A simple solvent blending coupled sonication technique for synthesis of polystyrene (PS)/multi-walled carbon nanotube (MWCNT) nanocomposites: Effect of modified MWCNT content

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The influence of carboxylic acid functionalized multi-walled carbon nanotubes (cMWCNTs) content on the properties of polystyrene (PS) nanocomposite (NC) films was investigated. The NC films were produced by a simple sonication assisted solvent blending technique. The interaction between the matrix (PS) and well dispersed filler (cMWCNT) was evaluated by different techniques involving Fourier transform infrared spectroscopy, Raman spectroscopy and X-Ray diffraction. Morphological images of the NCs were collected from Transmission electron microscopy. The thermal characteristics of the PS were found to be improved by the incorporation of the cMWCNTs, which was evident from the Thermogravimetric analysis (TGA) data. The thermal degradation activation energy evaluated by Coats-Redfern method and integral procedural decomposition temperature determined by Doyle’s method supported the thermal stability proposed by TGA of the NCs. The reaction mechanism of thermal degradation of neat PS and respective NCs was successfully predicted using Grado method. The rheological properties and hardness were found to be upgraded by the inclusion of nanotubes to the PS matrix.

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1. Introduction

Nanoparticles are proven as excellent reinforcing fillers for preparing polymer composites with improved morphological, thermal, mechanical, and electrical properties due to its nano-scale (small) dimensions and exceptionally high surface area, which aids in the desired improvement of properties even at low loadings of the nanofiller [1]. A blend of nanoparticles and polymer ensures improved multifunctional attributes of the nanocomposites (NCs) in contrast to conventional composites. Easy processability [1,2], fire retardancy [1,2], thermal resistance [2,3], mechanical strength [4,5], chemical resistance [2], electrical conductivity [1,2,5], optical clarity [1], gas barrier properties [3] make polymer nanocomposites exclusively popular field of research.

Carbon nanotubes (CNTs) have been extensively used as reinforcing materials due to its high tensile strength [4,6], elastic modulus [2,4,5], heat transfer coefficient, thermal stability [1], thermal conductivity [1], electrical conductivity [1,5], aspect ratio [6,7] and exceptionally high surface area [1]. In order to enhance the properties of polymer, a very low volumetric fraction of CNTs is required because of its high aspect ratio. In contradiction to theoretical studies, experimentally, polystyrene (PS) is not a perfect dispersant for CNTs. Additionally, compared to other fillers, the employment of CNTs as fillers is limited due to the difficulty in their dispersion faced during processing as well as poor interfacial interaction between the polymer matrix and nanotubes. The high flexibility and surface energy of the CNTs impart strong adhesive property, for which the CNTs tend to agglomerate [8,9]. Strong electrostatic forces and van der Waals interaction exist between the individual tubes, which do not allow their proper distribution in the matrix [1]. This is because uniform filler dispersion is essential for effective reinforcement of the NC. Physical or chemical interaction between the modifiers of CNT sidewalls and the polymer matrix can overcome the adhesive forces between the individual layers by interfacial stress transfer [8,10]. Often high frequency ultrasonication [1,11,12] assists dispersion by peeling off the individual nanotubes and maintaining them in the separated form. Interfacial affinity of nanofiller towards polymer matrix plays an important role in effective reinforcement preventing entanglement [13]. Hence, for better performance, nanotube surface functionalization
involving covalent bonding is adopted to increase the PS/cMWCNT interfacial interaction, which optimizes the filler dispersion [10,14,15].

PS is a thermoplastic polymer, which becomes pliable above a specific temperature. Hence, to make it suitable for high temperature applications, the softening temperature must be raised to a considerable high value. CNTs, which can withstand a temperature as high as 3500 °C, can be expected to increase the thermal stability of PS NCs by its incorporation. cMWCNT with an average Young’s modulus of 1.8 TPa [4] and a high bending strength of 14.2 GPa [16] can be used to prepare high performance NCs, since it can resist repeated twisting and bending. The high tensile strength and low density of the CNTs promote the fabrication of lightweight strong composite materials. Improvement in mechanical properties by CNT reinforcement has been reported by several researchers [3,10,17,18].

There are several works carried out for the synthesis of PS/cMWCNT NCs via in-situ polymerization and melt mixing, but very little progress is made for the synthesis using solvent blending. Literature proved that in-situ polymerization, anionic polymerization and atom transfer radical polymerization (ATRP) require high temperature, initiator and terminator [19–24]. The additional raw materials increase the process cost. Melt mixing gives good yield, but difficult to overcome viscous forces and process parameters make it complex [11]. Solvent blending is simpler, easy to control process and when aided by ultrasonication gives a good distribution of the nanotubes even at high loadings [1].

