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DESIGN AND DEVELOPMENT OF NOVEL FLEXIBLE BISMALEIMIDE TOUGHENED MULTI-WALLED CARBON NANOTUBE REINFORCED EPOXY NANOCOMPOSITES

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ABSTRACT

A novel water-soluble and flexible aliphatic bismaleimide resin (BMIDPE) was synthesized by using maleic anhydride and polyether diamine (PEA) and toughened with diglycidyl ether of bisphenol-A (DGEBA) with 4,4'-diamino diphenyl methane (DDM) as curing agent. This BMIDPE toughened DGEBA were further altered with various weight percentages (0.5, 1.0 & 1.5 wt %) of multi-walled carbon nanotube (MWCNT) to obtain MWCNT/BMIDPE/DGEBA nanocomposites. The thermal studies indicated that the MWCNT/DGEBA nanocomposites displayed improved thermal stability and decreased the glass transition temperature (T_g) than that of the neat epoxy matrix. The prepared nanocomposites displayed a better dielectric constant than that of the neat epoxy system. From XRD data, it is observed that MWCNT was exfoliated into BMIDPE toughened epoxy. The homogeneous fine dispersion of MWCNTs throughout the DGEBA matrix was ascertained by SEM. The result from mechanical analysis specifies that the inclusion of PEA into the epoxy system increases the toughness. Moreover, it was believed that this new type of BMIDPE toughened DGEBA/MWCNT nanocomposites would be utilized for high-performance applications.

Keywords: Carbon nanotube, flexible-bismaleimide, epoxy, thermal, electrical, mechanical and morphological properties.

INTRODUCTION

MWCNTs are attractive building blocks consisting of multiple concentric graphene cylinders with unique structure and properties[1]. Their exceptional electrical, thermal and mechanical properties were making them ideal composite reinforcement material[2-4], hydrogen containers[5], field emission sources[6], super-capacitors[7], molecular sensors[8] and scanning probe tips[9]. The current investigations have widely concentrated on the carbon nanotube reinforced epoxy resin nanocomposites as a result of their widespread applications in the aeronautics, astronautics and electronics industries[10]. However, the reinforcement role of CNTs in epoxy-based nanocomposites seems divergent. Some previous research reported the properties of carbon nanotube reinforced epoxy nanocomposites compared with the neat epoxy system[11-13]. Contributing attractive thermal/electric/mechanical properties, CNTs could represent a classical system for assessment of the potential to achieve a substantial improvement in comprehensive properties by adding nanoscale modulators at low weight percent.

Epoxy matrix is a versatile and extensively accepted resin used most frequently reinforced with nanotubes for unconventional composite uses, sealants, electronic circuit board materials, radomes hardware components and missile equipment components[14]. The resins of this class have dimensional stability, good stiffness, specific strength and chemical resistance and also display significant adhesion to the embedded matrix[15]. Many types of filler such as nanotubes, nanofibres and nanoparticles are now being tried as reinforcement material to produce better performance epoxy structures with increased properties[16].

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For improving its working performance in high-end engineering applications, chemical functionalization of the epoxy matrix has been primarily done to increase the impact resistance. Polymeric materials with flexible linkages such as carboxyl group-terminated acrylonitrile-butadiene (CTBN), hydroxyl-terminated acrylonitrile-butadiene (HTBN), amine-terminated acrylonitrile-butadiene (ATBN), polyacrylates and nitriles have generally been employed as impact converters used for epoxy matrices[17]. However, the modified epoxy resin can be brought its application well connected with corrosion coatings, weather resistant and structural adhesives. It was noted that the siloxane moiety incorporated epoxy matrix enhances the impacts owing to stress-strain properties of a minor change in glass transition behavior[18,19]. Progressiveness in thermo-mechanical behaviors was attained due to the inclusion of BMI core into epoxy matrix[20-24], siliconized epoxy[25] and unsaturated polyester resin[26].

BMIs are considered as a class of better temperature withstanding thermoset like polyimides and they find a wide range of applications in aerospace and electronics industries[27]. They hold high T_g, high char yield, high cross-linking ability, superior and specific modulus, low water absorption, excellent fire resistance, specific strength and high thermal stability[28]. The necessity of bismaleimide arose since the epoxies possess poor hot/wet performance in terms of applications. And, BMI linkages are capable to fabricate epoxy matrices and reveal capability of performing temperatures up to 230°C[29]. Though, the cured matrices are breakable owing to their aromatic structure and the high cross linking density of the network. Several efforts have been completed to increase the impact and fracture toughness of bismaleimide materials. Wang and his co-workers studied the introduction of the extended chain in the backbone of bismaleimide to decrease crosslink density[30]. Several investigators have efforted to subdue the inelastic nature of BMI through alteration of chemical configuration by including additional chemical groups[31]. One of the effective methods is done by using the high-molecular-weight prepolymers with chain-extension obtained via Michael addition synthesis reaction between diamine and BMI[32]. This is an efficient method of decreasing the brittleness of BMIs and the process will outcome the chain extended BMI-amine adduct to form the cross-linking structure. Also diamines and dithiols are the preferred bis-nucleophilic chain-extender since they have high basicity[33-35]. They reduce the brittleness of BMI because of their superior polymer segments which are offered core molecular movement after cross-linking. The crystallinity experimented for the developed MDA-modified BMI systems and its CNT composites[35]. There still a major disadvantage of using BMIs is difficulty in processing due to extremely aromatic chemical structures. In recent times, bismaleimides that have flexible bonds are commonly used as heat proof materials[36,37]. But the introduction of flexible networks into the bismaleimide monomers reduce the crosslink density[38,39] and thus resulted in the depressing of T_g and also the decomposition behavior of the final cured composite products. Consequently, a periodic analysis is requisite for considering the properties such as processibility, mechanical properties, morphology and crystallinity of the matrix and the carbon nanotubes reinforced nanocomposites.

In this context, a new type of chain extended BMI using a polyether amine, Jeffamine ED 2003, has been designed and BMI toughened epoxy/MWCNT nanocomposites were prepared and characterized their structure, thermal stability, crystallinity, mechanical and morphology properties.

EXPERIMENTAL

Materials

Bundled MWCNTs were purchased from Applied Science and Innovation Pvt. Ltd, Pune, India. The special surface areas were 40-500 m^2/g and their lengths were 1.0-40 μm and diameter of the MWCNTs was 20-45 nm. The received MWCNTs were treated by nitric acid and sulphuric acid and refluxed for 24 h, which as per the procedure reported[40]. The raw material such as DGEBA (LY556 equivalent [E] weight: 187) and 4, 4-diaminodiphenylmethane (DDM) was also bought from Huntsman Ltd India. Polyetherdiamine (Jeffamine ED 2003) M.Wt:2000, maleic anhydride (Fluka, 99%), acetone (Baker), acetic anhydride (B.D.H, UK) and N, N-dimethylformamide (DMF, SRL). All reagents were used without further purification except acetone and DMF, which were lately dried by standing over freshly, renewed type 4 Å molecular sieves for 24 h. Novel BMIDPEDPE was produced as per the reported method.

Functionalization of MWCNTs

The reason for functionalization was the debundling and dispersion improvement of the nanotubes during composite processing. Thus, the functionalization process was made in two steps: firstly, the oxidation of MWNT using a 3:1 (vol.) mixture of H_2SO_4: HNO_3 in order to purify the raw material from catalyst traces, to obtain carboxylic groups on their surface, as well as at the end by capping the semispherical ends. Thus 100 mg of MWNTs was added to 12 ml H_2SO_4: HNO_3 mixture, heated at 70°C in silicon oil bath and kept under stirring for 12h and then the product was filtrated on 0.22 μm pore Teflon membrane and washed until the pH reached neutral value and dried at for 48h at room temperature (RT)[40] to yield (MWNT-COOH).

