

Studies on Structural, Morphological, Thermal and Mechanical Properties of HPMC/GO-ZnO Hybrid Nanocomposites

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ABSTRACT

The nanocomposite films were prepared by joining Graphene Oxide-Zinc Oxide hybrid nanoparticles (GO-ZnO) into Hydroxypropyl methylcellulose (HPMC) polymer network. The films were prepared with various concentrations of GO-ZnO by using solution casting method. The films were characterized by its Structural, Mechanical and Thermal properties. It is observed that as the concentration of the GO-ZnO nanoparticles increases, there is a reduction in the mechanical & thermal properties of nanocomposite.

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Introduction

In current years, polymer nanocomposites fascinated the thoughts of many researchers because of their greater properties arising in the presence of nano fillers [1]. With the incorporation of nano estimated inorganic particles into the polymeric matrix, the new composite material will display changed physical, mechanical, thermal, optic, viable bactericidal capacity, intensive UV and infrared absorption, which enormously contrast from those of ordinary materials[2-4]. The properties of such nanocomposites rely upon the volume part, the size of nanoparticles, readiness technique and furthermore polymer/filler interface [5-6]. The disclosure of graphene and graphene-based polymer nanocomposites is a significant expansion in the zone of nano science and innovation [7-15]. From its first acquisition and abuse in polymer nanocomposites, graphene oxide has been contrasted with very notable, previously existing and high performing nano filler.

Graphene is a two-dimensional carbon allotrope, has been favored as nano filler over other nano fillers due to high surface area, aspect ratio, tensile strength, thermal and electrical conductivity and EMI protecting properties [16-20]. It is a one particle thick planar sheet of sp² fortified carbon iotas which are thickly stuffed in a honeycomb crystal lattice. Graphene is otherwise called the thinnest material known to man. Graphene has amazing properties, for example, extraordinarily high thermal conductivity, unrivaled mechanical properties and superb electrical bearing properties [16-20] with massive application potential [21-23]. These predominant properties of graphene can be reflected in polymer/graphene nanocomposites. In any case, the improvement in the physicochemical properties of the nanocomposites relies upon the dissemination of graphene sheets in the polymer framework and the interfacial communication between the graphene sheet and host polymer lattice. Then again graphene oxide (GO) is an oxidized type of graphene having hydroxyl, epoxy, diols, carboxylic and ketonic useful

functional groups. This oxygen bearing functional groups of GO can fundamentally influences the van der Waals interactions with organic polymers [19-20]. It contains both sp² and sp³ hybridized carbons bearing hydroxyl and epoxide functional groups on its "basal" plane [16] while the edges are for the most part enhanced via carboxyl and carbonyl functional groups [24]. Along these lines, GO is hydrophilic in nature and can be promptly dispersed in water as individual sheets to form stable colloidal suspensions [25]. In the mean time, these oxygen-containing groups present in GO sheets are liable for solid cooperation's with polar little atoms or polar polymers to form GO intercalated or exfoliated composites [26]. As the greater part of the synthetic polymers are non-biodegradable, so today in a situation sharpened age the uses of bio-degradable polymers are picking up enthusiasm for various applications. In any case, bio-degradable polymers have lower mechanical, thermal and water resistant properties thought about to engineered polymers. Thus to help the above said properties, bio degradable polymers can be mixed with engineered or normal polymers [27] or by including nano fillers, for example, GO [28] and furthermore by cross linking [29]. What's more, the functional groups of GO can likewise have improved similarity with organic polymers and for this reasons, GO has pulled in extensive consideration as a nano filler for creation of polymer nanocomposites. With this intrigue, GO has been utilized as a filler in the present investigation.

With coming of nanotechnology, a semiconductor nanoparticle has pulled in a lot of consideration because of their novel optical, electrical and mechanical properties. Among different semiconductor nanoparticles, nanosized zinc oxide (ZnO) particles are the most regularly considered in light of their enthusiasm for basic investigation and furthermore their applied viewpoints, for example, in solar energy conversion, varistors, radiance, photo catalysis, electrostatic dissipative covering, Transparent UV films and synthetic sensors. Beforehand, ZnO nanoparticles have been set up by strategies including

the sol-gel technique [30-31], precipitation [32], aqueous blend [33], and shower pyrolysis [34]. The mix of progress metal oxides, for example, ZnO with graphene-based materials, for example, GO to create polymer nanocomposites holds extraordinary guarantee as a viable method to improve the capacitance value. The fruitful intercalation of these metal oxides into graphene sheets may forestall the agglomeration and stacking which can prompt the development of superior novel composite materials [35]. Also, the examination on GO/ZnO hybrid based polymer nanocomposites is extremely restricted. Consequently, remembering this we have picked ZnO and GO hybrid material as filler in the present study.

