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Thermo-Mechanical Properties of Polyethyleneimine (PEI) Modified HNTs Filled ABS/PVC Composites

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Abstract

In this work, the surface properties of Halloysite nanotubes (HNTs) are successfully altered by using the Polyethyleneimine (PEI). Modified HNTs (m-HNTs) have successfully incorporated in Acrylonitrile-Butadiene-Styrene copolymer (ABS) and Poly Vinyl Chloride (PVC) blends with the help of injection molding machine, by melt mixing process. In order to enhance the thermo-mechanical properties of 90/10 ABS/PVC blends and its m-HNTs filled composites, the m-HNTs were varied in wt. % like 0.5, 1, 1.5 and 2. The enhanced mechanical and thermal properties of the 90/10 ABS/PVC blends were observed at 1.5 wt. % addition of m-HNTs. There was measurable difference in mechanical properties like tensile and impact strength of prepared composites, 74.46 % and 36.73 % respectively. However, it was also observed that thermal stability of the prepared blends in addition of m-HNTs was improved hand in hand which is explained with the help of Differential Scanning Calorimetry (DSC). The m-HNTs filled 90/10 wt. % ABS/PVC can be used in different areas like pipe fittings, electric applications, automobile etc.

Keywords: Acrylonitrile-butadiene-styrene copolymer (ABS), Poly Vinyl Chloride (PVC), Polyethyleneimine (PEI), PEI modified Halloysite Nanotubes (m-HNTs).

1. Introduction

Polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS) are most commonly synthesized polymer blend for enhancing impact and tensile properties [1]. PVC has good mechanical properties; still its applications are restricted in niche areas owing to its poor impact strength. Typically, addition of rubbery material like ABS in PVC results in enhanced impact strength of PVC [2]. Although, an excellent mechanical property of ABS makes it most suitable for commodity range, still poor tensile strength limits its use in some specific applications [8]. Addition of ABS in PVC yields in improved toughness [9-15].

Thus, melt mixing of PVC and ABS in a definite quantity can give better impact and tensile strength for blended polymer [2-14]. Mechanical properties of the polymer matrix not only depend upon the morphology development but also depend upon the addition of filler materials and compatibilization [1-8, 17]. The improvement in mechanical properties of plastic blends and nanofiller filled composites depends on the interfacial reaction amid the fillers and the matrix [18]. Nevertheless, the equal dispersion of the nano filler contributes in improving the mechanical properties of nano material filled plastic blends and their composites [8]. HNTs are used as filler in polymer blends due to their good dispersion properties and low cost. HNTs have attracted minds of many researchers owing to their unique chemical properties on external surface of the polymer composites. HNTs are naturally occurring alumino-silicates, mostly found in tropical areas, used as natural filler. They are biocompatible and found in bio-application such as filling the cracks in bone. However, HNTs has Van der Waals forces on external surfaces, which might

create aggregations when filled in polymer or polymer blends, and results non-uniform properties of polymer matrix [16]. To overcome such issues, typically, the surface of HNTs is modified with different materials like Polyethyleneimine (PEI), quaternary ammonium salt, Heda, Chitosan etc. Modified HNTs filled polymer blends and their composites results in better dispersion and, hence, impart better thermo-mechanical properties [18]. In comparison with other nano fillers, like Carbon nanotubes (CNTs), HNTs are mostly used due to its low cost and readily availability, unique external surface property as well as its better dispersion. The incorporation of m-HNTs in ABS/PVC blends will be of global interest for lightweight structure applications [26].
In this work, 90/10 (WT/WT %) ABS/PVC blend system is taken for study, as it gives rise to matrix-droplet morphology, which is successful in producing good tensile and impact properties of ABS/PVC blends. In order to enhance the dispersion of HNTs in 90/10 (WT/WT %) ABS/PVC blends, the surface of HNTs is altered with the help of branched polyethyleneimine (PEI) [24-26]. The PEI modified HNTs filled ABS/PVC blends and its composites are prepared with the help of twin-screw extruder and injection molding. The characterization of prepared composite materials has been carried out using TEM, SEM, DSC, XRD, FTIR etc. In addition, the impact and tensile test were carried out using impact and tensile testing equipment's.