Synthesis of Bis-maleimidodiaminopolyether (BMIDPE)

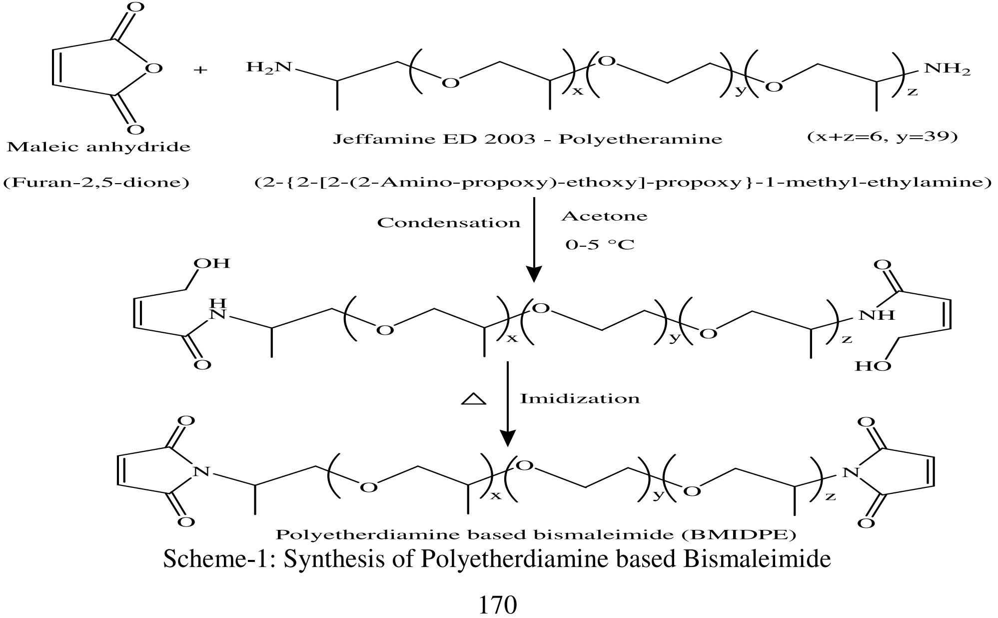
A three-way RB flask purged with nitrogen fitted out with a dropping funnel and a solution of polyetherdiamine (Jeffamine ED 2003) (20, 0.01mol) in 8 ml of acetone[28, 41,42] were poured as per the procedure reported somewhere (Scheme-1).

The RB flask was cleaned with N_2 and then maleic anhydride solution (1.96g, 0.022mol) in 10 ml of acetone was further added dropwise to the above blend. The reaction released excess heat (exothermic), the addition was subsequently done in a water/ice bath. This mixture was then stirred well for 4 h at 0-5°C and at room temperature for an extra 1 h.

The above solution was then refluxed with a preheated solution (60-65°C) of sodium acetate (0.1 g), acetic anhydride (10 ml) and triethylamine (2 ml) were further added to the preheated solution and the reaction product was agitated for 6h. The solution was later cooled to RT and then slowly added into ice water on stirring. The mixture was further stirred and allowed the tin salts to completely hydrolyze by adjusting the pH to basic with the addition of sodium bicarbonate (5%). The aqueous solution was then separated with extra $CHCl_3$ and carefully washed with brine solution and dried using sodium sulphate. Evaporation of the additional solvent leaves a dark brown viscous liquid with a yield of 85% (Scheme-1).

Preparation of Blends

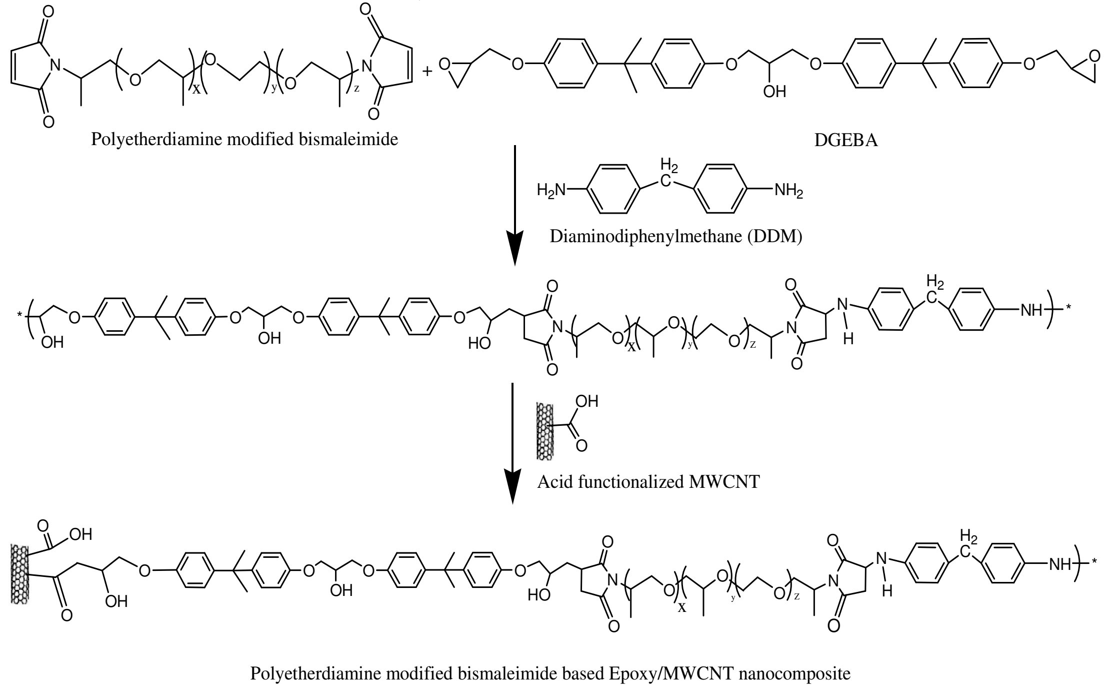
The DGEBA/BMIDPE blends were prepared by mix blending technique, and their compositions are shown in Table-1. The obtained blends were cured with aromatic amine curing agent DDM in a stoichiometric amount equivalent to epoxy resin. The reaction was carried out in a thermostatic oil bath to maintain the constant temperature. Initially, the BMIDPE resins were weighed and dissolved in the absence of a solvent with the pre-weighed quantity of liquid epoxy matrix at a temperature of 120°C for 2 h[13]. After, the desired amount of curing agent (dried at 80°C) was added into the synthesized blend and mixed with help of stirrer because polymer starts to become gel above this temperature, until ensuring the homogenous and visually transparent mixture.



Scheme-1: Synthesis of Polyetherdiamine based Bismaleimide

Casting of Composites

Composites were obtained by mixing a stoichiometric quantity of the curative agent DDM respective to DGEBA/BMIDPE and blended with the (MWNT-COOH at RT[43].



Scheme-2: Schematic representation of Synthesis of the BMIDPE/DGEBA/MWCNT Nanocomposites

Prior to Curing, the trapped Air from Product was eliminated by Vacuum. The Curing Process was carried in Two Steps Thermal Treatment: One Step for 3h at 120°C and the Later Step for 2h at 180°C to Complete this Reaction.

The method used to obtain the epoxy/MWNTs nanocomposites samples is illustrated in Scheme-2. The casting was then lastly detached from the mould and studied their properties.