Hydroxyl propyl methyl cellulose (HPMC) is a bio-degradable and bio-good polymer and broadly utilized for various applications [36]. It is likewise water dissolvable. In this way, we have favored HPMC for getting ready nanocomposites films with GO/ZnO nanohybrids fillers. The GO/ZnO hybrid nanocomposite is with nanosized 50.94 nm (from XRD) and good thermal, optical and conductive properties are evaluated in my own published paper [37], which we have used for preparing polymer nanocomposites. Henceforth, the primary target of the present investigation is to plan new polymer/inorganic nanocomposites dependent on one of a kind mix of two nano fillers, for example, GO and ZnO and furthermore to augment the application window of GO/ZnO filled HPMC polymer nanocomposites. The scattering of nano-fillers into polymer grid was analyzed utilizing distinctive logical methods. The far reaching examination of HPMC-GO/ZnO nanocomposites was prepared by solution casting method and contemplating their basic structural, thermal, morphological, mechanical, optical and dielectric properties. The work involved the characteristic change of the bio polymer HPMC by the addition of hybrid nano particle GO-ZnO where it will be applicable for different common fields of usage like packing.

Experimental

The commercial grade HPMC utilized in this work and was acquired from Central Drug House, Delhi. HPMC was as white powder, having inexact molecular weight of 120,000 Dalton. GO-ZnO nanoparticles were prepared in our lab by using wet chemical method and the size of the nanoparticles used for this study is 50.94 nm [37]. Solution casting is a simple and adaptable strategy to deliver nanocomposite films in lab scale. In the arrangement projecting of polymer nanocomposites, 4 gram of polymer HPMC is dissolved in 100 ml water and mixed with GO-ZnO nanoparticles which is the same medium by using sonication (30 minutes) and continues stirring for one hour. The homogeneous solution was poured in to glass plate. The solvent phase is taken out by evaporation and there on the dried film is peeled off from the substrate and stored in a desiccators for further studies.

FTIR spectroscopy (Fourier-transform infrared spectroscopy) of HPMC/GO-ZnO nanocomposites films was completed with Fourier Transform Infrared Spectrophotometer in the wave number range 400 – 4000 cm^{-1} . X-ray diffraction (XRD) investigations of HPMC/GO-ZnO nanocomposites films were gotten with a scanning velocity and step size of $1^\circ/\text{mm}$ and 0.01° separately utilizing Bruker center progressed X-beam diffraction meter. The outputs were taken in the 2θ range from $10-70^\circ$ utilizing $\text{Cu K}\alpha$ radiation of frequency $\lambda = 1.54060 \text{ \AA}$. The surface morphology and microstructure of HPMC/GO-ZnO nanocomposites films were additionally inspected by

scanning electron microscope (SEM). Warm stability of HPMC/GO-ZnO nanocomposites films was contemplated utilizing TGA/DSC; the tests were carried up to 800°C at a rate of $10^\circ\text{C}/\text{min}$. The mechanical properties of HPMC/GO-ZnO nanocomposite films were explored utilizing Bench top UTM. The tests with the dimension of $20 \times 20 \times 0.05 \text{ mm}$ were utilized for mechanical testing

Results and Discussion

FTIR analysis of HPMC/GO-ZnO nanocomposites

FTIR spectroscopy is extremely helpful and advantageous strategy to examine the communication between at least two segments of nanocomposites. In the current examination, FTIR investigation of HPMC/GO-ZnO nanocomposite films was done to dissect the practical gatherings, the idea of holding and to comprehend the basic changes in the nanocomposites because of the joining of GO-ZnO nano fillers. Figure 1(a) shows the FTIR spectrum of HPMC. The band at 3429.65 cm^{-1} is attributed to OH stretching vibrations. The band at 2916 cm^{-1} is due to symmetric stretching vibrations of methyl and hydroxyl propyl group. The band at 2328 cm^{-1} is attributed to O-H stretching vibrations or intra molecular hydrogen bonding. The band at 1645 cm^{-1} is due to stretching vibrations of C=O groups present in HPMC. The peaks for the hybrid Nanomaterials were observed in the HPMC/GO-ZnO nanocomposite films in Fig. 1(b-d). Graphene oxide the peaks at 1455.63 cm^{-1} and 1374.49 cm^{-1} are attributed to -CH₂ scissoring and O-H bending vibrations respectively [38]. The broadband at 1049 cm^{-1} is attributed to C-C and C-O vibrations of cellulose. The peaks at 1053.45 cm^{-1} , 1268 cm^{-1} , and 1645.87 cm^{-1} were seen which compares to C-O bending and C=O stretching vibration individually [39,40] The FTIR peaks at 1374.62 cm^{-1} and 2331 cm^{-1} were likewise seen in the range of ZnO which are credited to the extending vibrations of C=C and C-H gatherings. Other little tops at 1220 cm^{-1} , 1546 cm^{-1} and 1735 cm^{-1} are ascribed to the adsorbed carbonate moieties [41-42]. FTIR range of HPMC/GO-ZnO nanocomposite films shows attributes peaks of the apparent multitude of components, demonstrates that the nanocomposites are effectively prepared.