2. Experimentation

2.1. Material

PVC was purchased from Fine Flow Plastic Industries, Mumbai, India. ABS was purchased from Strylotion, India under the trade name Terluran GP-22. HNTs were supplied by Imerys Tableware, New Zealand. Ethyl alcohol AR (99% purity) is used as solvent. The branched polyethyleneimine (PEI) was brought from Sigma Aldrich, India whose Mn amount is 60,000/- [26].

- Physical Properties of HNTs-

  Physical Properties of HNTs are provided in Table 1.

Table 1. Physical properties of HNTs [8]

Chemical formula	Surface area (m^2/g)	Pore volume (mL/g)	Density (kg/m^3)	Refractive index
$Al_2Si_2O_5(OH)_4.nH_2O$	65	1.25	2540	1.54

- EDX spectrum acquired for HNTs-

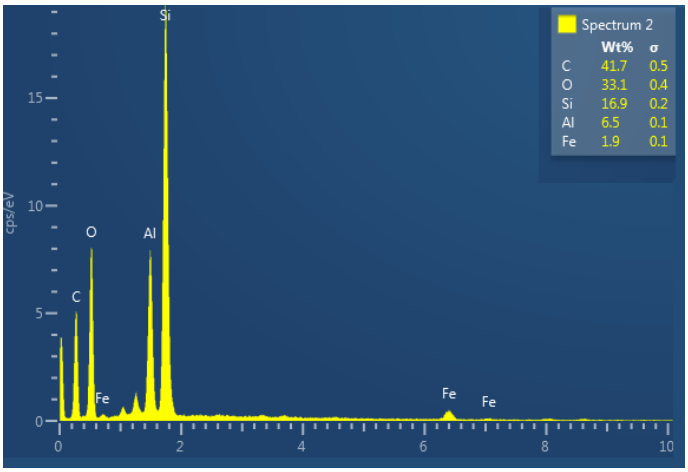

Fig. 1. EDAX spectra of Halloysite Nanotubes (HNTs)

Energy Dispersive X-Ray Analysis (EDX) also called as EDS or EDAX. EDX is used to characterize the elemental composition of target material Fig.1 shows EDX spectrum of HNT which is used as filler material in present study. Table 2. Shows the wt. % composition of different elements present in HNT as follows:

Table 2. Elemental composition of HNTs

Elements	C	O	Si	Al	Fe
Wt. %	41.5	33.1	16.9	6.5	1.9
Σ	0.5	0.4	0.2	0.1	0.1

From above table, it can be deduced that, HNT majorly consist of carbon, oxygen, silicon and aluminium and small fraction of ferrous.

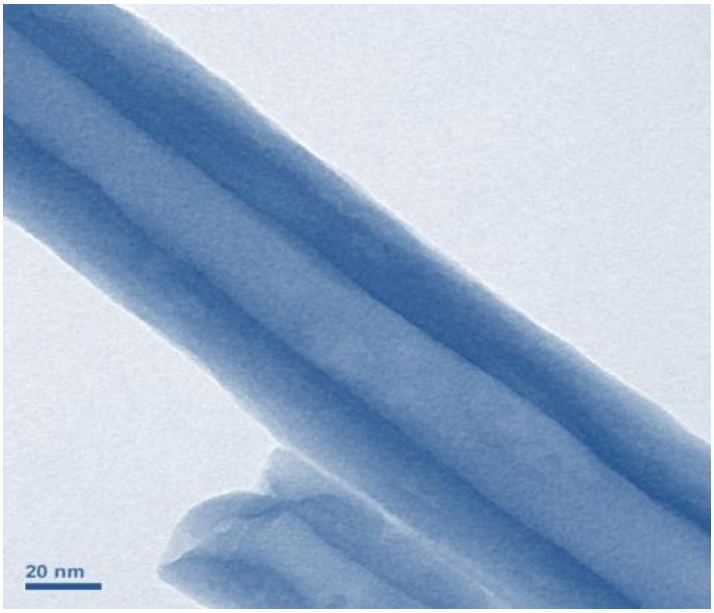

Fig. 2. TEM of Halloysite Nanotubes (HNTs) [18,19]

Fig. 2 shows the TEM micrograph of HNTs (performed on high resolution JEOL JEM 2100) having tubular structure with external diameter in the range of 60-80 nm.