Characterization

Physicochemical Studies

Fourier Transform (FT-IR) infrared spectral data of MWCNT incorporated Epoxy nanocomposites were recorded between 400 and 4000 cm^{-1} on a Perkin Elmer 6X FT-IR spectrophotometer. Approximately 100 mg of optical-grade KBr was finely ground with the adequate amount of the polymer sample to make 1.0 wt% mixture for making KBr pellets. At least 16 scans were made for all samples at a resolution of ±4 cm^{-1} after the sample was loaded. JEOL 500 MHz NMR spectrometer was employed to record ^{1}H and ^{13}C NMR analyses. Samples were diluted and analyzed by using $CDCl_3$ and TMS as an internal standard.

Thermal Studies

A differential scanning calorimeter (DSC-200, Netzsch) in the temperature range between 50 and 400ºC at a heating rate of 10ºC min^{-1} was used to determine the glass transition temperature (T_g) of the samples under a constant flow of nitrogen. Thermal analysis (TGA) was also carried out in a DSC-2920 from TA Instruments combined with a TA-2000 control system. The calibration of the instrument was done using calcium oxalate and aluminum delivered by Netzsch. The samples (about 50 mg) were heated up to 80°C under a continuous supply of nitrogen (60 mL min^{-1}), at 10ºC min^{-1}.

X-Ray Diffraction Studies

Wide-angle X-ray spectra were obtained using an X'Pert PRO PANalytical (Model 3000) diffractometer (with Cu $K_{\propto}$radiation (θ= 0.15406 nm) for the ground powder of cured composites. The spectral window ranged from 2 θ= 0^{o} to 70^{o}.

Water Absorption Behavior

ASTM D 570 was used to test the water absorption properties of the nanocomposite films. The nanocomposite specimens (dimensions: 100 mm square, 3 mm thickness) were immersed in distilled water for 48h and the films were removed and weighed to an accuracy of 0.0001g.

Mechanical Properties

The mechanical properties such as tensile, flexural, impact and hardness were measured. The tensile properties were determined as per ASTM D 3039 for specimens of the width of 25 mm, length of 200 mm, and thickness of 3 mm. The specimens having dimensions 3 mm in depth, 10 mm in width, and 100 mm in length was used for flexural strength measurement at 5 mm min^{-1} cross-head speed using HTE-series-H50 K-S Model (Hounsfield test equipment Ltd, UK) as per ASTM D 790. The samples of nanocomposites were analyzed as per ASTM D 256-88 to determine the impact strength. A Durometer-Type D and Hardness was calculated using the specimens of 3 mm thickness as per ASTM D 2240.

Dielectric Constant

The dielectric constant behavior was studied using an impedance analyzer (PSM1735 NumetriQ) at room temperature (RT). The polymer samples were made in the form of a film (1 mm thickness × 13 mm dia.), by applying a pressure of 3.5 tons for impedance measurements using platinum (Pt) electrode in the frequency range at 1 MHz. The dielectric constant of the samples was determined using ε' as the standard relations.

Morphological Properties

The SEM of the fractured surfaces was carried out using a JEOL JSM Model 6360 microscope. The specimens were coated with platinum and were exposed to an accelerating voltage of 20 kV. The hybrid film morphology was also studied using SEM.

RESULTS AND DISCUSSION

FT-IR Spectral Analysis of BMIDPE

The FT-IR spectrum (Fig.-1)of flexible linkage aliphatic bismaleimide show a strong absorption corresponding to imide ring around 1,720 cm^{-1} due to the asymmetric and symmetric C=O stretching vibration. C-N-C stretching vibration of imide ring is also observed as bands around 1,350 cm^{-1} and the band CH_3 group showed a symmetric stretching around 2866 cm^{-1}. Further, the C-O-C bond (alkoxy) shows a strong absorption band[44,45] at 1,030 cm^{-1}. The appearance of new absorption peaks at 2953 cm^{-1} (C-H stretching) and 1457 cm^{-1} (C-H bending) also specified the formation of bismaleimide ring[41].

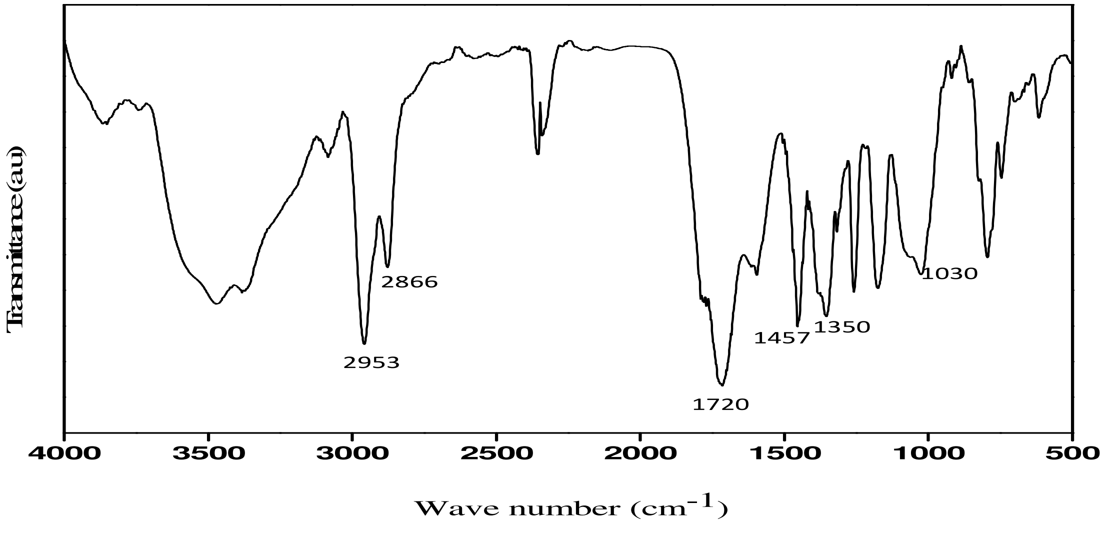


Fig.-1: FT-IR Spectrum of Polyetherdiamine based Bismaleimide

FT-IR Spectral Analyses of Nanocomposites

The FT-IR spectral data of BMIDPE toughened DGEBA epoxy matrix resins and MWCNT-incorporated BMIDPE blended DGEBA epoxy matrix resins are listed as shown in Fig.-2.