Formation of polymer NCs with properly dispersed and incorporated nanotubes was inferred by Raman spectroscopy [25] and a D-band at 1329 cm⁻¹ (FTIR) Spectroscopy [19,29]. Raman spectroscopy of MWCNT-COOH showed a G-band and a D-band at 1329 cm⁻¹ respectively [25]. A N/D/IG ratio of 1.254 was obtained from the peak at 1715 cm⁻¹ [25], whereas the bands appearing at 3400 cm⁻¹, 1732 cm⁻¹, 2910 cm⁻¹ and 2850 cm⁻¹ respectively [28]. Thermogravimetric Analysis (TGA) showed a 31 °C increment in the thermal stability for the PS NCs with 3 parts per hundred of MWN, as compared to PS [31] and a temperature corresponding to maximum degradation (T_max) of 377 °C for PS NCs, same as that of PS [29]. A sharp increase in micro-hardness of the NCs was seen for CNTs content below 1.5 wt.%) [18]. NCs showed more solid-like stress relaxation behaviour, decrease in wear resistance, and increase in elastic modulus and yield strength with a corresponding decrease in failure strain, with increasing MWN content [32–37].

It is apparent from the above extensive literature review that the dispersion quality of nanofillers in polymer matrices plays a key role in altering the properties of polymer nanocomposites. However, there is a lack of studies on better dispersion of CNTs in PS matrix by simple means of approach. Therefore, this work aims at introducing a facile solvent blending coupled ultrasonication, technique for the synthesis of a polymer nanocomposite, which can improve the properties of the nanocomposite to a degree comparable with commonly used methods like melt mixing and radical polymerizations, at very low filler loadings. Greater emphasis has been given on dispersing the filler used because it influences the enhancement of the desirable traits to a great extent. Ultrasonication has been employed for two turns of short time intervals (to control the cost concern), expecting well dispersed modified MWCNT in PS matrix. The influence of cMWCNTs on the structural, thermal and rheological properties of the NCs is also investigated.

2. Experimental

2.1. Materials

Polystyrene (PS) and xylene were purchased from National Chemicals Ltd., Gujarat and Merck Specialities Pvt. Ltd., Mumbai, respectively. Carboxylic acid (<8%) functionalized multiwalled carbon nanotubes (cMWCNTs) were procured from Sigma—Aldrich, USA. All the materials were used as-received without further purification.

2.2. Preparation of PS/cMWCNT nanocomposites

PS, cMWCNT, xylene were used for the experiment. PS nanocomposite films with different loadings of cMWCNT such as PS: 0.1 (0.1 wt.%), PS: 0.3 (0.3 wt.%), PS: 0.5 (0.5 wt.%), and PS: 0.7 (0.7 wt.%), were prepared by solvent blending method using xylene as a solvent. The fabrication was conducted by following four steps: PS was kept in a hot-air oven for 6 h to remove the moisture present in it. Moisture-free PS was mixed in suitable proportion (depending on loading) with xylene by continuous stirring for 2 h using a magnetic stirrer. cMWCNT was mixed with xylene in appropriate proportions (depending on loading) by stirring for 2 h in a magnetic stirrer. Then the solution was sonicated in bath sonicator (REMI R-24 Ultrasonicator, Mumbai) for 2 h to ensure proper dispersion of the nanotubes in the solution. The sonicated cMWCNT solution was slowly transferred to the PS solution with continuous stirring for 2 h. Then it was sonicated using tip sonicator (Sonics Vibra-cell, USA) for 2 h for uniform dispersion to avoid any agglomeration. The solution was slowly poured and uniformly spread in a petridish and kept under undisturbed circumstance for 24 h. After that, it was heated at 60 °C to evaporate the residual solvent. After complete solvent removal, the film was slowly pulled out from the petridish and used for characterization. The respective stages of NC preparation are clearly illustrated in Fig. 1.