2.2. Surface modification treatment of HNT with branched Polyethyleneimine (PEI)

HNTs were successfully coated with polyethyleneimine (PEI). The branched PEI has very good cationic charge density [26]. They have –ve charge when the pH is more than three, as well as they become iso-electric at three, and have +ve charge when pH is smaller [26]. For modification of HNTs with PEI, the pH value should be in between eight to nine and is controlled by addition of NaOH. The HNTs get modify with the help of PEI due to the cation exchange ability of HNTs and interaction between HNTs and PEI (anion cation exchange ability between them), the PEI are adsorbed on the HNTs. The FTIR studies was carried out using: IRAffinity; SHIMADZU with resolution 0.5 cm^{-1} for the samples in the scanning range of 400 to 4000 cm^{-1}. Fig. 3 (b) clearly depicts the surface treatment/modification of HNTs. The peaks can be observed at 3692 & 3619 cm^{-1} which are the peaks of HNTs and m-HNTs i.e., PEI modified HNTs respectively. However, the intensities of the said peaks are different which clearly messages that the HNTs are successfully modified by branched PEI. Along with this, the peak at 3543 is of interlayer H_2O of the HNT. The said peak is subdued in the branched PEI spectrum which is because of the chemical interaction between PEI and HNT. Fig. 3 (b) clearly depicts the layer of PEI on HNT surface due to the adsorption of PEI. The quantity of the said layer can be found using the Equation:

$$R_a = 0.028M_n0.5 \qquad \ldots\ldots (1)$$

Wherein, the R_a is a radius of gyration, M_n is a quantity of average molecular Wt. of the layer which is adsorbed on HNT [18-19, 26]. The amounts of PEI utilized in research is 60,000. Hence, the R_a is found as 6.85 nm.

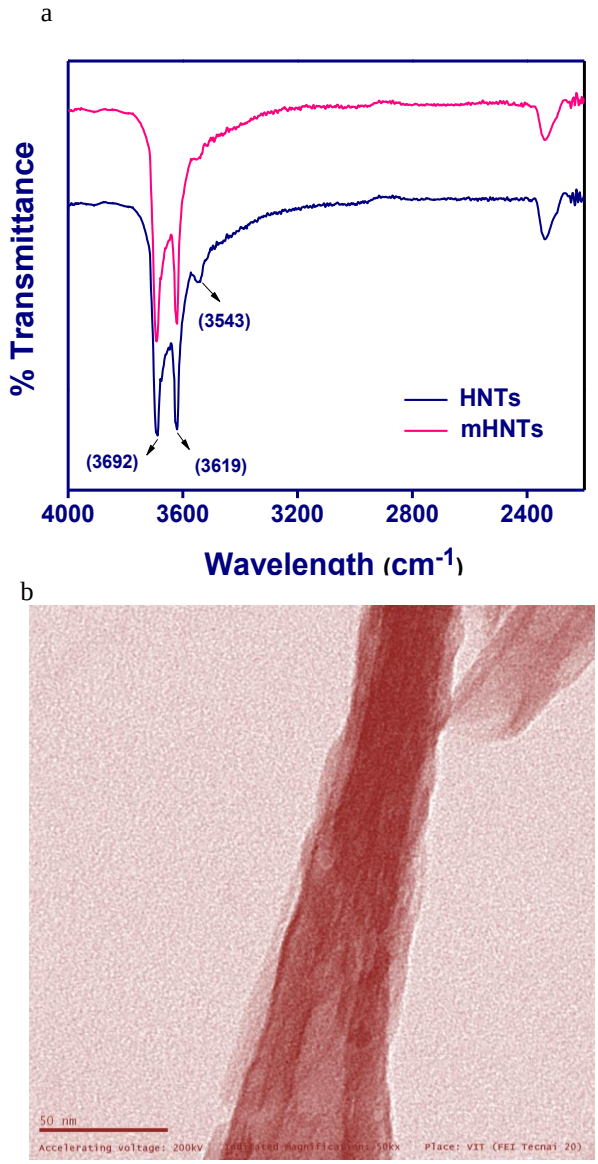

Fig. 3. (a) FTIR of HNT and PEI modified HNTs; (b) TEM of m-HNTs [26].