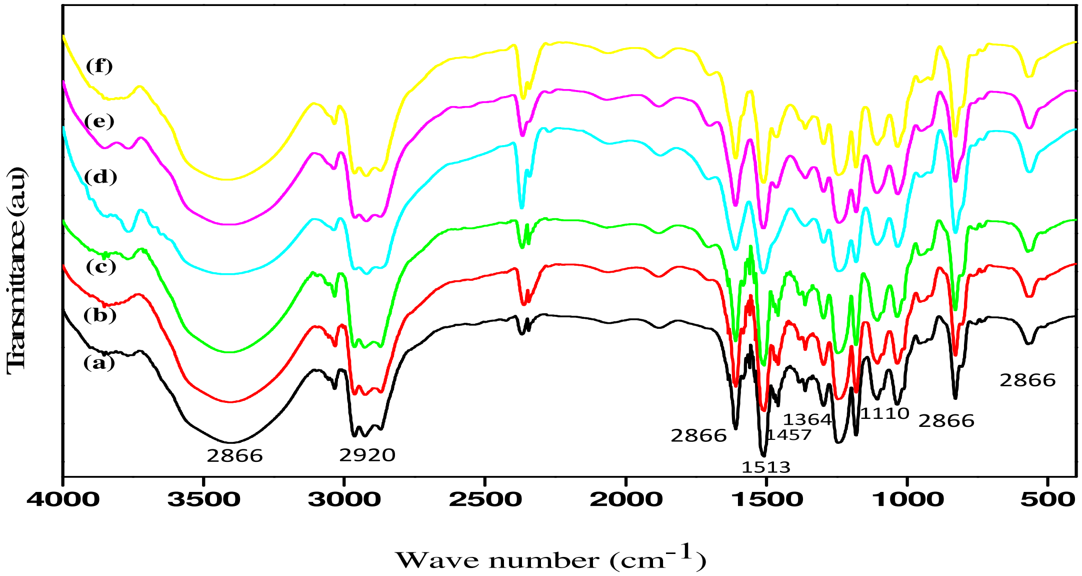


Fig.-2: FT-IR Spectra of the Neat BMI/DGEBA and BMI/DGEBA/MWCNT Nanocomposites

The ring opening reaction of epoxy of was ascertained by the disappearance of an absorption peak corresponding to oxirane group of the epoxy matrix at 914 cm^{-1}. The thermal imidization was then confirmed by an absorption band at 1364 cm^{-1} (-C-N in the imide groups). The peak was observed at 1110 cm^{-1} corresponding to CH_2wagging of imide rings. There, an anti-symmetrical deformation of CH_3 was observed at 1457 cm^{-1}. The presence of aliphatic C-H group was confirmed by a peak around 2920 cm^{-1} [47,50]. The other important peaks are 1513 cm^{-1} which is because of the C-N-C stretching respectively[50]. The completion of curing of the BMI chains was indicated from the absorption band in the range of 1000-500 cm^{-1} with a reduced number of peaks[41-42]. Upon the addition of MWCNT to DGEBA, the formation of MWCNT/DGEBA is confirmed by the disappearance of the peak at 1610 cm^{-1}due to the amide groups. These observed absorption bands revealed that MWCNT was successfully incorporated into DGEBA matrices and coincided very well with the reported earlier[50] data.

Thermal Properties

Differential Scanning Calorimetric Analysis

The glass transition temperatures (T_g) of the conventional DGEBA epoxy system, BMIDPE/DGEBA epoxy and MWCNT/BMIDPE/DGEBA epoxy systems were determined from DSC analysis and are listed in Table 1 and Fig.-3.The values of T_g were reduced with the rise in the concentration of BMIDPE content into DGEBA epoxy systems, as shown in Table 1.The BMI toughened DGEBA displays T_g around 145 ºC than those of neat epoxy 165-168ºC. On adding 5%, 10%, and 15% of BMI into the epoxy matrix, T_g values are 185.4ºC, 146.4ºC, and 134.8ºC, respectively. The presence of the chain extended and aliphatic flexible units decreased the effective crosslink density, which in turn reduces the curing temperature by accelerating the reaction rate. The segmental mobility of molecules established by extra free volume in the matrix system leads to a drop in the values of T_g. This kind of an intercross linking network formation between BMIDPE and epoxy was ascertained from the single T_g[34, 41].

The incorporation of MWCNT into BMIDPE-toughened DGEBA epoxy matrices also increased the T_g value. For example, the incorporation of MWCNT (1.5 wt %) into 10% BMIDPE-blended DGEBA epoxy resin matrix possess the T_g value of 254.8ºC and that of the BMIDPE - blended DGEBA epoxy resin system displayed 146.4ºC (Table-1). It is suggested that the increase in T_g value of MWCNT-filled BMIDPE-toughened DGEBA epoxy nanocomposites may probably due to the reinforcement of the

MWCNT with the crosslink density and thus the access of the molecules of epoxy resin DGEBA is hindered, which results in a higher degree of cross-linking and as a consequence a higher $T_g$value[46-48].

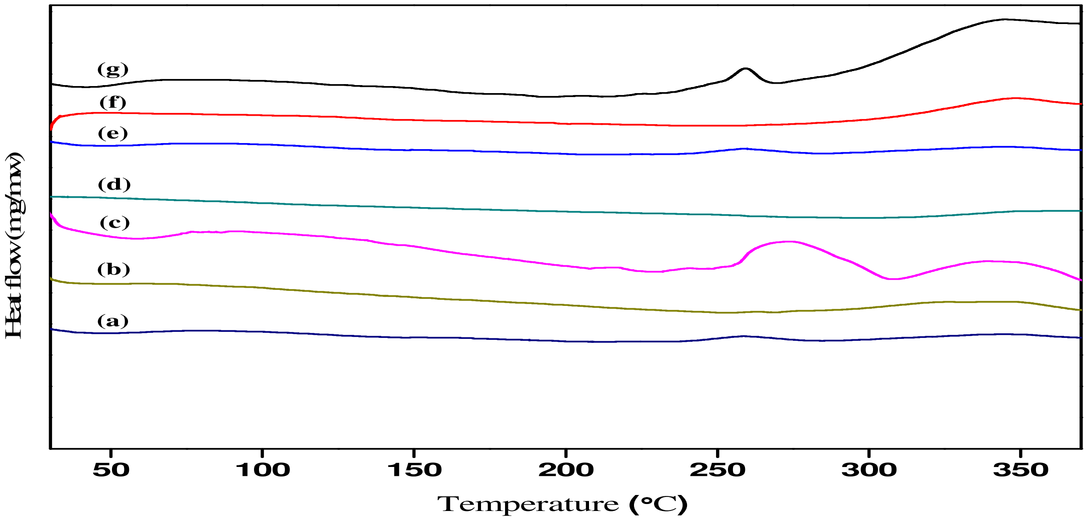


Fig.-3: DSC Thermogram of the Neat BMI/DGEBA and BMI/DGEBA/MWCNT Nanocomposites

Table-1: Thermal and Dielectric Data of the Neat BMI/DGEBA and BMI/DGEBA/MWCNT Nanocomposites

Systems	Percentage Composition (Wt %)	The temperature for Weight Loss @ 50%(°C)	Glass Transition (°C)	Char Yield %	Dielectric Constant (ε')
DGEBA/BMI Composite	100/00/00	370	190.2	0	3.5
	100/05/00	425	185.4	0.9	3.8
	100/10/00	465	146.4	1.5	4
	100/15/00	438	134.8	2.1	4.3
DGEBA/BMI/ MWCNT Composite	100/10/0.5	476	237.5	17	5.2
	100/10.1.0	491	244.2	36	5.7
	100/10/1.5	700	254.8	41	6.4

Thermogravimetric Analysis

The thermal stability and degradation temperature of BMIDPE into DGEBA epoxy matrices were augmented as the concentration of BMIDPE were increased. The cross-linked structure and the entangled network of BMIDPE/DGEBA epoxy resin systems which delayed the degradation temperature caused by the BMIDPE moiety[48]. Furthermore, the incorporation of COOH-MWCNTs into epoxy matrices boosted thermal stability since nanocomposites act as a heat-proofing and mass transport barrier to the volatile products generated during decomposition. With the increasing percentage concentration of MWCNT, the degradation temperatures of MWCNT incorporated BMIDPE/DGEBA systems were increased. The MWCNT-filled BMIDPE/DGEBA epoxy resin systems exhibited the superior thermal stability and greater char yield than that of neat BMIDPE/DGEBA epoxy systems (Fig.-4).

It was also found out that the MWCNT-filled BMIDPE-toughened DGEBA matrix nanocomposites which are more thermally stable than those of the BMIDPE-toughened DGEBA nanocomposites because of their hindering effect of vastly crosslinked structure in the matrix. However, the addition of COOH-MWCNTs slightly improves the thermal stability of DGEBA/MWCNT system[47] observed from Fig.-5.