XRD analysis of HPMC/GO-ZnO nanocomposites

The XRD (X-Ray Diffraction) example of pure HPMC Fig. 2 (a) shows a solitary wide peak at $2\theta = 20.21^\circ$ demonstrating that HPMC is an amorphous polymer [43]. The solid diffraction peak of GO was observed at $2\theta = 12.9^\circ$ and the peaks after $2\theta = 25^\circ$ explains the peak of ZnO. Figure 2(b-d) shows the XRD pattern of HPMC/GO-ZnO nanocomposite films and all the XRD peaks of GO-ZnO hybrid nanoparticles were seen in the trademark diffraction peaks of HPMC/GO-ZnO polymer nanocomposite films; however the trademark peaks of ZnO decreased. This show that the ZnO segments were uniformly connect with the GO and the mixture nano filler was homogeneously blended in the HPMC polymer network.

SEM analysis of HPMC/GO-ZnO nanocomposites

The SEM (Scanning Electron Microscopy) micrographs of HPMC/GO-ZnO nanocomposites are appeared in Fig. 3(a-d). It very well might be proposed from Fig. 4b that the nanocomposite with extremely low GO-ZnO content (1 wt %) shows a homogeneous and smooth surface morphology, very like pure HPMC (Fig. 3a). As we continue expanding the wt% of GO-ZnO (3 and 5 wt%) as appeared in Fig. 3c

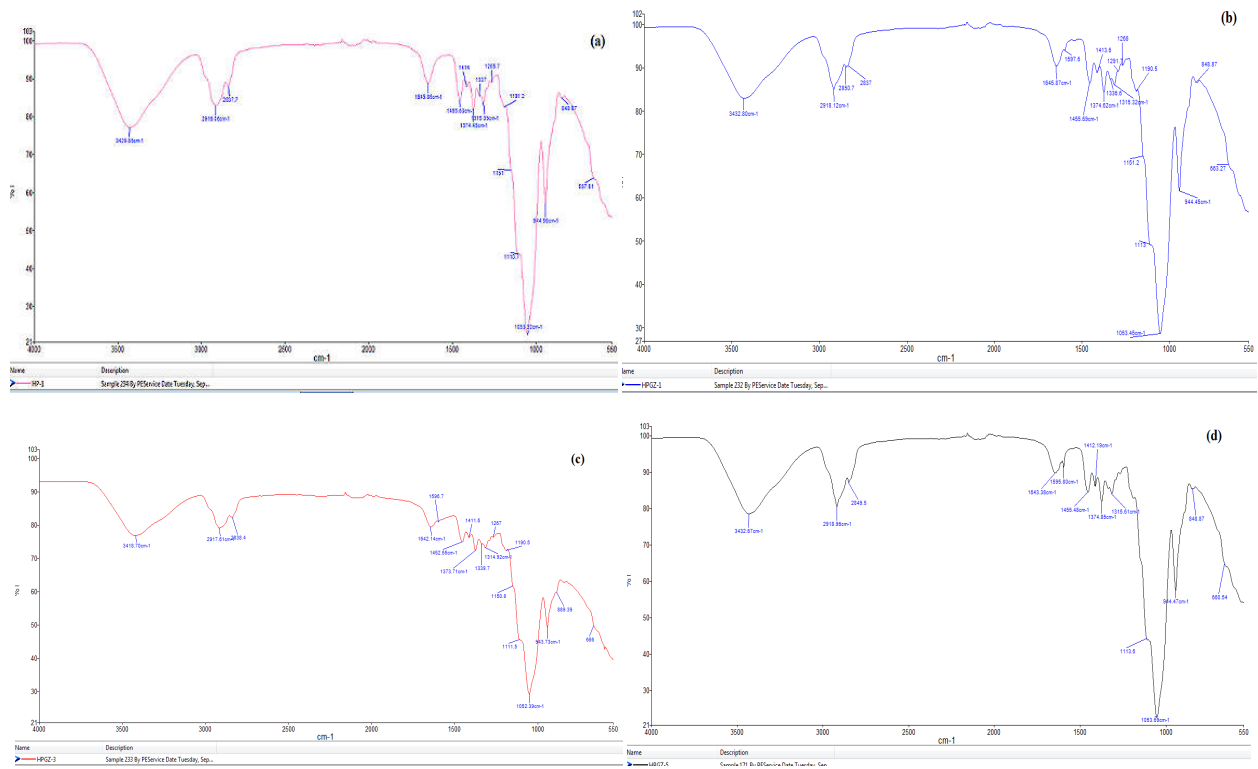


Figure 1: FTIR Spectra of a) Pure HPMC b) HPMC/GO-ZnO (1 wt %) c) HPMC/GO-ZnO (3 wt %) d) HPMC/GO-ZnO (5 wt %)