2.3. Preparation of composites

The ABS/PVC blends were prepared primarily by drying the ABS (in the form of granule) and PVC powder in the hot air oven at round about 75ºC for 1.5 hrs. to remove all the moisture from them. As decided the quantities of m-HNT (0.5 wt. %) were taken in 45 ml of ethanol and stirred for the proper mixture. Further, the ABS and PVC 90/10 wt. % were mixed and the m-HNTs with ethanol solution were poured in it. The mixture was stirred and mixed properly with the spatula. In order to extract the ethanol from the said mixture, the mixture was kept in a hot air oven for 24 hours at 85ºC. The extrusion process was used to mix the m-HNTs added ABS/PVC, after which the injection molding was used to prepare the samples of the constituents with varying wt. % of modified HNTs. The

samples with different wt. % of modified HNTs were prepared as per the ASTM standard (D638, ASTM D256) in order to carry out tensile and impact test on it, the same process was used for preparing samples with different weight percent of modified HNTs filled ABS/PVC blends and its composites. The samples with designation code and the weight percentages of modified HNTs are shown in Table 3.

Table 3. Physical properties of HNTs

Sr. No.	Sample code	ABS (wt. %)	PVC (wt. %)	m-HNTs (wt. %)
1	AP	90	10	-
2	AP+ 0.5 wt. % m-HNTs	90	10	0.5
3	AP+ 1 wt. % m-HNTs	90	10	1
4	AP+ 1.5 wt. % m-HNTs	90	10	1.5
5	AP+ 2 wt. % m-HNTs	90	10	2

3. Results and discussions

3.1. Mechanical characterization

- Tensile Properties:

It is but obvious that the development in the morphology, nature of crystal structure and the reaction between the interface matters in imparting better mechanical properties of the nano filler filled polymer blends and its composites. It was noticed that incorporation of modified HNTs (1.5 wt. %) in polymer blends, α in the monoclinic and β in trigonal condition are obtained. The SEM image of tensile fractured samples is shown in Fig. 5, which clearly depicts the fibrils in very small size which is an outcome of improved restriction to the elongation of chains. However, the nano-fillers are added in matrix of the polymer, results in increased crystallinity and decrease of spherulite size. The tensile properties were highest at 1.5 wt. % of m-HNTs in 90/10 ABS/PVC.

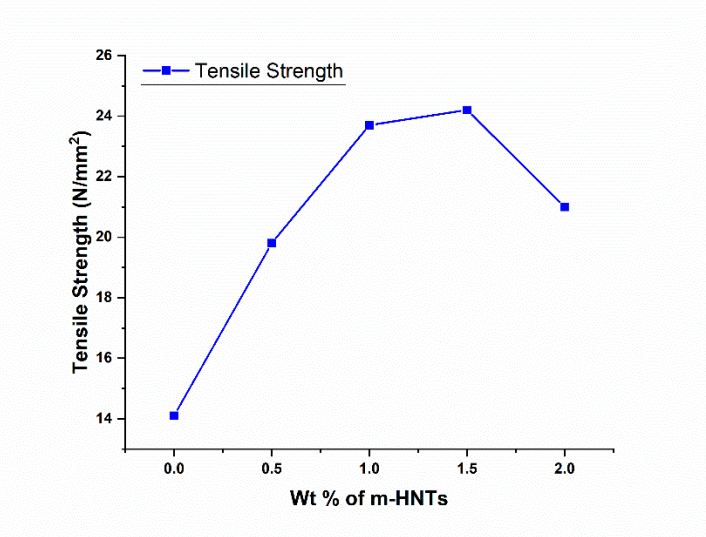

Fig. 4. Tensile strength of m-HNTs filled 90/10 ABS/PVC composites

The tensile results of m-HNTs filled 90/10 ABS/PVC composite under different weight percentage of m-HNTs when applied the pull force is shown in Fig. 4 which clearly depicts that, 1.5 wt. % m-HNTs incorporation imparts highest tensile strength, whereas beyond 1.5 wt. % the tensile strength reduces due to aggregation of HNTs which is clearly visible in Fig. 4. Fig. 5 (b) depicts the SEM image of tensile fractured sample at 2 wt. % m-HNTs which shows the aggregation of HNTs which is the reasons of reduction in mechanical properties especially tensile

strength. Tensile strength was increased from 14.1 to 24.6 N/mm^2 at 1.5 wt. % m-HNTs further the descending trend was observed at higher loading of m-HNTs.