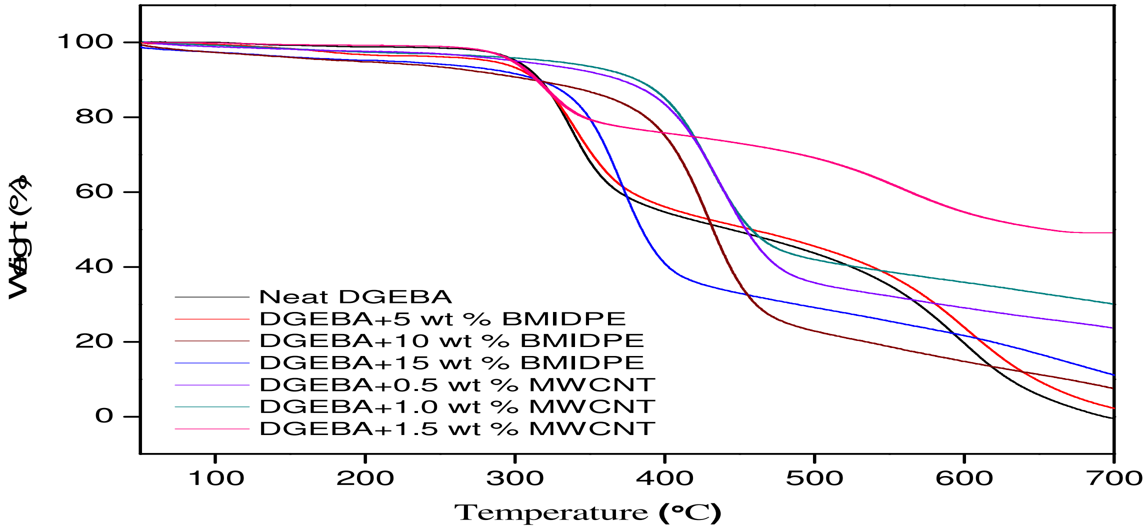


Fig.-4: TGA Thermogram of the Neat BMI/DGEBA and BMI/DGEBA/MWCNT Nanocomposites

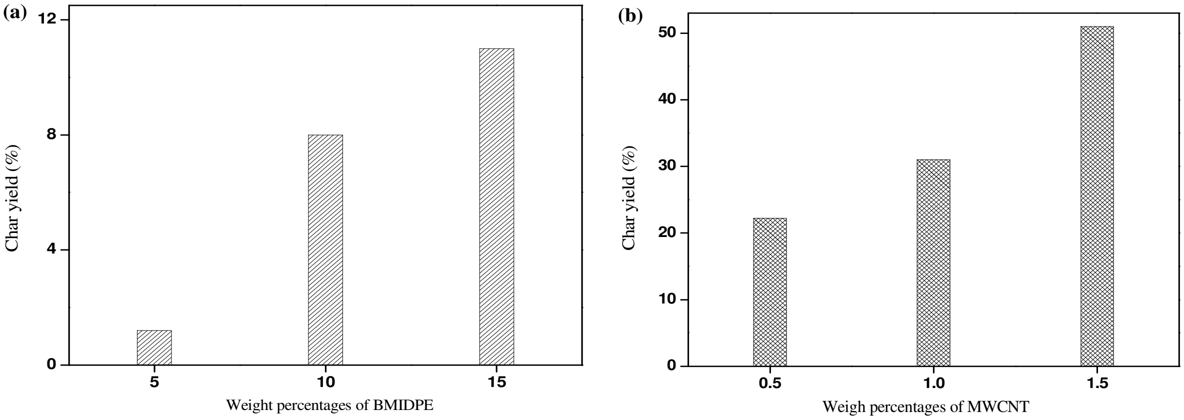


Fig.-5: Char Yield Comparison of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

X-Ray Diffraction Analysis

The XRD behavior of the BMIDPE toughened DGEBA resin systems and BMIDPE toughened DGEBA/MWCNT nanocomposites are shown in Fig.-6. The diffractogram of BMIDPE/DGEBA matrix gives a broad peak showing that the epoxy is blended with BMIDPE which assigned the structure of the epoxy systems to amorphous. On adding MWCNTs into the BMIDPE/DGEBA matrix, this peak respective to $2\theta = 18.5°$ shifted towards slightly higher value in turn clearly shows that the incorporation of MWCNTs into epoxy matrix refines the microstructure of the composites by the means of interfacial interaction between the MWCNTs and epoxy matrix.

From the diffractograms, it can be shown that the MWCNT has well reacted with the BMI/DGEBA system, thus results in a broad peak. The disappearance of the small sharp peak has also confirmed that the formed MWCNT reinforced DGEBA nanocomposites are amorphous and highly exfoliated in their end form also homogeneous dispersion of MWCNT.

Water Absorption Behavior

The BMI incorporation into epoxy resin matrix resulted in lower water uptake property according to their concentration (Fig.-7a and b). This is hence because of the creation of intercross linking structure formed between inherent water repellent bismaleimide and the epoxy resin matrix. The reduction in water uptake percentage of the BMI blended epoxy resin matrix is due to the characteristic water repellent nature of BMI networks[48].

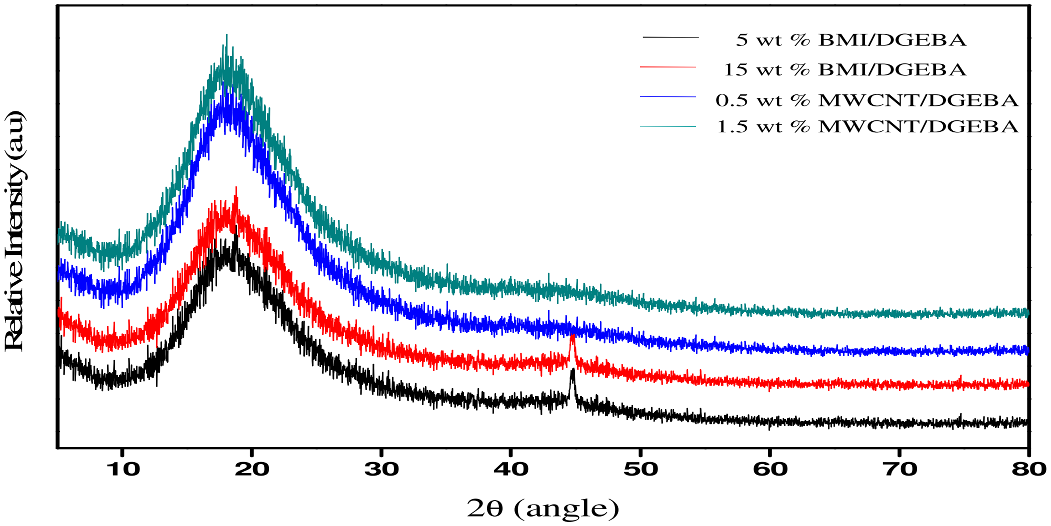


Fig.- 6: XRD Pattern of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

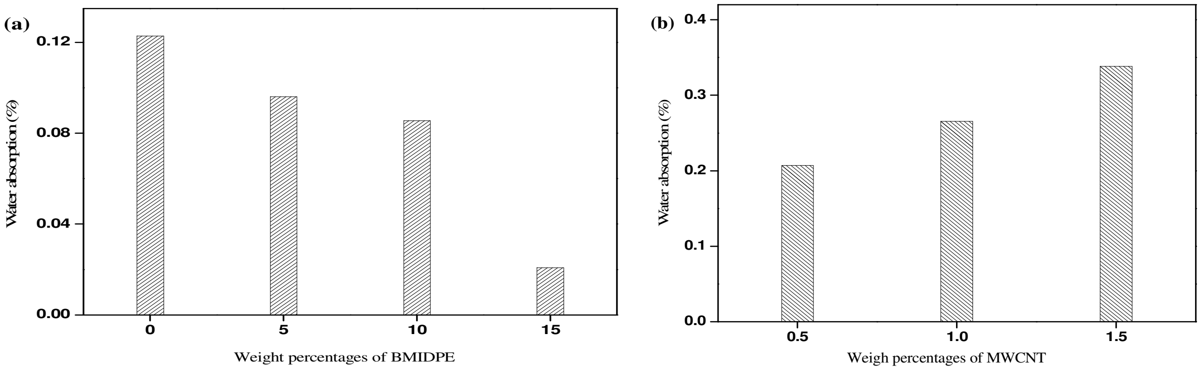


Fig.-7: Water Absorption Behaviour of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

Hence, it is indicated that the BMI offers a significant role in enhancing the resistance to water absorption of nanocomposites[23]. However, the reinforcement of 0.5, 1.0 and 1.5 wt% of MWCNT into 10 % BMIDPE-DGEBA epoxy matrix increased the water absorbing properties. This is supported by the presence of hydroxyl groups in the MWCNT networks.

