nm was observed for the fly ash nanoparticles (Khan *et al.* 2011). This may be due to the characteristic of surface plasmon absorption of fly ash nanoparticles. Further the nature of the spectrum indicated the narrow size distribution of the particles. This is further supported by TEM study.

3.3.4 EDX analysis of the fly ash

EDX provides the chemical composition of the fly ash. The EDX spectrum (Fig. 5) clearly reveals the presence of various metals and oxides, carbonates and sulfides of metals. This is in accordance to the XRD results.

3.3.5 SEM study

To observe the morphology of the nanocomposites, the nanofly ash dispersion was studied by SEM which provides a visualization of the morphology of the nanocomposites as well as the pristine polymer (Fig. 6). From the SEM micrographs, it is seen that the surface of the pure resin was almost smooth. But the micrographs for the nanocomposites showed rough surface morphology with the dispersion of the particles of the nano fly ash, which was a good indication of toughness. The particles are irregular to spherical shaped and distributed uniformly throughout the matrix.
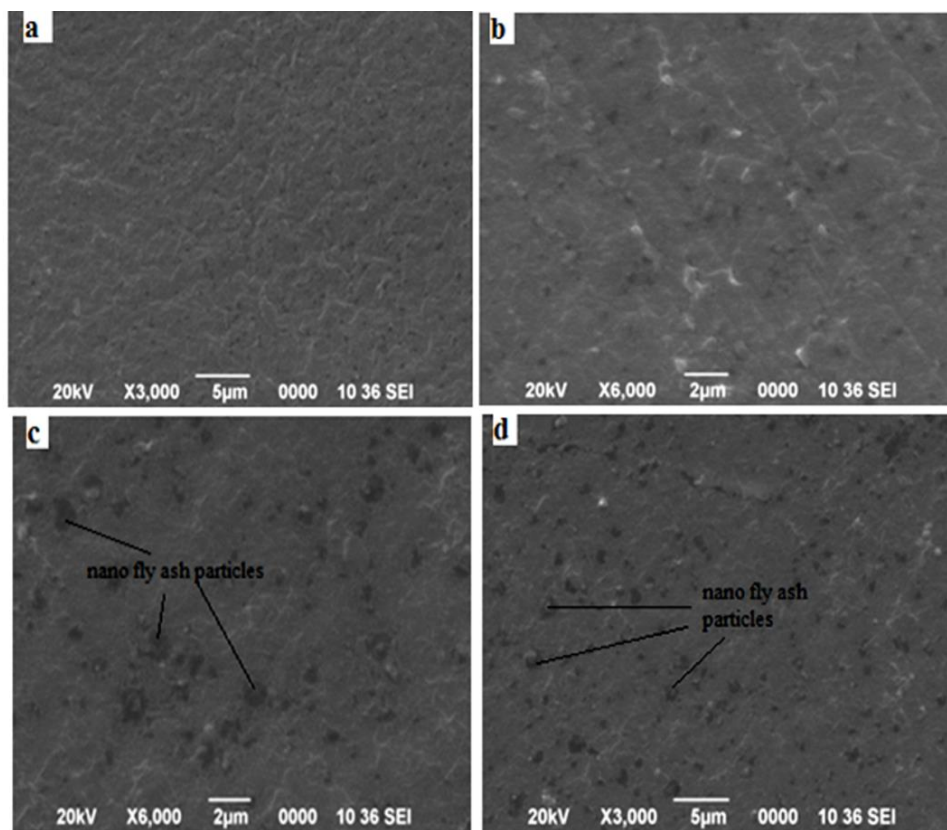

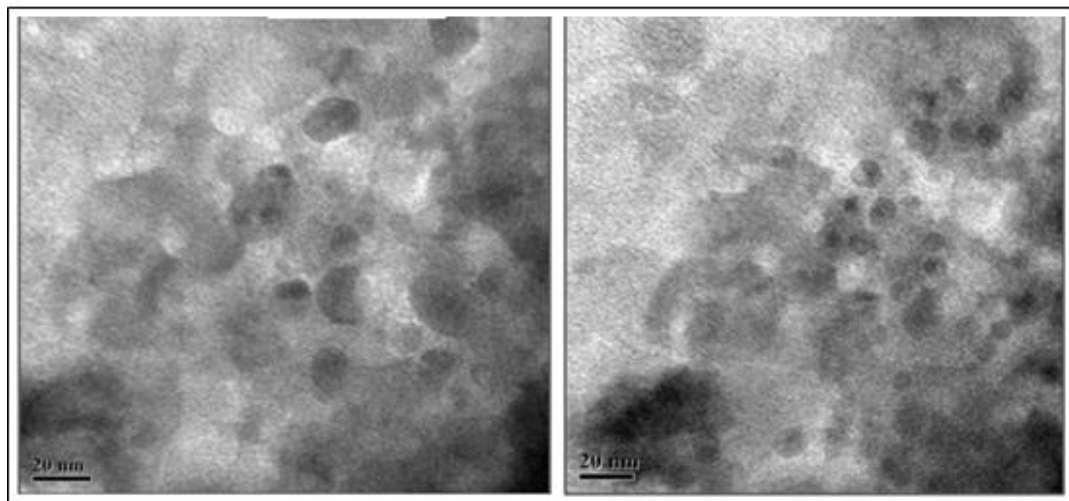Fig. 6 SEM micrograms of (a) PENC0, (b) PENC1, (c) PENC 5, and (d) PENC10