2.3. Characterizations of PS/cMWCNT nanocomposites

Structural analysis of pure PS, cMWCNT and PS NCs at different cMWCNT loadings was carried out by XRD. Micro Raman spectroscopy and FTIR spectroscopy. X-ray diffraction acted as a supporting tool in confirming the proper incorporation of nanotubes in the PS matrix. XRD analysis was performed to determine the effect of the nanotubes on the crystallinity of PS. The patterns were recorded for a 20 range of 5 to 80° with scanning rate of 2°/min, on a Bruker D8 Advanced X-ray diffractometer. Raman spectroscopy provides detailed information about the specific structure of the analysed species by probing individual chemical bond vibrations. Measurements were conducted on laser micro Raman spectrometer (Horiba JobinVyon, LabRam HR) using the Argon laser beam at a wavelength of 540 nm. The beam was focused at a magnification of 100× at different orientations of the sample and the scattering results were observed. FTIR analysis was carried out (IR Affinity-1, Shimadzu Corporation) in order to identify the different functional groups present and their bonding after the formation of composite. TEM was conducted on JEOL JEM 2100 to confirm the perfect incorporation and dispersion of nanotubes in the PS matrix. The improvement in...
thermal stability was proved by Thermogravimetric (TG) analysis. Thermograms were recorded in a nitrogen environment maintained at a flow rate of 40 ml/min, for a temperature range of 30–700 °C, at a heating rate of 10 °C/min, by TG 209 F1, Libra Analyser. The sample weight (measured by internal balance) was kept at around 7 mg. Hardness test was carried out by a Shore Durometer to account for hardness improvement by cMWCNT addition. For rheological study, sample films were subjected to oscillatory force by sandwiching between two parallel plates of Anton Paar, Physica MCR 301 rheometer, and heated to 190 °C. Experiments were conducted yielding the results explaining the rheological property change for an angular frequency range of 0.01–100 rad s⁻¹.

3. Result and discussion

3.1. XRD analysis

XRD provides information about the nanotube structure starting from single nanotube to nanotube bundle. MWCNTs consist of several layers of graphene rolled in the form of concentric cylinders. This layered structure makes it sensitive to X-ray diffraction. The diffraction pattern shows two prominent peaks at 2θ values of 25.9° and 43.2° (Fig. 2(a)), which represent the (002) and (100) reflections of graphite, respectively. In contrast to normal graphite (2θ = 26.5°) [30], the intense peak of cMWCNT at 2θ value of 25.9° shows a downward shift, which is attributed to the increase in sp² C=C layer spacing. The comparatively low intensity peak at 2θ = 43.2°, corresponding to (100) in-plane reflection shows an asymmetric profile, due to the presence of different crystalline species scattering X-rays from different orientations at a non-uniform intensity. The variation in d-spacing of the nanotubes, can be calculated from Bragg’s Law,

\[ d = \frac{n\lambda}{2\sin\theta} \]  

(1)

Considering, 2θ = 25.9° for (002) plane, \( \lambda = 0.1504 \) nm (for X-rays) and \( n = 1 \), \( d_{002} \) is found to be 0.3347 nm, which is in good agreement with previous reports.
agreement with that of graphite (0.335); the slight decrease is attributed to the presence of multiple layers of graphite and functionalization of sidewalls by additional organic group (carboxyl group).

XRD of pure PS displays only one broad peak at 19.4° and a small peak at 10.9°, as depicted in Fig. 2(b). The XRD profiles of PS NCs show prominent peaks of PS denoting its presence in the NC in abundance, with progressively decreasing intensities with loading of MWCNT (see Fig. 3). However, peaks typical for cMWCNTs are not observed in the diffraction pattern (Fig. 3), which can be justified, either by the very low cMWCNT content of the NCs or the perfect dispersion of the nanotubes. The absence of cMWCNT peaks can be attributed to the fact that nanotubes are properly incorporated, which decreases the d-spacing to an extent not detectable individually as a separate entity by XRD. The results obtained are in good conformity with reported literature [28,30,34].

3.2. Raman spectroscopic analysis

A good dispersion only can be anticipated from XRD, which requires Raman spectroscopy analysis for further confirmation, which is very sensitive to modifications of the nanotube surface by surface functionalization or charge-transfer effects. Fig. 4 depicts Raman spectra of cMWCNT and pure PS. Raman spectrum of cMWCNTs exhibits the characteristic bands of sp² hybridized carbon systems: The D-band and the tangential G-band (Fig. 4(a)). The D-band or the Dispersive band, depending on the wavelength of the exciting laser beam (at about 1351 cm⁻¹), is associated with the randomness found in sp²-hybridized systems and hence is activated by presence of defects. The G-band or the Graphitic band occurs at around 1591 cm⁻¹, which signifies the C=C bond stretching (in-plane stretching) in graphitic carbon systems. All kinds of sp²-hybridized carbon systems exhibit a strong peak depending on the excitation frequency of the laser beam called the G’-band or 2D-band at about 2697 cm⁻¹, which is typical for graphene systems. The I_D/I_G ratio of the cMWCNT is found to be 1.287 (greater than 1), indicating the presence of many defects in it [25].