Mechanical Properties

Tensile Behavior

The tensile properties of neat DGEBA, BMIDPE/DGEBA epoxy systems and MWCNT filled DGEBA epoxy resin systems are presented in Table-1 and Fig.-8a and d. The inclusion of BMIDPE into DGEBA epoxy matrices suppressed the tensile behavior with 5, 10 and 15% BMIDPE into the DGEBA epoxy matrix comparing with those of unmodified epoxy matrices.

Table-2: Mechanical Properties of the Neat BMI/DGEBA and BMI/DGEBA/MWCNT Nanocomposites

Sample	Percentage Composition	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Hardness (MPa)	Izod-unnotched Impact Strength (J/m)	Water Absorption (%)
DGEBA/ BMI systems	100/00/00	61.20	2721	107.0	1813	84.3	101.7	0.1229
	100/05/00	54.21	1910	32.7	2670	159.3	108.5	0.0961

	100/10/00	55.57	2088	35.6	2910	117.9	133.3	0.0856
	100/15/00	60.59	2179	37.6	3070	83.8	166.7	0.0209
BMI/DGEBA/ MWCNT systems	100/10/0.5	31.30	2131	34.5	2810	87.2	138.3	0.2069
	100/10/1.0	54.59	2228	31.4	2560	112.6	200.1	0.2656
	100/10/1.5	58.78	2248	28.1	2290	136.3	233.3	0.3381

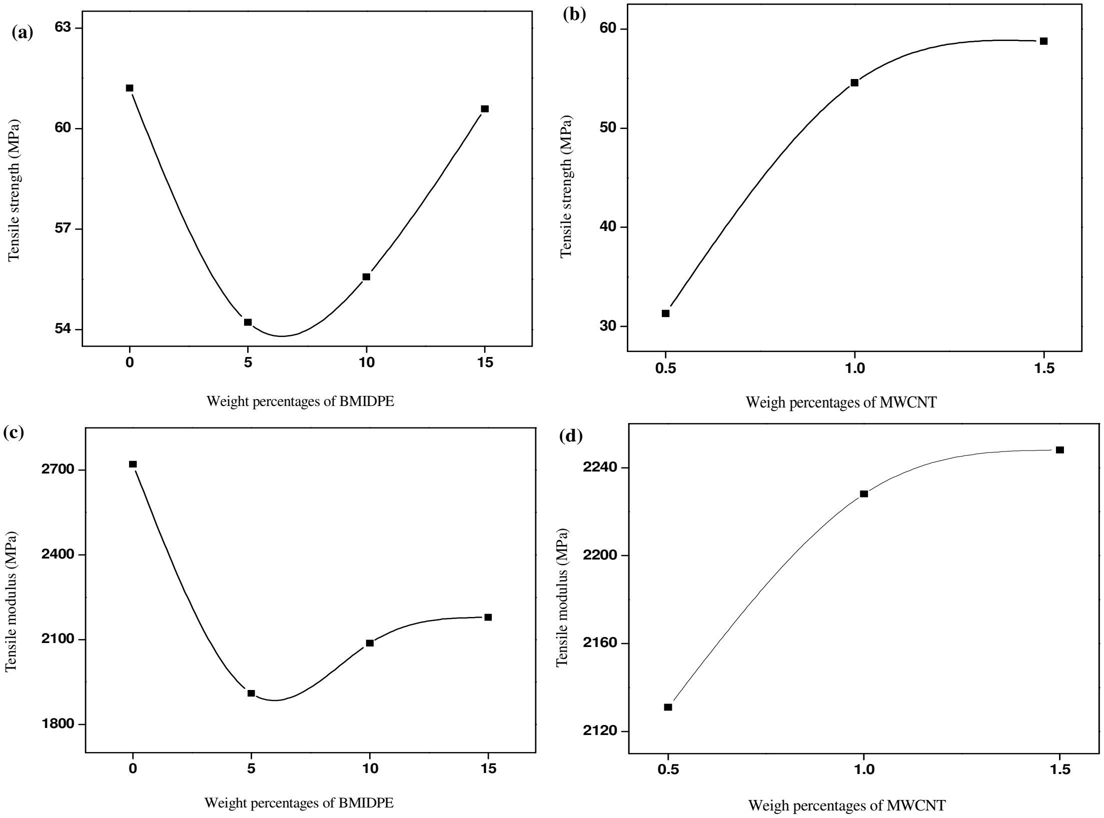


Fig.-8: Tensile Strength of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites and Tensile Modulus of (c) Neat BMI/DGEBA and (d) BMI/DGEBA/MWCNT Nanocomposites

The tensile strength of BMI-epoxy matrices are decreased with the increased BMI content whereas, it increased with increasing MWCNT content for BMIDPE-DGEBA/MWCNT nanocomposites. The introduction of 1.5 wt % of MWCNT into 10 % BMIDPE-DGEBA epoxy resin matrix enhanced the tensile strength by 7 %, respectively. The increase in the compatibility between the BMI and the carbon nanotubes through the chain extending reaction of DDM has increased the tensile strength of MWCNT/BMI/DGEBA nanocomposites[43].

Flexural Behavior

The Table-2 and Fig.-9a to d represent the flexural properties of neat DGEBA, BMIDPE-toughened DGEBA epoxy and MWCNT/DGEBA epoxy nanocomposites. The flexural strength of the epoxy is considerably increased with the newly introduced BMIDPE matrix in the epoxy resin as a result of the network formed between the BMIDPE and epoxy system.

The values of flexural strength according to nature and percentage incorporated bismaleimide are enhanced as witnessed as in the case of tensile strength. The rise in flexural strength is remarkably influenced by the homopolymerization of BMI and an interpenetrating network structure between the epoxy resin and BMI formed[34]. The flexural modulus of the nanocomposites was raised to an extreme amount of 70% for the modified BMI as compared to the neat BMI.

It has been hypothesized that MWCNT inhibits dissolution in the modified resin-based composite, which in turn altered the brittle or crystalline nature into a semi-crystalline or amorphous structure and thus resulted in the reduction of flexural strength of the nanocomposites.