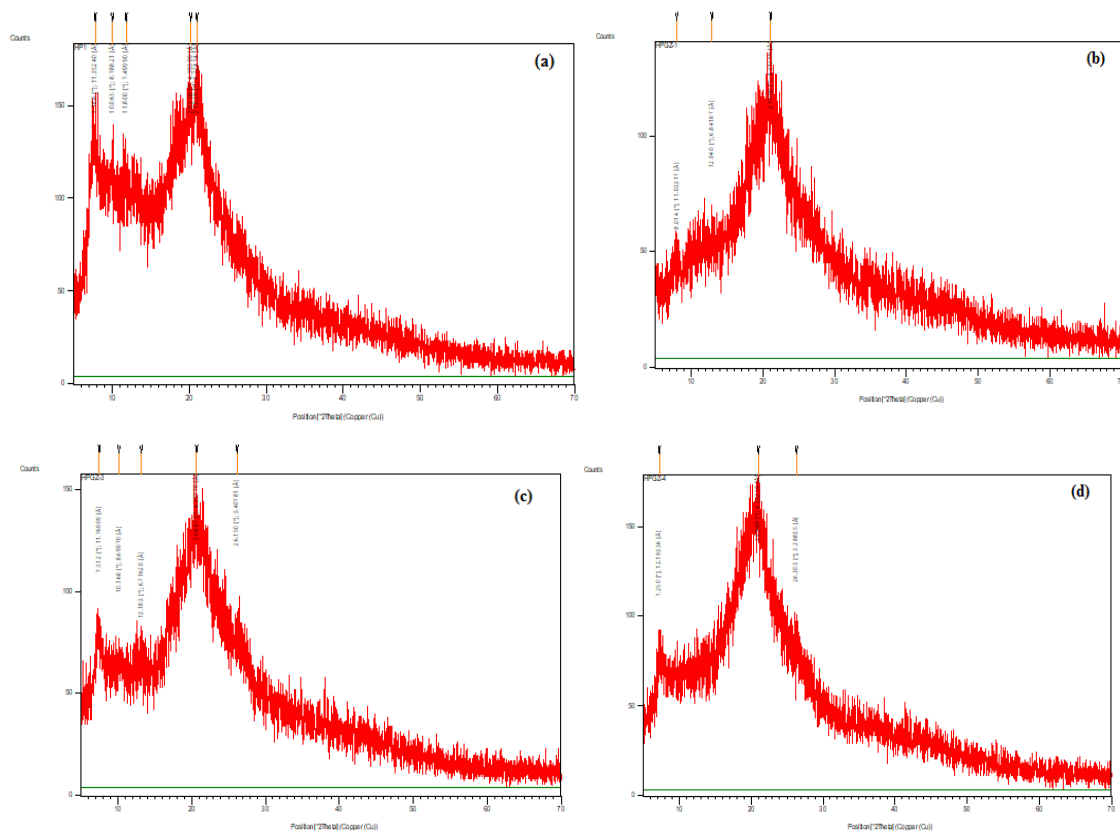


Figure 2: XRD Chromatogram of a) Pure HPMC b) HPMC/GO-ZnO (1 wt %) c) HPMC/GO-ZnO (3 wt %) d) HPMC/GO-ZnO (5 wt %)

and d, the nanocomposites uncover a similarly unpleasant and coarse kind of surface morphology which is very conspicuous on account of Fig. 3d crediting to the way that the GO-ZnO nanoparticles are colossally adhere to the

HPMC network. It very well may be also demonstrated that the peeled nanocomposites delineates a decent level of scattering of GO-ZnO in the HPMC matrix. Overall the nanocomposites with more prominent GO-ZnO content