Fig. 7 TEM images of PENC5

3.3.6 TEM studies

To understand the actual pattern of dispersion of fly ash nanoparticles in the polymer matrix, representative TEM images were recorded (Fig. 7). The TEM analysis of PENC5 revealed that the uniform dispersion of the fly ash particles in the polyester matrix. The particles were irregular to spherical in shape with average size of about 20 nm.

3.4 Curing and swelling studies of the resins

The hyperbranched resins were converted to nanocomposites, by the process of crosslinking with epoxy resin as curing agent and poly(amido amine) as the hardener. The swelling test was done in THF solvent. It was noticed that the curing time was drastically reduced after the formation of nanocomposite. Non-drying oil based polyester resin needs long time for curing due to the crosslinking reaction by radicals with the help of atmospheric oxygen. The drying time of the polyester resin drastically improved because of using epoxy curing agent. Also, there is a possibility of crosslinking reactions of hydroxyl/epoxide of epoxy resin and amine groups of the hardener with the hydroxyl/ester groups of polyester resin (Kokane 2002). Also, in this case hydroxyl groups of fly ash in the nanocomposites assisted the crosslinking reaction by forming H-bond with epoxide of epoxy resin and hydroxyl groups of polyester resin along with amine group of the hardener. As a result, cure rate of polyester nanocomposites increased with the nano fly ash loading compared to the pristine resin.

3.5 Performance characteristics of the nanocomposites

The values for tensile strength, elongation at break, gloss, impact resistance and scratch hardness of the cured films of polyester resin and its nanocomposites are given in Table 1. It was found that both the tensile strength (TS) as well as the elongation at break (EB) of polyester/fly ash nanocomposites improved to a noticeable degree with the incorporation of nano fly ash. The tensile strength of the nanocomposites increased from 3.55 MPa to 8.74MPa, whereas EB changed

Table 1 Performance characteristics of nanocomposites

Properties	PENC0	PENC1	PENC5	PENC10
Curing (h)	3.5	2.5	2.5	2
Swelling (%)	28	25	23	21
Gloss value at 60°	93	98	96	86
Impact hardness (cm)	85	90	95	90
Scratch hardness (kg)	7	8	>10	9
Tensile strength (MPa)	3.55	8.62	8.74	6.15
Elongation at break (%)	114	133	254	144

from 114 to 254% with increase of nano fly ash content from 0 to 5 wt%. These improvements in TS and EB of the nanocomposites indicated that the polyester matrix was strengthened by the incorporation of homogeneously dispersed nano fly ash. Elasticity (elongation at break) may also be increased by the presence of the aliphatic polyester moiety of the hyperbranched polyester due to the plasticization effect. The dispersion of the particles of the fly ash offered the maximum surface for strong interaction through H-bonding with the polymer chains. Again, all the particles are not perfectly spherical and possessed uneven surface as observed in TEM analysis (as discussed earlier). This allowed more surface area to be exposed to the polyester matrix for efficient interaction to take place. This strong interfacial interaction between polymer chains and nano-level dispersed particles of nano fly ash formed shear zones when the materials were under stress and strain (Pramanik *et al.* 2003). This interaction contributed to the increase in tensile strength and elongation at break of the nanocomposites. Further, increase of crosslinking density as supported by swelling (Table 2) with the increase of fly ash loading enhanced tensile strength. However, when relatively high fly ash content (more than 5 wt%) was used more and more nano fly ash might aggregate instead of being uniformly dispersed, which resulted in a deterioration of the mechanical properties.