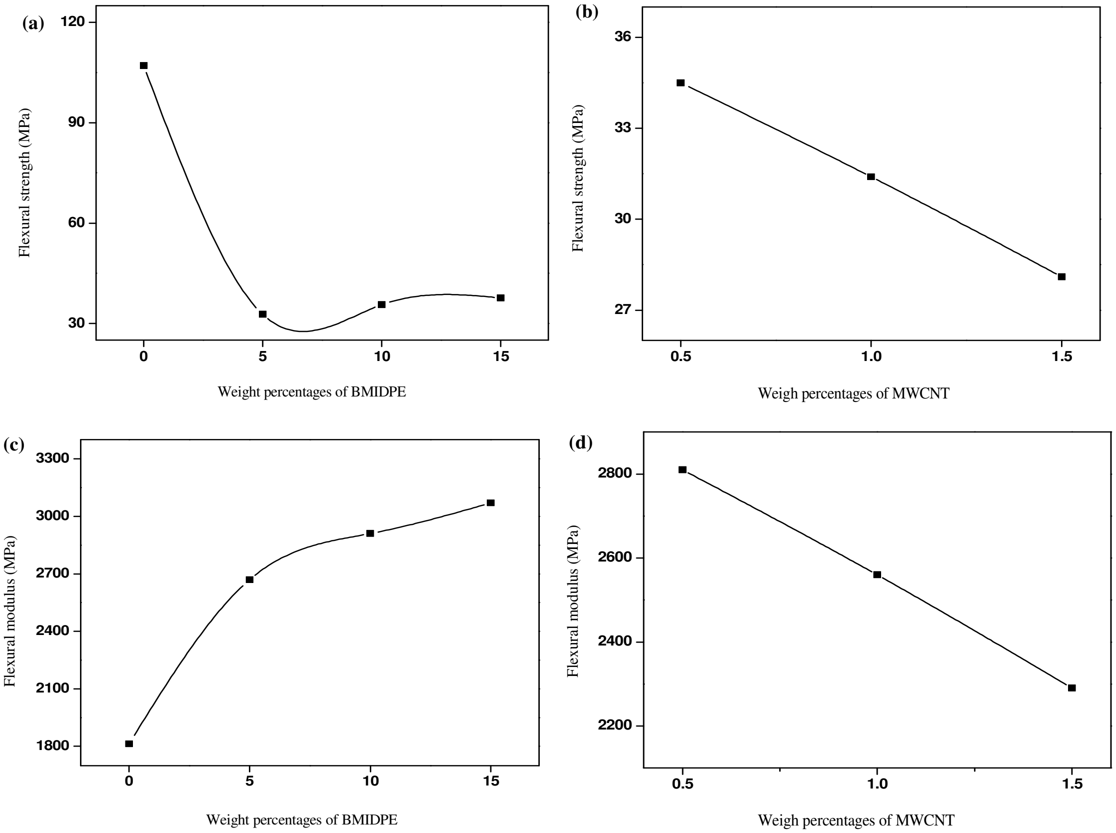


Fig.- 9: Flexural Strength of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites and Flexural Modulus of (c) Neat BMI/DGEBA and (d) BMI/DGEBA/MWCNT Nanocomposites

Impact Behavior

The impact properties of neat DGEBA, BMIDPE-toughened DGEBA epoxy and MWCNT filled DGEBA epoxy nanocomposites are presented in Table-2 and Fig.-10a and b.

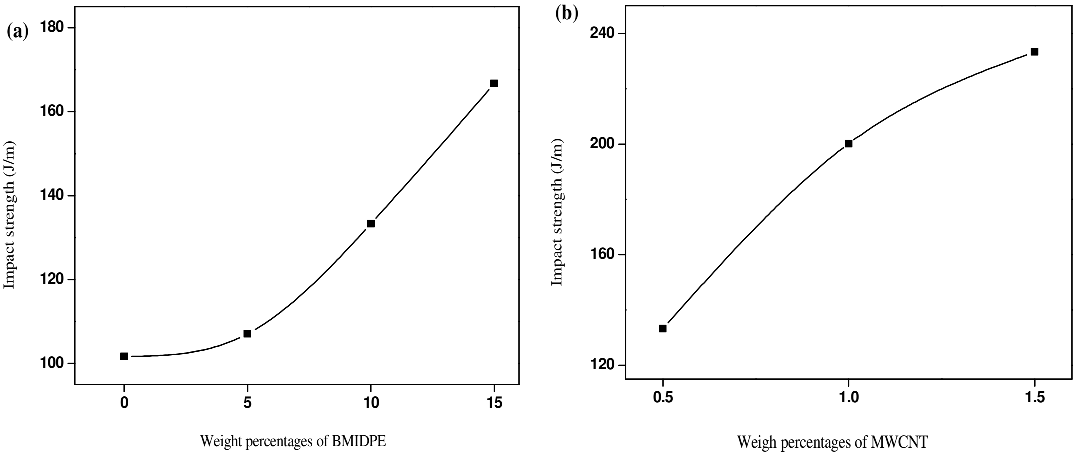


Fig.-10: Impact Strength of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

This enhancement is described as a result of the chain enlargement by the incorporation of polyether amine and the creation of the flexible structure within the matrix system. Furthermore, the existence of ether linking in the polyether amine structure is also accountable for the better improvement of the impact strength owing to its unrestricted molecular movement. But, the magnitudes of impacts of BMI/epoxy are superior to unmodified epoxy matrix.[34, 41]

The introduction of 0.5, 1.0 and 1.5 wt% of MWCNT into10 % BMIDPE-DGEBA epoxy resin matrix elevated the impact strength by 3, 50 & 75% correspondingly. This was ascribed to the flexibility exerted due to the higher stiffness and strength of the MWCNT, which act as tiny and arbitrarily dispersed tubes. On comparing the values of impacts of the BMIDPE/DGEBA system with the BMIDPE/DGEBA epoxy based MWCNT nanocomposites, they displayed higher values than that of BMIDPE caused by the existence of higher cross linking density. This may be elucidated by the improved flexibility of the network of BMIDPE/DGEBA than that of BMIDPE/DGEBA. The extended chain develops toughness and processibility of BMI because of the expansion of the chain length that has a tendency to increase the toughness of the BMI system. On the other hand, the crosslinked structure through Michael-addition reaction is formed by the reaction of bis-nucleophilic species with the BMI system. According to the percentage content of BMI, the fusion of BMI into epoxy resin matrix increases the toughness, owing to the suppressed crosslinked structure density and a larger percentage of flexible ether network[50].

Hardness

Comparing with DGEBA resin, a significant increment of hardness is obtained for BMI/DGEBA nanocomposites (Fig.-11a and b).It is seen that the inclusion of BMI into epoxy matrix reduces the hardness to remarkable value. The hardness of the neat epoxy system is observed as 84 MPa, whereas the 5%, 10% and 15% BMI modified epoxy show 159.3, 117.9 and 83.8 MPa.

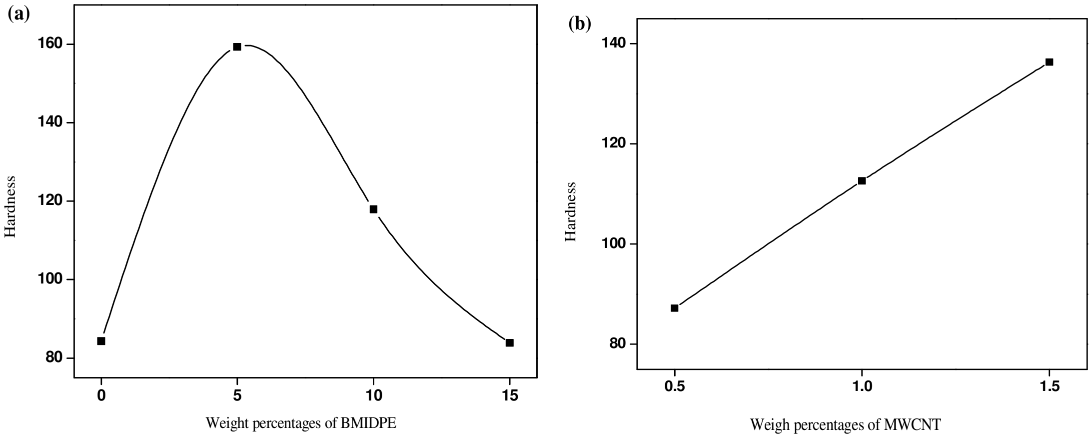


Fig.-11: Hardness of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

This may be ascribed to the inherent flexible molecular structure of BMI and the inclusion of flexible linkage between BMI and the epoxy resin matrix. Furthermore, this existence of homopolymerization of BMI and the establishment of intercross linking structure between the BMI and epoxy resin matrix are both remarkably responsible for the hardness. Epoxy/MWCNT nanocomposites resulted in the hardness value of 136.3 MPa which is 16% more that of BMIDPE/epoxy sample. The reinforcement of nanotube and its derived high strength may effect in forming a network structure that expands the hardness of the composites.