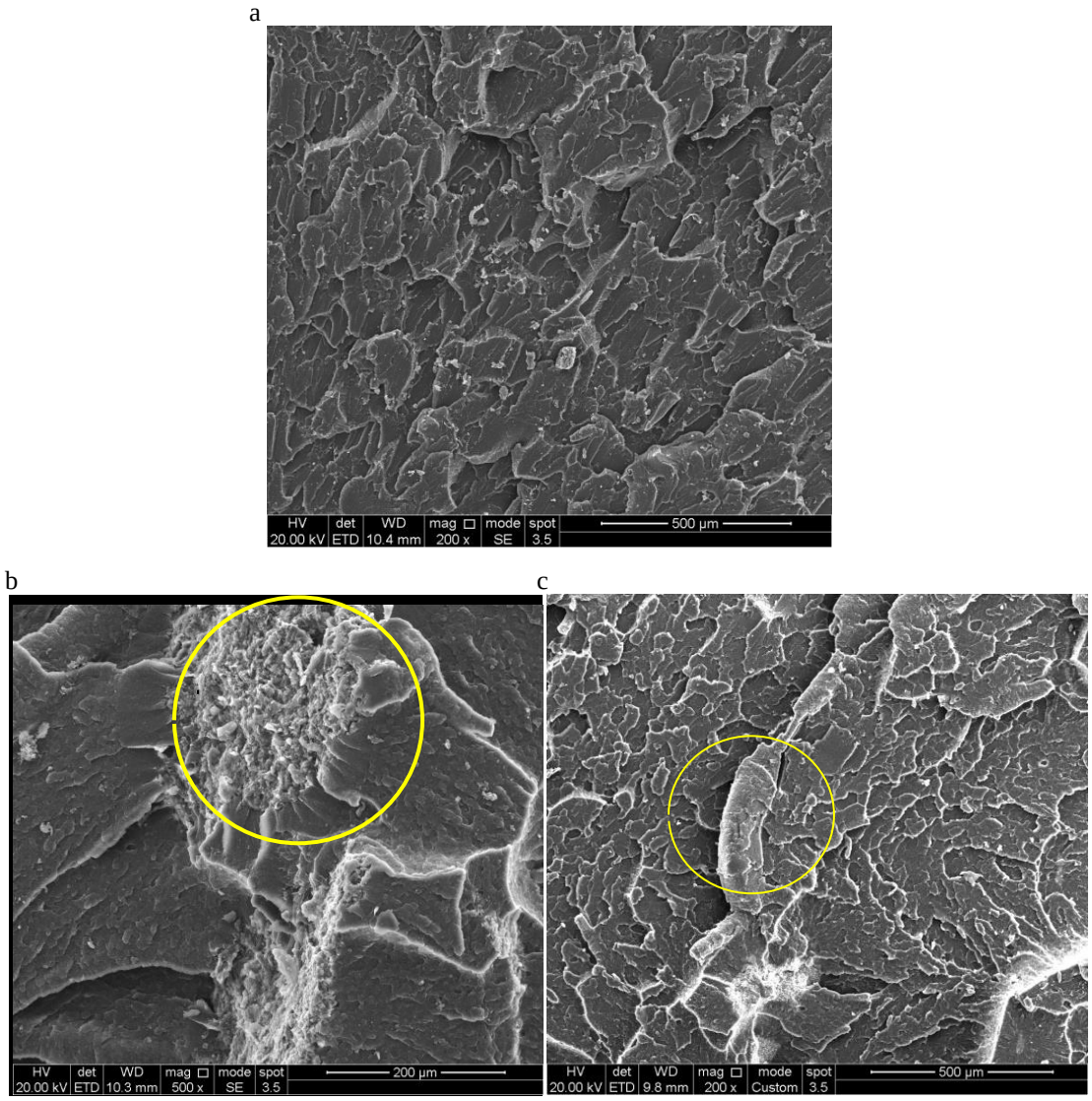

Fig. 5. Scanning electron microscopy (SEM) of tensile fractured samples; (a) 90/10 ABS/PVC blend (b) 2 wt. % m-HNTs (c) 1.5 wt. % m-HNTs added 90/10 ABS/PVC Composite.