The Raman spectrum of PS is complex due to molecular asymmetry and presence of different C–H bond types, as observed in Fig. 4(b). The vibration frequencies depend on the atomic masses of the species involved and their bond strength. Strong bonds and atoms with low masses have high Raman shifts, whereas weak bonds and heavy atoms show low shifts. Since, hydrogen is lighter than carbon; the C–H vibrations have a higher frequency than the C–C vibrations. The vibrations of carbon atoms connected by strong double bonds (C=C) occur at a higher frequency than weaker (C–C) single bonds. However, the prime value of Raman spectroscopy lies in considering the vibrations of heavier atoms, like the ‘breathing’ (expanding/contracting) mode of the aromatic carbon ring of PS, which can be observed at 1000 cm⁻¹ in the spectra.

cMWCNTs have distinct Raman bands in the PS NCs (Fig. 5). It is observed that the G-band splits up into G’-band and G−G−bands in the spectra of PS NC. The frequency of the D-bands and G’-G−bands in the Raman spectra is presented in Table 1. In contrast to the cMWCNT, the position of D-band in the Raman spectra of PS NC is shifted approximately by 0.3 cm⁻¹ (as inferred from Table 1). No appreciable shift of the D-band is found with the minor increase in weight percent of filler in PS NC. The G-band splits into G− and G’-bands in the NC spectra with a band width of 9.7 cm⁻¹. The I_D/I_G ratio of the NCs at different loadings is also presented in Table 1. Compared to the pristine cMWCNT (I_D/I_G), the NC structure is expected to be less defective owing to the decrease in I_D/I_G ratio, by increasing the filler loading (Table 1), with the ratio remaining close to or less than 1. The increase in mechanical stresses among the cMWCNTs affects the disorderliness and hence its dispersion. This confirms the alignment of nanotubes in the PS matrix due to the increased PS-cMWCNT bonding caused by greater interaction between filler and matrix with loading. The usual three bands of cMWCNT are observed in Raman spectra, which prove the preservation of cMWCNT structure in PS NCs. The observed results are in good agreement with previous reported studies [27,35–37].
3.3. FTIR spectroscopic analysis

FTIR spectroscopy was performed to identify the carboxyl modification of the surface of MWCNTs as well as to prove the extent of incorporation of cMWCNT in the PS matrix. Absorption bands characterizing cMWCNT and PS are shown in Fig. 6(a) and (b), respectively. Two peaks at 3854 cm\(^{-1}\) and 3740 cm\(^{-1}\) indicate the presence of hydroxyl group (O\(\sim\)H stretch) in the cMWCNT structure. A small peak at 2885 cm\(^{-1}\) signifies the C\(\sim\)H stretching vibrations of cMWCNTs. Prominent peaks are obtained denoting carbon–carbon double bond (1511 cm\(^{-1}\)) and triple bond (2381.7 cm\(^{-1}\) and 2311.8 cm\(^{-1}\)) stretching vibrations of cMWCNT. Two peaks obtained at 1689 cm\(^{-1}\) and 1702 cm\(^{-1}\) can be assigned to the C\(\sim\)O stretch of COOH group, which confirms the surface modification of MWCNTs. Significant peaks at 3031.5 cm\(^{-1}\) and 2868 cm\(^{-1}\) represent the aromatic and aliphatic C–H stretching of pure PS, respectively. Peaks at 1594 cm\(^{-1}\) and 1538.4 cm\(^{-1}\) are designated the aromatic C–C stretching vibration. An intermediate peak at 2945.4 cm\(^{-1}\) indicates the methylene (–CH\(_2\)) group stretching of pure PS.

The FTIR spectra of PS NCs are illustrated in Fig. 7. It is clearly observed that the intensity of peaks (% transmittance) of pure PS is much greater than that of cMWCNT. Prominent peaks of PS are observed in the PS NC spectra, with progressively decreasing intensity with an increase in filler loading (Fig. 7), indicating the increase in the incorporation of the nanotubes in the NCs. However, at low loadings, the cMWCNT peaks are suppressed by the high intensity peaks of the abundant PS. But at higher loadings (greater than 0.5), new peaks (3740 cm\(^{-1}\), 1515 cm\(^{-1}\) and 1078 cm\(^{-1}\)) are observed in addition to PS peaks, which are contribution of the cMWCNTs. The intensities of the latter peaks are found to increase with loading, confirming the increase in cMWCNT content in the NCs. Peaks specific to pure PS and cMWCNT found in the NCs are enlisted in Table 2. The obtained results are in harmony with reported literatures [38–40].
3.4. TEM analysis