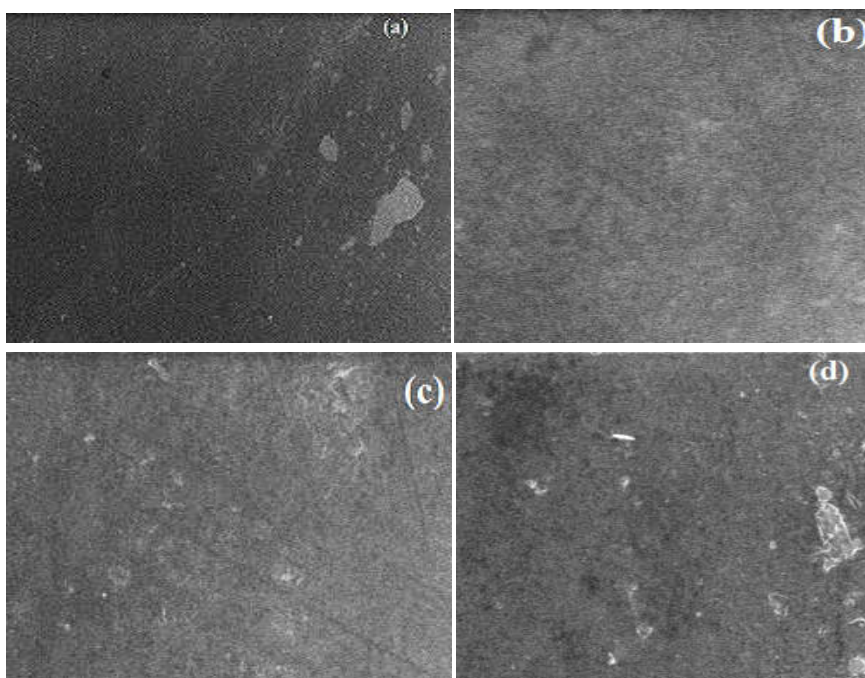
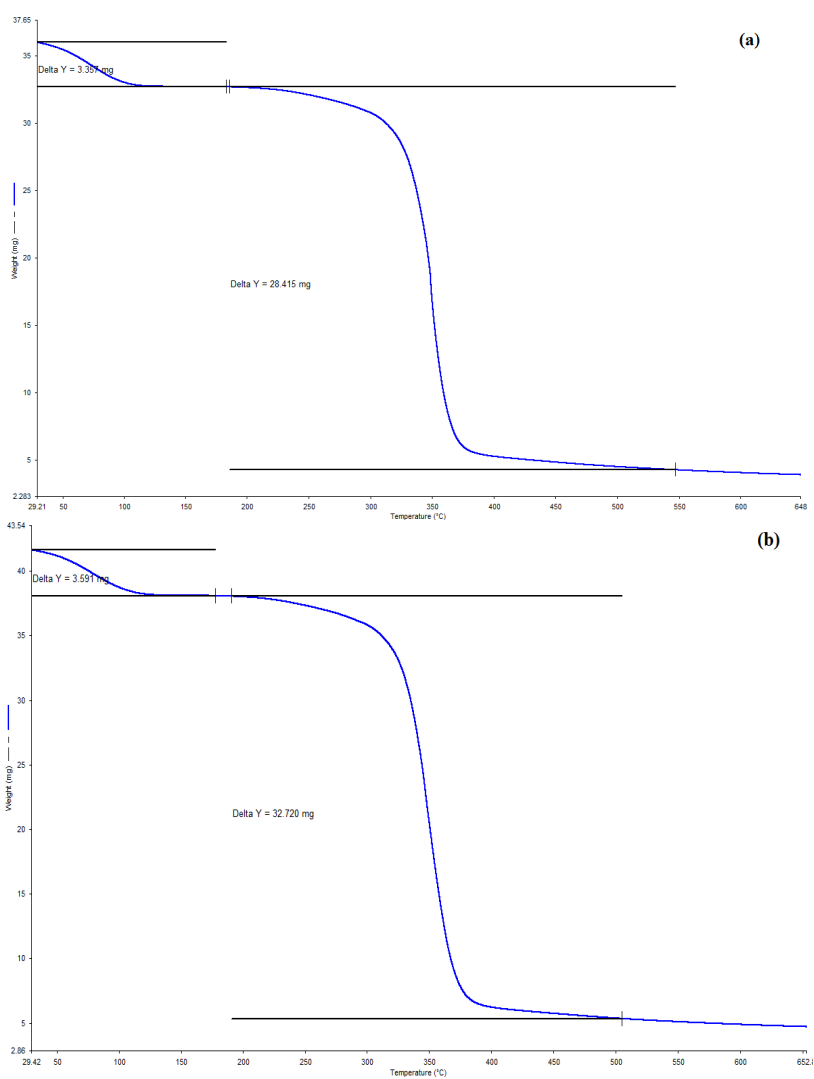


Figure 3: SEM images of a) Pure HPMC b) HPMC/GO-ZnO (1 wt %) c) HPMC/GO-ZnO (3 wt %) d) HPMC/GO-ZnO (5 wt %)