Dielectric Properties

The dielectric constant values of the BMIDPE-toughened DGEBA/MWCNT epoxy nanocomposites were higher than neat epoxy (Table-1 and Fig.-12a and b). This increment was due to interfacial polarization exerted in MWCNTs. The low-frequency dielectric constant values of the composites have substantially influenced by the polymer flexibility. Especially, the existence of dipole nature in the polymer resin matrix and their movement strongly impact the dielectric constant. The amount of the dielectric loss also improved with the growing polarity of the polymer component.[51,53]

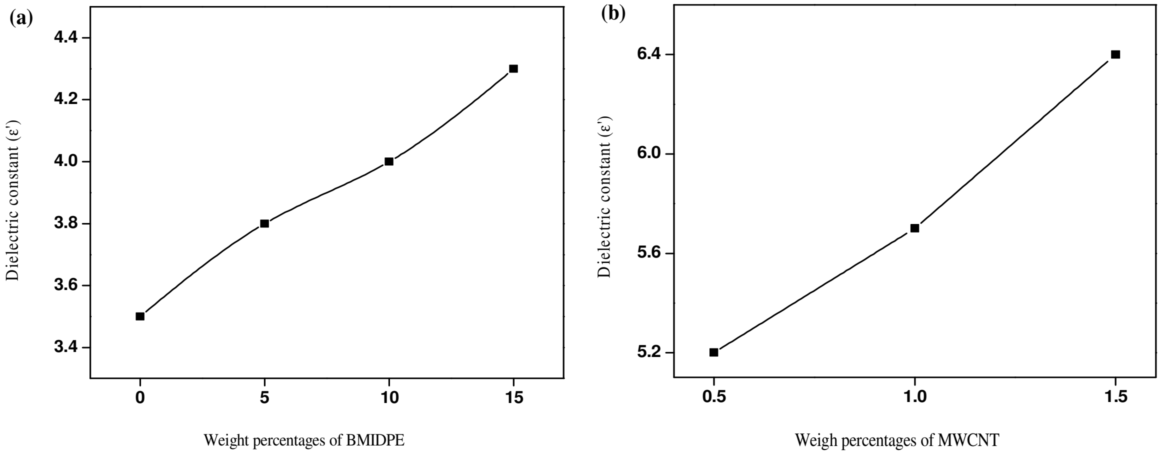


Fig.-12: Dielectric Behaviour of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

Morphology

The morphological behavior of the epoxy resin nanocomposites was studied by SEM and the rough surfaces of the neat DGEBA epoxy and MWCNT/epoxy resin nanocomposites are shown in Fig.-13. The neat BMIDPE-toughened DGEBA epoxy systems display a relatively fine fracture surface even at the upper magnification[34, 41,52] from Fig.-13a and b.

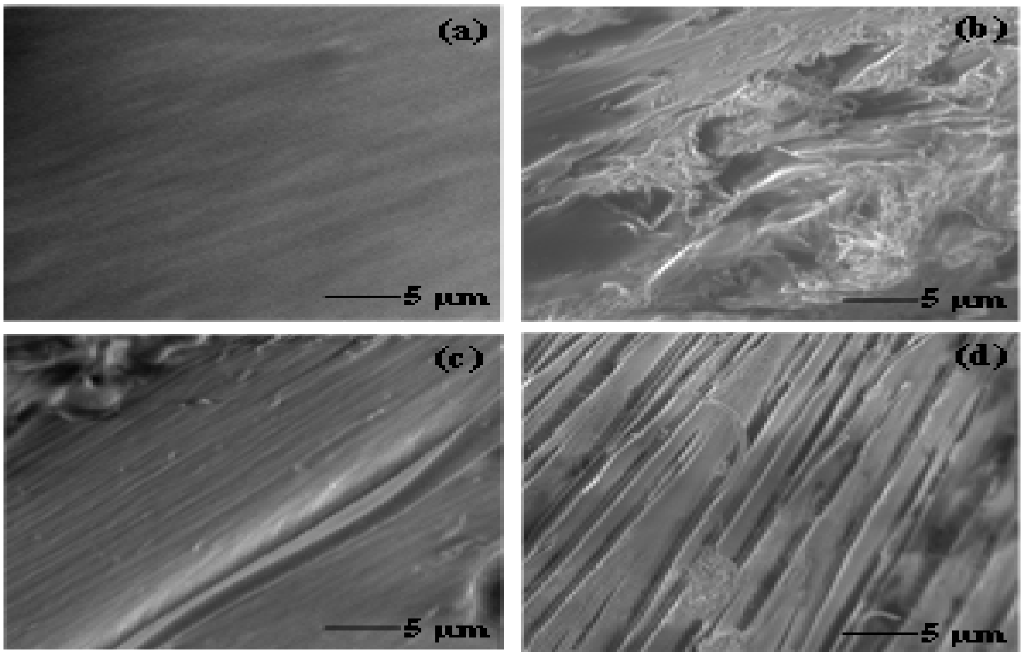


Fig.-13: SEM Images of the (a) Neat BMI/DGEBA and (b) BMI/DGEBA/MWCNT Nanocomposites

The rough surfaces of the nanocomposites show noticeably no apparent fractographic separation between the MWCNT and epoxy resins was noticed. The rough surfaces of the nanocomposites are coarse with the MWCNTs added into the epoxy system as seen Fig.-13c and d. In addition, the transparent and homogeneous morphology of MWCNT clearly indicates the effective miscibility of MWCNT in the epoxy system. The miscibility could be arisen due to the covalent bond formation between the acid-modified MWCNT and the epoxy matrix and led to the development of nanocomposites with exfoliated structures[43].

CONCLUSION

A novel bismaleimide toughened multi-wall carbon nanotube reinforced epoxy nanocomposites has been structurally designed, developed and characterized. The reinforcement efficiency of MWCNTs filler in the epoxy matrix was assessed along with the thermal stability and T_g. The tensile strength of the nanocomposite was improved to 7% with merely 1.5 wt% loading of acid modified carbon nanotubes than the neat BMI/DGEBA matrix. The developed nanocomposites showed substantial changes in Young's modulus than that of neat epoxy. This substantial enhancement recommended an efficient way to recognize an industrial application of nanotubes reinforcing epoxy nanocomposite. With only 1.5 wt% loading, the flexural modulus of MWCNT/epoxy composite was drastically augmented by 70% whereas the flexural modulus of the neat epoxy matrix was only improved by 32%. The reduction in water uptake properties for the BMI/epoxy matrix is due to the intrinsic water repellent nature of bismaleimide linkages which ascertain water repellent properties of the composites. The incorporation efficiency of MWCNTs fillers in the epoxy matrix was assessed along with the electrical and mechanical properties. In addition, MWCNT/epoxy nanocomposites resulted in better-enhanced impact strength and hardness representing that there is effective load transfer between the polymer matrix and the reinforced nanotube at the nanolevel. The dielectric constant values of the resulted nanocomposites were enhanced by means of increased weight percentages of MWCNT into the epoxy matrix. SEM microphotographs revealed that MWCNT was thoroughly impregnated in the polymer matrix with the presence of the chemical bonding between MWCNT and the epoxy matrix. Such a unique combination of thermal, mechanical and dielectric properties opens the door for developing nanocomposites eventually with multi-functionalities.

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