- Impact Properties

The impact test results of m-HNTs filled 90/10 ABS/PVC composites are shown in Fig. 6. The impact strength was found highest especially at 1.5 wt. % m-HNTs incorporation in 90/10 ABS/PVC blends and its composites because of strong interfacial interaction between the constituents. Modification imparts strong interaction, dispersion and hence imparts better impact strength to the composite. The SEM image (Fig. 7) does not show the fibrils showing the brittle fracture. Furthermore, the impact strength shows descending trend beyond 1.5 wt. % addition of m-HNTs and is due to the aggregation of m-HNTs due to the poor interfacial interaction between the constituents.

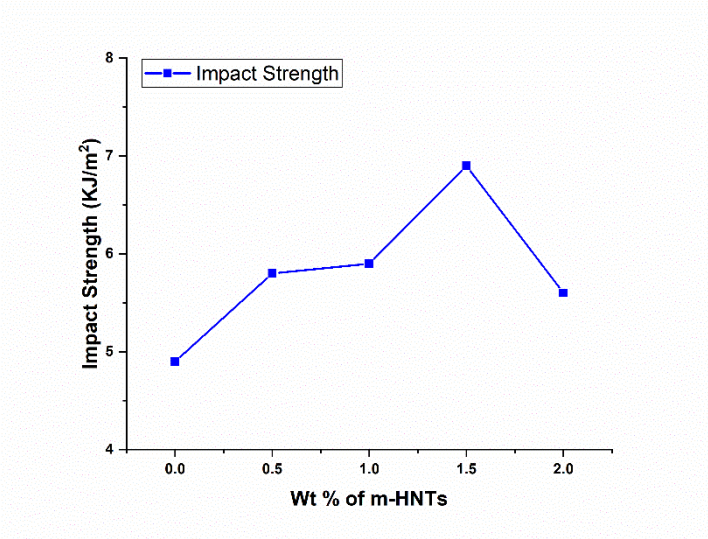

Fig. 6.Impact Strength of m-HNTs filled 90/10 ABS/PVC Composite

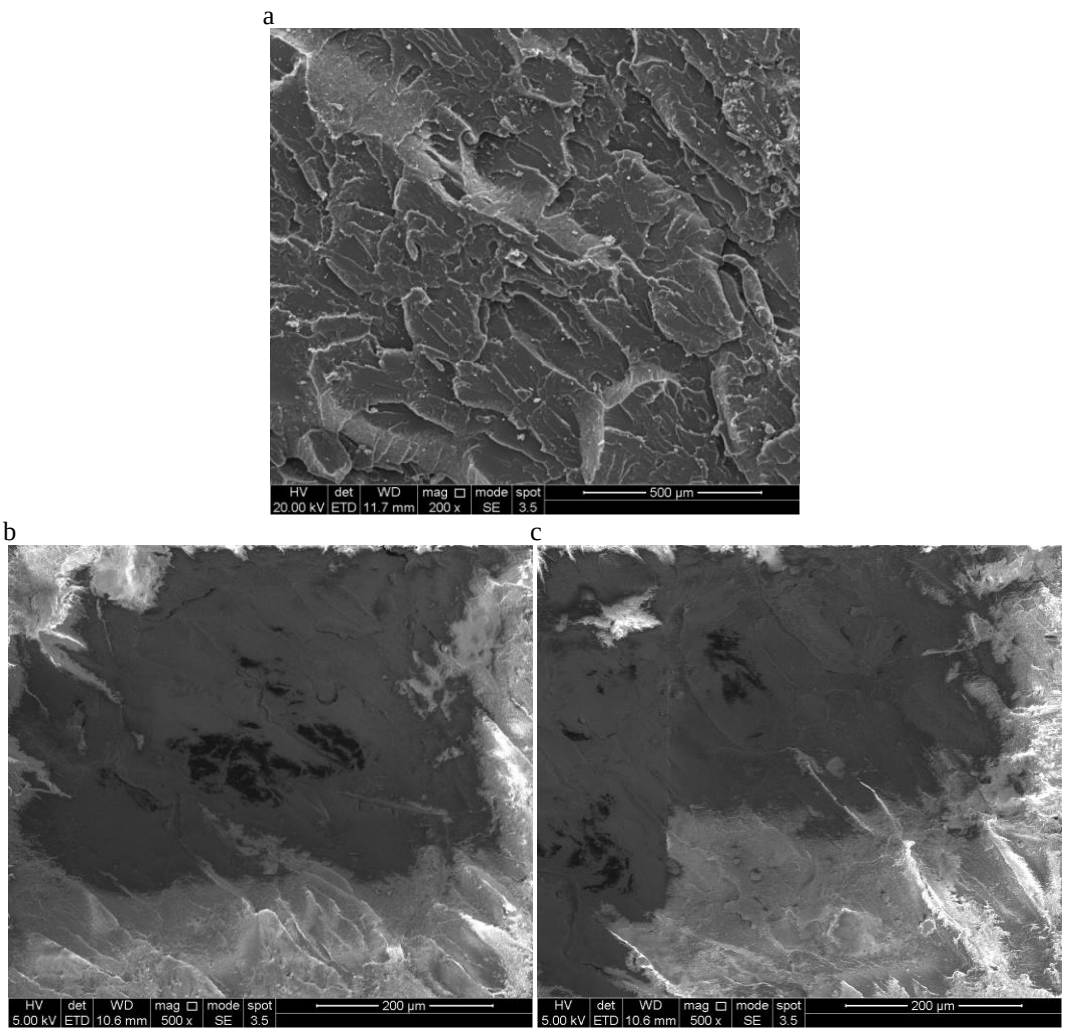

Fig. 7. Scanning Electron Microscopy (SEM) of Impact fractures samples (a) 90/10 ABS/PVC blend (b, c) 1.5 wt. % m-HNTs added 90/10 ABS/PVC Composite.

- Thermal properties

The DSC of 2 wt.% m-HNTs filled ABS/PVC 90/10 wt. % composite is shown in Fig. 8. It is the very clear from the endotherm that, when there is change in the crystal arrangement or the structure always