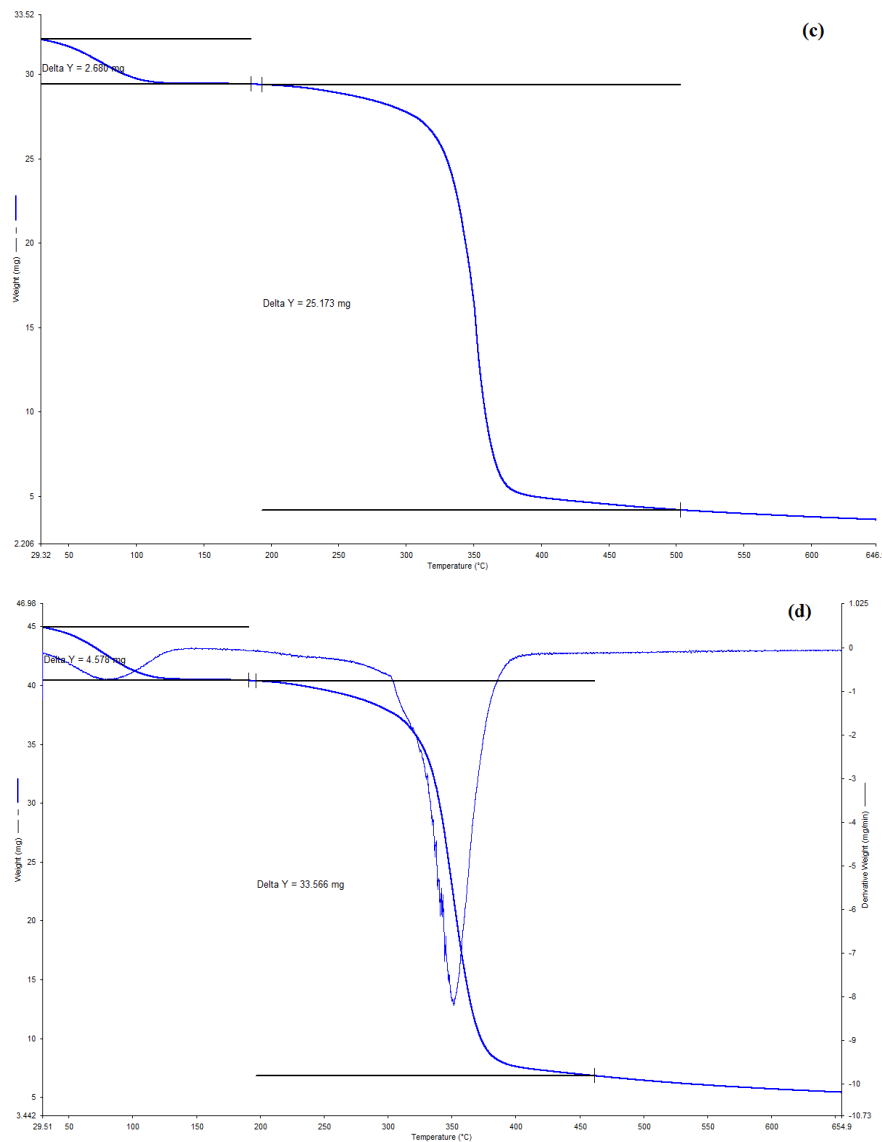


Figure 4: TGA Spectra of a) Pure HPMC b) HPMC/GO-ZnO (1 wt %) c) HPMC/GO-ZnO (3 wt %) d) HPMC/GO-ZnO (5 wt %)

Table 1. Percentage of weight loss of HPMC/GO-ZnO hybrid nanocomposites at various temperatures

Sample code	Percentage of weight loss at various temperature						
	100° C	200° C	300° C	400° C	500° C	600° C	Residue
Pure HPMC	8.39	9.45	14.63	85.42	87.54	88.77	3.89
HPMC/ GO-ZnO (1%)	7.04	8.81	14.01	85.07	87.11	88.27	4.70
HPMC/ GO-ZnO (3%)	7.32	8.52	13.51	84.62	86.86	88.10	3.62
HPMC/ GO-ZnO (5%)	8.19	10.27	16.02	83.08.	85.70	87.31	5.41

Table 2. Mechanical properties of Pure HPMC and HPMC/ GO-ZnO nanocomposites

Sample code	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
Pure HPMC	374.43	99.82	13.23
HPMC/ GO-ZnO (1%)	388.77	9.84	12.77
HPMC/ GO-ZnO (3%)	418.22	9.9	11.36
HPMC/ GO-ZnO (5%)	340.765	9.98	11.05

shows surfaces distending GO-ZnO covered with HPMC demonstrating the solid interfacial bond among HPMC and GO-ZnO nanoparticle.