TEM micrographs of PS NC surfaces (PS: 0.3 and PS: 0.5) at same magnifications are shown in Fig. 8. The nanotubes are found to be strongly held by the PS matrix proving strong interfacial aromatic interaction between the PS and nanofillers. The short size of the nanotubes is visible in the micrographs. The nanotube fibres are found to be in the coiled form, embedded in the PS matrix. Several reports revealed that the method of preparation and chemical surface modification of nanotubes are the prime cause of such a phenomenon [40]. Homogenous distribution of cMWCNT in the PS matrix is evidenced from the micrograph of PS: 0.3, with diameter in the range of 12–20 nm. However, an aggregated CNT mass is observed in few regions at higher loading, which is evident in the micrograph of PS: 0.5 (see Fig. 8(b)). Overall, the TEM images demonstrate a good dispersion of nanotubes in the PS matrix and similar trends were also observed previously by other researchers [11,22].

3.5. Thermal analysis

The thermal degradation stability of the PS NCs was characterized by TG analysis (TGA). The recovered NC film is graded in the form of powder prior to analysis. The cMWCNT suffers dual-step decomposition (Fig. 9(a)). The first inflection point of TGA traces at 175 °C can be attributed mainly to the thermal breakdown of the modifying –COOH group, since in a nitrogen environment (in absence of an oxidizing environment), the nanotubes will not undergo appreciable degradation initially. The first inflection point of DTA graph (Fig. 9(a)) occurring at 59 °C is associated with the moisture removal. The second inflection point at 739 °C (temperature at which the maximum degradation occurs, T_{max}) corresponds to the oxidation of the cMWCNTs by the oxygen released to the system environment, as a product of –COOH decomposition. The latter phenomenon occurs at a very high temperature, which indicates that cMWCNTs are very stable. Hence, it can be expected that its use as reinforcing filler can enhance the thermal stability of PS. PS undergoes single-step degradation, the breakdown of the polymer chains starting at 350 °C and continues till 450 °C (Fig. 9(b)). It can be observed that PS degrades completely at about 457 °C, with a T_{max} of 417 °C (Fig. 9(b)).

The TG curves for PS NCs at different cMWCNT loadings are plotted along with those for pure PS and cMWCNT to draw a comparison (see Fig. 10). Beyond 450 °C, there is no change of wt.% of the NCs. Around 0.4 wt.% of PS NCs remaining undecomposed is referred as the residue. The temperature for which the NCs decompose lies in the range of 350 °C–450 °C. The thermal stability of the PS NCs with respect to pure PS is improved, which is mainly due to the combined effect of nano-confinement and barrier effect of the incorporated nanofillers. The delay in weight loss is due to enhanced interfacial interaction of cMWCNT with PS, with a reduced mass loss rate due to the formation of a barrier preventing mass transfer and providing thermally insulation to the underlying PS [41,42]; cMWCNTs come to the surface at temperatures lesser than decomposition temperature owing to their high surface energy, contributing more to the thermal stability of the polymer. The best explanation can be of nano-confinement, which causes the individual monomer radicals formed after breakdown of the polymer (PS) chains to be together for a greater period of time, thus adding to its stability, for a greater range of temperature as
compared to pure PS [43]. Table 3 represents the increase in degradation temperature with rise in cMWCNT content in NCs for different extents of mass loss of the sample (as evident from Fig. 10). When 20% weight loss is taken as a point of comparison, the PS NCs demonstrate the improved thermal degradation temperature by 11–26 °C over pure PS. It is propitious with the fact that thermal stability is consistently enhanced with cMWCNT loading. The increase in degradation temperature with nanotube content of the NC further confirms the thermal stability enhancement of PS by cMWCNT reinforcement. The results are analogous to reported literatures [31,44,45].

3.5.1. Thermal degradation kinetic analysis

The influence of cMWCNT loading on the thermal degradation can be observed by determining kinetic parameters like order of the reaction (n), pre-exponential factor (A) and chiefly activation energy (E) by using the Coats Redfern kinetic model [46]. Further, the mechanism of degradation can be inferred from the Criado method [45,46]. The rate of a reaction is proportional to the concentration of the reacting species at that point of time. Hence, if \( \alpha \) (Eq. (2)) amount has converted, then \( (1-\alpha) \) amount remains, which is the current concentration of the species.

\[
\alpha = \frac{W_0 - W_t}{W_0 - W_{\infty}}
\]  

(2)

where, \( W_0 \) is the initial mass of the sample, \( W_t \) is the current mass of the sample (at a reaction time \( t \)), \( W_{\infty} \) is the final mass of the sample.