Gloss characteristic of the films after the formation of nanocomposite may be due to good crosslinking of the cured films which resulted in smooth surfaces. This improvement may be due to better compatibility of nano fly ash with the polyester due to the unique hyperbranched architecture. The gloss value increased with the nano fly ash loading as large amount of light was reflected from the smooth surface. But it was seen that at a higher loading of 10 wt% nano fly ash, the gloss property decreased which might be due to the agglomeration of the fly ash nanoparticles.

The scratch hardness increased with the increase in nano fly ash loading. This is due to the highly compact structure formation of the nanocomposite with the incorporation of nanoparticles. The interaction between the nano fly ash particles and the hyperbranched polyester matrix, prevented the easy indentation by the load. However, at the highest nanoparticle loading, the scratch resistance was decreased. This may be because at higher nano fly ash loading, the particles may not be well dispersed and form clusters in the polyester matrix. Hence a highly compact structure formation may be prevented, as all of the particles may not form strong interactions with the polymer chains.

The impact resistance of the prepared nanocomposites increased as the amount of nano fly ash increased from 1 to 5 wt%. The nano fly ash particles formed a tortuous pathway for crack propagation and act as crack stoppers resulting in higher impact energy. However at still higher nano fly ash loading there may not be efficient number of particle-polymer interaction which may

Table 2 Chemical resistance of nanocomposites

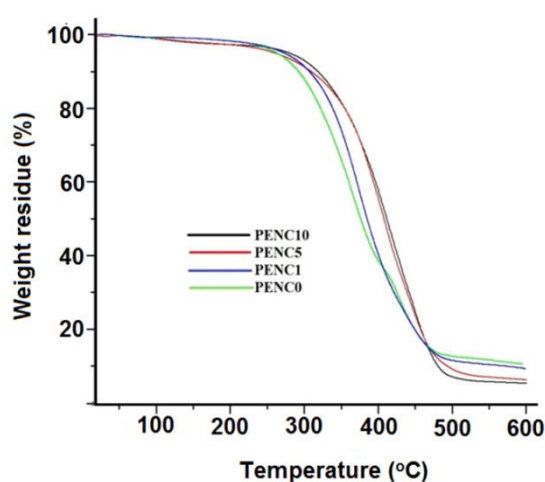| Types of medium	Weight loss (%)			
	PENC0	PENC1	PENC5	PENC10
5% aqueous NaOH	6.23	3.86	3.12	4.36
5% aqueous HCl	1.33	0.58	0.511	0.63
10% aqueous NaCl	1.12	0.47	0.39	0.51
10%aqueos ethanol	0.8	0.59	0.43	0.42
Water	0.6	0.4	0.42	0.52

Fig. 8 TGA thermograms of PENC0, PENC1, PENC5 and PENC10

lead in deterioration of property.

The chemical resistance of the cured polyester resin and its nanocomposites was performed in various chemical environments viz. 5% alkaline NaOH solution, 5% HCl solution, 10% NaCl solution, 10% ethanol solution and water for 15 days at room temperature. The data (Table 2) indicated that the resistivity towards dilute HCl solution, aqueous NaCl solution and water increased significantly after nanocomposites formation. However, the alkali resistance of the hyperbranched resin was poor due to the presence of alkali hydrolysable ester group. But in case of nanocomposites as the nano fly ash loading increased, the resistance towards all the media increased which may be due to compact and crosslinked structure of the nanocomposites. The nano fly ash particles are bonded to the polyester matrix. The permeability was also reduced due to dispersion of the nanoparticles in the matrix of the nanocomposites, so the different ions or species present in different media were not able to easily penetrate the surface and hence the the results.

3.6 Thermal properties

The thermal stability of the nanocomposites significantly improved upon incorporation of nano fly ash in the hyperbranched polyester matrix as compared to the pristine system. This was evident from TGA thermograms as shown in Fig. 8. The initial thermal degradation temperature of polyester was improved from 270 to 320°C by the formation of nanocomposite. This improvement

of thermal stability of the nanocomposites systems was related to the well-dispersed nano fly ash particles which hinder the diffusion of volatiles and assist the formation of char after thermal decomposition. Also, the nano fly ash particles act as good insulator and hinder the escape of volatile products generated during combustion which enhance the overall thermal stability (Park *et al.* 2008).

5. Conclusions

In this study we demonstrated a low cost castor oil-based hyperbranched/ bitumen modified fly ash nanocomposite as a surface coating material. The nanocomposites showed that incorporation of the bitumen modified nano fly ash into the polyester matrix results in an improvement of the mechanical performance like tensile strength, impact and scratch resistance. The chemical resistance and the thermostability of the nanocomposites were also improved as compared to the pristine hyperbranched polyester system. This indicates the nanocomposites may be used as environment friendly surface coating materials.

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