Thermal Analysis of HPMC/GO-ZnO nanocomposites

The thermal studies of polymer nanocomposites are a significant property on the grounds that these nanocomposites are frequently utilized as superior designing plastics. Figure 4(a-f) shows TGA (Thermo gravimetric Analysis) thermograms of HPMC/GO-ZnO nanocomposites. It very well may be noticed that HPMC films shows decomposition in three phases. The principal disintegration phase of HPMC was begun at temperature moderately under 100 c and went up to 150 c which is because of the presence of moisture in the example. The subsequent corruption stage saw in the temperature range 150 C -350 C can be due to the decay of polymer chains. The third stage was seen in the temperature range 360 - 500 c which is credited to the disintegration of remaining carbon. This decomposition temperature shifts towards little higher temperature as the GO-ZnO nanoparticle fixation increments.

The level of weight reduction of and HPMC/GO-ZnO mixture nanocomposite films at different temperatures is given in Table 1. The TGA thermograms of HPMC (Fig.4 a) and HPMC/GO-ZnO polymer nanocomposite films (Fig.4 b-d) show the development of GO-ZnO filler to HPMC network fabricates the warm security of the polymer. At 500°C the degree of weight decrease of HPMC neat film is 88.77 % and it reduces to 87.31% when it is added with 5% of GO-ZnO. This likewise confirms the extension in thermal stability of HPMC film after the expansion of GO-ZnO. Only At 200° C and 300° C the weight reduction is increased and it may be due to the agglomeration of the GP-ZnO nanoparticles at 2% and 3% loading.

The DSC (Differential Scanning Calorimetry) thermograms of the HPMC and HPMC/GO-ZnO nanocomposite films are appeared in Fig 5 (a-d). The glass Transition temperature (Tg) of the HPMC pure film was at 88.09 ° C. As the pace of Hybrid nano filler rate builds the Tg of the Hybrid polymer nanocomposite film decreases. The Tg of the decreases to 82.94 with the addition of 5 wt% of GO-ZnO hybrid nanoparticle to the HPMC matrix. The crystallinity of the polymer network increases by the addition of the GO-ZnO nano particles lead to the reduces in the Tg.