For nth order of the reaction, Coats Redfern method is governed by Eqs. (3) and (4).

\[
\ln \left( - \frac{\ln (1-\alpha)}{T^2} \right) = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} n = 1
\]  

(3)

\[
\ln \left( \frac{1-(1-\alpha)^{-1/n}}{(1-\alpha)^{-1/n}} \right) = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} n \neq 1
\]  

(4)

where, \( T \) is the absolute temperature, \( R \) is the universal gas constant and \( \beta \) is the heating rate. Generally, the logarithmic term on the right part of the above equations is considered as constant. Plots of left hand side (LHS) versus (1/T) were made for different values of \( n \) for pure PS and its NCs as shown in Fig. 11. Linearization of the plot data gives straight lines with negative slopes governed by the equations Eqs. (3) and (4). The value of \( n \) for which the correlation coefficient (R²) value of the linearization is the maximum gives the order of reaction followed by the concerned material. The activation energy and pre-exponential factor can be determined from the slope and intercept values of the straight lines (specific to the determined order), respectively and the obtained results are presented in Table 4. The advantage of the method lies in the fact that single heating data is sufficient for the analysis. The activation energy is found to increase with the addition of cMWCNT, providing an evidence for the delay in thermal degradation; more the loading, higher is the activation energy and the thermal stability.

3.5.2. Thermal degradation mechanism determination

Criado et al. [46] proposed a method to determine the solid phase reaction mechanism (at a definite heating rate), utilizing the activation energy calculated by Coats Redfern method, with Eqs. (5) and (6) [46,47] governing the method.

\[
Z(\alpha) = \frac{\beta}{A} G(\alpha) \frac{d\alpha}{dT} e^\alpha
\]  

(5)

\[
Z(\alpha) = \frac{d\alpha}{dT} R \left( \frac{e^{-x}}{x} x^3 + 18x^2 + 86x + 96 \right)
\]  

(6)

where, \( Z(\alpha) \) is the Criado function and \( G(\alpha) \) is the solid-state mechanism function. \( Z(\alpha) \) versus \( \alpha \) plots are made from Eq. (5) (Fig. 12), with the \( G(\alpha) \) function given by different mechanisms (see Table 5). Then these plots are compared with the experimental \( Z(\alpha) \) versus \( \alpha \) plot governed by Eq. (6), to predict the reaction mechanism (which gives a profile similar to the experimental curve) of the thermal degradation reaction. The
### Table 3
TGA results of PS NCs.

| S. no. | Sample name | Temperature at 20% weight loss | ΔT20% | Temperature at 50% weight loss | ΔT50% |
|--------|-------------|-------------------------------|-------|-------------------------------|-------|
| 1      | cMWCNT     | 503                           | -     | 736                           | -     |
| 2      | PS         | 373                           | -     | 405                           | -     |
| 3      | PS: 0.1    | 384                           | 11    | 409                           | 4     |
| 4      | PS: 0.3    | 392                           | 19    | 412                           | 7     |
| 5      | PS: 0.5    | 396                           | 23    | 413                           | 8     |
| 6      | PS: 0.7    | 399                           | 26    | 414                           | 9     |

### Fig. 11.
Thermal degradation kinetic profiles of pure PS and its NCs by using Coats Redfern method.
results suggested that thermal degradation of both PS and its NCs follows F1 reaction mechanism (random nucleation having one nucleus on individual particle, i.e. the identical probability of nucleation occurring at each active site) at the initial stage and gradually moves toward D1 mechanism (One-D diffusion) at higher conversion ($\alpha > 0.7$).

3.5.3. Integral procedural decomposition temperature (IPDT)

IPDT is an index evaluating the thermal stability by considering the entire shape of the TGA curve. It expresses temperature tolerance of the sample in terms of decomposition temperature. However, the factor is calculated empirically and is influenced by sample nature and thermal decomposition reaction conditions [48]. It is

| Name of sample | Reaction order (n) | Activation energy (E kJ/mol) | Correlation coefficient ($R^2$) | IPDT (°C) |
|----------------|-------------------|------------------------------|-------------------------------|-----------|
| PS             | 0.1               | 96.05                        | 0.995                         | 378.8     |
| PS: 0.1        | 0                 | 105.89                       | 0.96                          | 381.0     |
| PS: 0.3        | 0                 | 120.63                       | 0.96                          | 389.2     |
| PS: 0.5        | 0                 | 133.17                       | 0.96                          | 397.6     |
| PS: 0.7        | 0                 | 134.82                       | 0.96                          | 399.2     |

**Table 4**

Result of Coats Redfern method and IPDT applied to TGA.

