ABSTRACT

The objective of the present work is to focus on the synthesis and characterization of different functionalized polybenzoxazines and to improve the properties of polybenzoxazines by hybridizing them with nano-sized organically modified montmorillonite clay (OMMT) and multiwalled carbon nanotubes (MWCNT) to meet the requirements of high performance applications. The aromatic diols (1,1-bis(3-methyl-4-hydroxyphenyl) cyclohexane (BMHPC), bis(3-hydroxyphenyl)phenyl phosphate (BHPP), bis(3-hydroxyphenoxy) phenyl phosphine oxide (BHPPO), bis(3-hydroxyphenoxy)diphenyl silane (BHDPS) and bis(3-hydroxyphenoxy) dimethyl silane (BHDMS)), N-(4-hydroxyphenyl)maleimide (HPM), cyanate ester (1,1-bis(3-methyl-4-cyanatophenyl)cyclohexane (BMCPC)), bismaleimide (bis(4-maleimidophenyl)methane (BMPM)), aromatic diamine (bis(3-aminophenyl)phenyl phosphine oxide (BAPPPO)), bifunctional benzoxazine monomers (1,1-bis(3-methyl-4-hydroxyphenyl)cyclohexane benzoxazines (CBs), 4,4'-sulfonyldiphenol benzoxazines (SBs), bis(4-maleimidophenyl)benzoxazines (BMPBs), phosphorus diol benzoxazines (BHPPB and BHPPOB) and silicon diol benzoxazines (BHDPSB and BHDMSB)) and epoxy resin (silicon containing epoxy (SE), siliconized epoxy (EP-HTPDMS)) were synthesized using appropriate chemical intermediates and were used for the development of polymer matrices such as polybenzoxazines, polybenzoxazine-bismaleimide/cyanate ester hybrid polymers and benzoxazines modified epoxy hybrid polymers. The resulting hybrid polymer matrices were then reinforced with organoclay and MWCNT nanofillers to prepare polybenzoxazine based nanocomposites. The purity and structure of the benzoxazine monomers (CBs, SBs, BMPBs, BHPPB,
BHPPOB, BHDPSB and BHDMSB) and other organic monomers such as BMCPC, BMPM, BAPPPO and HPM were confirmed by FT-IR and NMR spectral analysis.

The benzoxazines were prepared from aromatic and aliphatic amines (aniline (Ani), 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylether (DDE), 4,4'-diaminodiphenylsulphone (DDS), bis(3-aminophenyl)phenyl phosphine oxide (BAPPPO), 1,2-ethylenediamine (ED) and 1,6-diaminohexane (DH)). The 1,1-bis(3-methyl-4-hydroxyphenyl)cyclohexane benzoxazines (CBs), 4,4'-sulfonyldiphenol benzoxazines (SBs) and bis(4-maleimidophenyl)benzoxazines (BMPBs) were prepared using the above mentioned amines except BAPPPO, DDS and Ani respectively. The bis(3-hydroxyphenyl)phenyl phosphate (BHPP), bis(4-hydroxyphenoxy)diphenyl silane (BHDPS) and bis(4-hydroxyphenoxy)dimethyl silane (BHDMS) based benzoxazines were prepared by using 4,4'-diaminodiphenylmethane (DDM).

The polybenzoxazines containing cyclohexane (PCBs), sulfone (PSBs), maleimidophenyl (PBMPBs), phosphorus (PBHPPB and PBHPPOB) and silicon (PBHDPsb and PBHDMSB) skeleton were prepared and their thermal properties were characterized. The bis(4-maleimidophenyl) polybenzoxazines (PBMPBs) showed higher thermal stability and char yield due to presence of both maleimidophenyl group and oxazine ring structure in BMPBs when compared to those of PCBs and PSBs. Polybenzoxazines containing phosphorus and silicon linkages exhibited higher glass transition temperatures (DSC), better char yield and high thermal decomposition temperatures (TGA) respectively, when compared to those of conventional polybenzoxazines due to the flame retardant nature of phosphorus and silicon.
The organoclay reinforced skeletal modified polybenzoxazine nanocomposites (PCBs/PSBs-organoclay) were prepared by solvent method using a sonicator. Thermal (DSC, TGA) and morphological (XRD, SEM) properties of organoclay reinforced polybenzoxazine nanocomposites were investigated. The incorporation of organoclay into polybenzoxazine (PCBs and PSBs) lowers the glass transition temperature ($T_g$) with an increase in decomposition temperature and char yield when compared with those of unmodified polybenzoxazine matrices. The enhancement in thermal stability of the nanocomposites was noticed up to 5 wt% of clay loading. The partial exfoliation (XRD) and homogeneous surface morphology (SEM) were observed for organoclay reinforced PCB and PSB nanocomposites.

The DDM based 1,1-bis(3-methyl-4-hydroxyphenyl)cyclohexane benzoxazine (CB$_{DDM}$), BAPPPO based bis(4-maleimidophenyl)benzoxazine (BMPB$_{BAPPPO}$), bis(4-maleimidophenyl)methane (BMPM) and 1,1-bis(3-methyl-4-cyanatophenyl)cyclohexane (BMCPC) hybrid polymer matrices were prepared by solution method. DSC and TGA analysis showed that the resulting hybrid polymers possess much higher glass transition temperatures than those of individual homopolymers. The organoclay and acidified MWCNT were used to prepare polybenzoxazine hybrid nanocomposites based on benzoxazines (CB$_{DDM}$ and BMPB$_{DDM}$) modified DGEBA epoxy matrix systems in order to improve thermal, mechanical and electrical properties of hybrid polymer matrices.

The organoclay reinforced benzoxazines modified DGEBA epoxy hybrid nanocomposites were prepared via in-situ polymerization of diglycidyl ether of bisphenol-A epoxy (DGEBA)-CB$_{DDM}$/BMPB$_{DDM}$ with 4,4'-diaminodiphenylmethane (DDM) as a curing agent using varying percentages (upto 5 wt%) of organoclay. Similarly, MWCNT reinforced
benzoxazines modified DGEBA epoxy nanocomposites were prepared by solvent method using a sonicator. Thermal (DSC, TGA), thermo-mechanical (HDT, DMA, CTE), mechanical (tensile strength, flexural strength and impact strength), electrical (dry arc resistance, dielectric constant and dielectric loss), water absorption and morphological (XRD, SEM and TEM) properties of benzoxazines modified DGEBA epoxy nanocomposites were studied and discussed.

The PBMPB, PBHPPB, PBHPPOB, PBHDPSB and PBHDMSB matrix systems exhibit better thermal stability and high char yield when compared to those of PSBs and PCBs matrix systems. The BMPB/BAPPPO/BMPM and benzoxazines modified DGEBA epoxy hybrid matrices show better properties than those of other hybrid matrices. The PSBs-organoclay nanocomposites exhibit improved glass transition temperature and thermal stability than those of PCBs-organoclay nanocomposites. The organoclay reinforced benzoxazines modified DGEBA epoxy nanocomposites possess high thermal stability, high impact strength, high storage modulus and low dielectric properties. The MWCNT reinforced benzoxazines modified DGEBA epoxy nanocomposites possess better thermal, mechanical and high dielectric properties. The data obtained from different studies such as thermal, mechanical, thermo-mechanical, morphological and electrical, it is concluded that the organoclay/MWCNT reinforced benzoxazines modified DGEBA epoxy nanocomposites possess superior characteristic properties than those of unmodified DGEBA epoxy resin. These hybrid nanomaterials can be effectively used in the form of coatings, adhesives, matrices and composites for high performance industrial and engineering applications under severe and harsh environments with improved longevity.