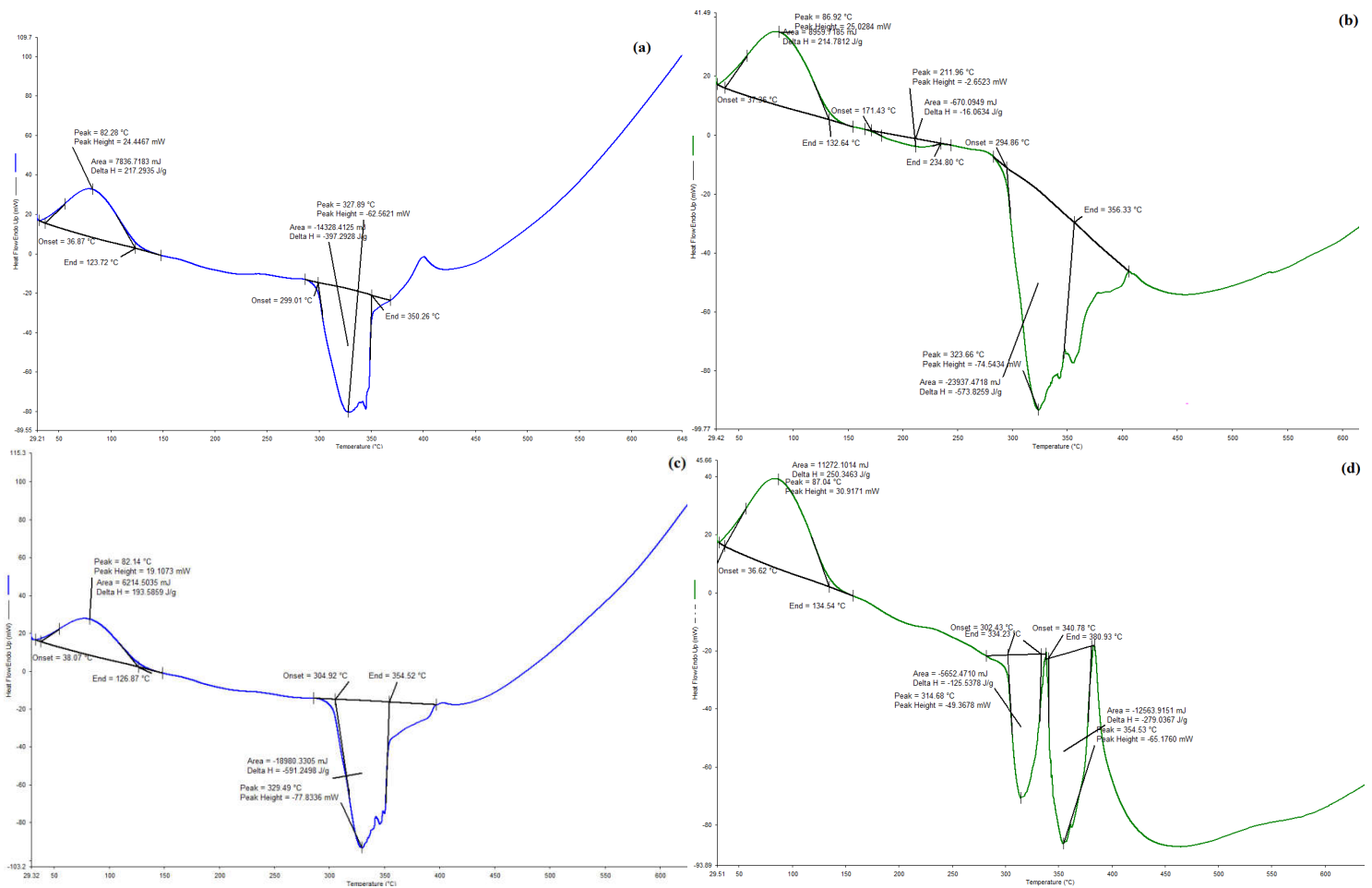


Figure 5: DSC Spectra of a) Pure HPMC b) HPMC/GO-ZnO (1 wt %) c) HPMC/GO-ZnO (3 wt %) d) HPMC/GO-ZnO (5 wt %)

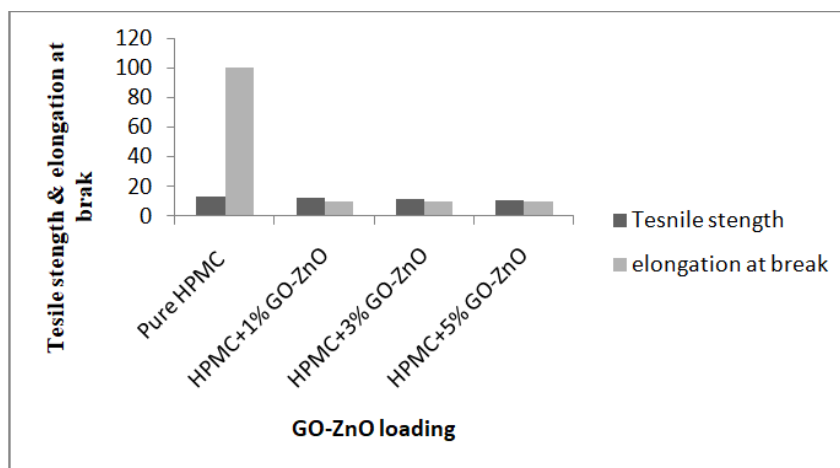


Figure 6: Mechanical properties of Pure HPMC and HPMC/GO-ZnO nanocomposites

Mechanical studies of HPMC/GO-ZnO nanocomposites

The impacts of GO-ZnO Hybrid nanoparticle on the mechanical properties of the HPMC nanocomposite films were assessed up to their failure. Table 2 shows the Tensile strength, the Young's modulus and elongation at break of the pure HPMC and HPMC/GO-ZnO nanocomposite materials. The Tensile strength and Young's modulus of the pure HPMC film were 13.2 MPa and 374.43 MPa separately. The elongation at break of same film was 99.82 %. Single direction showed that the expansion of GO-ZnO nanoparticles to HPMC films brought about a huge effect in mechanical properties. As the GO-ZnO focus builds, the Tensile strength, Young's modulus and stretching diminishes and is clearly drawn in fig 6. The expansion of GO-ZnO to the HPMC films didn't bring about any improvement in mechanical properties and rather we noticed drawback impact. This could be because of strain field's occurs at polymer lattice because of presence of GO-ZnO nanoparticles. This is additionally a sign of less connection at the interface of the two segments because of the lower surface area [44].

Conclusions

The results obtained revealed that there are changes, both in mechanical and thermal properties, in HPMC films when GO-ZnO hybrid nanoparticles were added. Tensile strength, Young's modulus and rate of weight loss diminish as the GO-ZnO fixation increments. The mechanical properties decline in view of weakening of intermolecular van der Waal's force and furthermore because of the formation of strain fields because of unpredictable scattering of nanoparticles in the network of HPMC.

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