**Fig. 12.** Thermal degradation mechanism profiles of pure PS and its NCs.
Table 5

| G(α) expressions for common solid state reaction mechanisms [43]. |
|------------------|------------------|
| Mechanism        | G(α)             | Solid state process                     |
| A2               | [−ln(1−α)]^{1/2} | Nucleation and Growth: Avrami equation 1 |
| A3               | [−ln(1−α)]^{1/3} | Nucleation and Growth: Avrami equation 2 |
| A4               | [−ln(1−α)]^{1/4} | Nucleation and Growth: Avrami equation 3 |
| R2               | 1−[(1−α)^{1/2}]  | Phase boundary controlled reaction: contraction area |
| R3               | 1−[(1−α)^{1/3}]  | Phase boundary controlled reaction: contraction volume |
| D1               | α^2              | One-D Diffusion                         |
| D2               | (1−α)×ln(1−α)+α  | Two-D Diffusion                         |
| D3               | [1−(1−α)^{1/2}]  | Three-D Diffusion, Jander Equation       |
| D4               | [1−(2/3)α]×[(1−α)^{2/3}] | Three-D Diffusion, Ginstlinge Brounstein Equation |
| F1               | [−ln(1−α)]      | Random nucleation having one nucleus on individual particle |

associated with the volatile parts of the polymer [48]. According to Doyle, IPDT is given by Eq. (7) [49,50].

\[ IPDT = K \times A' (T_f - T_i) + T_i \]

where, \( K = \frac{A_1 + A_3}{A_1} \); \( A' = \frac{A_1 + A_3}{A_1 + A_2 + A_3} \)  

An increase in activation energy (as inferred from Coats Redfern method) anticipates an increase in IPDT values with rise in cMWCNT content. All NCs have higher IPDT values than pure PS (378.8 °C). PS: 0.7 is found to have the highest IPDT (399.2 °C) succeeded by PS: 0.5 (397.6 °C), PS: 0.3 (389.2 °C) and PS: 0.1 (381.0 °C), preserving the consistency with Coats Redfern method results (see Table 4). This increment can be attributed to the increase in thermal stability of the sample with proper nanofiller incorporation and dispersion [50,51].

3.6. Hardness determination

Hardness can be defined as the resistance of the material to permanent or plastic deformation by measuring the indentation depth suffered by a material in response to a given consistent force. The durometer scale is a measure of hardness developed by employing a Shore durometer. This depth is influenced by viscoelastic properties and strength of the material. The indentation depth decreases gradually with an increase in cMWCNT content, under a fixed load. This signifies an increased resistance to permanent or plastic deformation. Incorporation of the nanofillers in the microstructure hampers the movement of molecular chains during deformation, reducing the strain recovery during unloading period. A strong interfacial strength and physical bonding between the matrix and the filler leads to the rise in hardness [52]. Fig. 13 illustrates the hardness profiles of pure PS sample and its NCs as a function of cMWCNT loading. The averaged hardness value increases by about 7.5%, from 66.9 MPa to 71.9 MPa for a very minor increase in the filler content (from 0 to 0.7 wt.%). This indicates an increase in wear resistance of the sample with cMWCNT addition [52,53].

3.7. Melt rheological analysis

Melt rheology is a reliable tool for the inspection of effect of reinforcing filler on the chain relaxation and mobility of polymers. The significance of rheological analysis of the NCs lies in gathering information about their microstructure and dynamics [54]. Factors influencing rheological performance include the properties of the filler used, its aspect ratio and effectiveness of dispersion and polymer-filler interfacial interaction [54].

Viscoelastic behaviour is characterized by relaxation and unwinding of few portions of the polymer chain under stress during the initial loading period. Hence, the deformation is evident, which is designated as viscous behaviour. The unwinding creates a back stress on the polymer chain. When the back stress equals the original stress acting on it, relaxation stops accompanied by a drop in viscosity, and the material starts regaining its original form. This is designated as the elastic behaviour. Storage modulus indicates the amount of energy stored prior to deformation, when it is subjected to a deforming force. Hence, the increase in storage modulus suggests an increase in resistance to plasticity or permanent deformation, and the storage of energy provides evidence for rise in elasticity in response to deforming force. In contrast, loss modulus gives the measure of energy dissipated while deforming under the action of an external impressed force. Loss of energy indicates an increase in chain relaxation and molecular mobility, which attributes to viscous behaviour. Hence, the rise in loss modulus denotes viscous property of the material, losing energy when activated by a load. Fig. 14(a) and (b) show the increase in storage modulus and loss modulus in response to cMWCNT loading with angular frequency, respectively. For a particular cMWCNT concentration, a greater increment is obtained at high frequencies. The convergence of the graphs at higher frequencies signifies liquid-like to solid-like transformation due to the decrease in mobility of the polymer chains by geometric confinement of CNTs. The liquid-like rheology shows prominent increment of storage modulus and viscosity with CNT content as opposed to solid-like behaviour characterized by negligible variation of loss modulus and storage modulus with
loading. The higher elasticity and delayed relaxation of NCs is influenced by filler–filler interactions and matrix–filler interfacial interactions. An increase in CNT concentration allows greater inter-particle and interfacial interactions at lower frequencies. For lower frequencies, the graphs display a sensitive response with CNT content, since more time is available for the interactions to occur. The filler concentration at the point of transition is called the rheological percolation threshold [55].

Complex viscosity is a frequency-dependent viscosity function, which denotes the simultaneous effect of frequency and viscosity during forced harmonic oscillation of shear stress. This contains both real and imaginary parts. Complex modulus \( (G^*) \) is the resultant of storage \( (G') \) and loss moduli \( (G'') \) and similar to a complex number is expressed as Eq. (8).

\[
G^* = G' + iG''
\]  

(8)

Complex viscosity \( (\eta^*) \) is the ratio of complex modulus \( (G^*) \) to angular frequency \( (\omega) \) (Eq. (9)). Hence, magnitude of complex viscosity can be given as Eq. (10).

\[
\eta^* = \frac{G'}{\omega} + i\frac{G''}{\omega} = \frac{G'}{\omega} + i\frac{G^*}{\omega}
\]  

(9)

\[
\eta^* = \left( \frac{G'}{\omega} + \frac{G^*}{\omega} \right)^{1/2}
\]  

(10)

Fig. 14(c) shows a decrease in complex viscosity as can be predicted from Eq. (10) which signifies greater improvement of elasticity than viscosity.

4. Conclusion

The present work successfully examined the impact of cMWCNT on the PS with its NCs prepared by solvent blending method coupled with ultrasonication. The structure of PS NCs was meticulously studied by various analytical techniques. X-ray diffraction confirmed the strong interaction and dispersion of the nanotubes in the PS matrix from the absence of peaks specific to cMWCNT, in the PS NC profiles. Defect density reduction of the NCs as compared to the pure matrix, inferred from micro Raman analysis further provided the evidence of effective nanofiller incorporation. FTIR results showed prominent cMWCNT peaks, which demonstrated that the MWCNTs are carboxylic acid functionalized in the NC. TEM verified the dispersion of cMWCNT peaks, which demonstrated that the MWCNTs are carboxylic acid functionalized in the NC. TEM verified the dispersion of cMWCNT peaks, which demonstrated that the MWCNTs are carboxylic acid functionalized in the NC. TGA proved a significant improvement of thermal stability of PS with cMWCNT loading. The activation energy evaluated by Coats-Redfern method strengthens this argument. The rheological and hardness improvement with nanotube inclusion was evidenced from this investigation.

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Nomenclature

\( T_{\text{max}} \) temperature corresponding to maximum thermal degradation  
\( R \) universal gas constant  
\( \beta \) heating rate  
\( E \) activation Energy  
\( A \) pre-exponential factor  
\( n \) thermal degradation reaction order  
\( T \) thermal degradation reaction temperature (absolute)  
\( W_0 \) thermogravimetric analysis initial sample weight  
\( W_{\infty} \) thermogravimetric analysis final sample weight  
\( W_t \) thermogravimetric analysis sample weight at the time instant \( 't' \)  
\( t \) thermogravimetric analysis reaction time  
\( T_f \) final temperature of thermal degradation reaction  
\( T_i \) initial temperature of thermal degradation reaction  
\( A' \) thermogram area ratio

Fig. 14. (a) Storage modulus, (b) Loss modulus and (c) Complex viscosity plots of pure PS and its NCs.
thermogram area ratio coefficient
K
complex modulus
G^*
storage modulus
G' loss modulus
G'' complex viscosity
η^ω angular frequency

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