there is change in melting temperature (T_m) too. The addition of modified m-HNTs increases the crystallinity of ABS phase. It was observed that the crystallinity of modified HNTs (PEI modified HNTs) is less than the unmodified HNTs and is because of the improved dispersion of modified HNTs, on which more amount of amorphous ABS chains being adsorbed. Such results were addressed by many of the researchers. At 212^{o}C we can see the transition in the graph due to which there is the change from glassy to rubbery [25-26]. Also, the endothermic peak was observed at 216^{o}C and it was because of the addition of 2 wt. % of m-HNTS in the said polymer blends which imparts better thermal stability also [26].

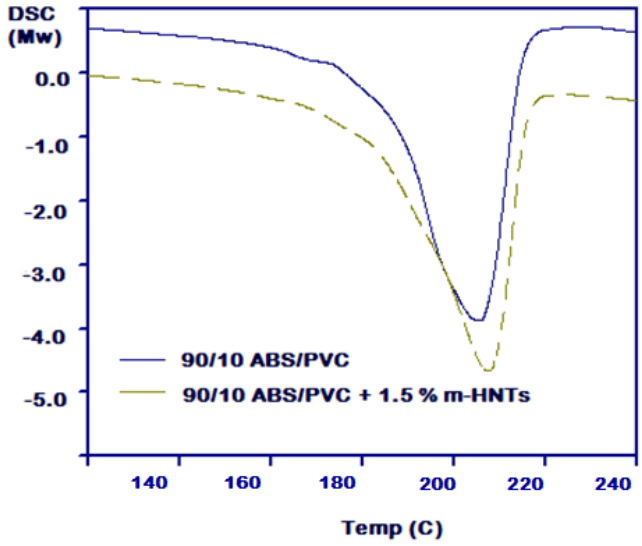

Fig. 8. DSC Melting endotherms of pure blend and branched PEI modified HNTs (m-HNTs) filled 90/10 (wt/wt %) ABS/PVC blends and its composites.

4. Conclusion

The external surface of HNTs can be successfully changed with the help of branched PEI. The PEI modified HNTs resulted in a better crystallinity of PVC phase in comparison with the pure blend and also better dispersion of m-HNTs was observed. The refinement in droplet morphology was observed when PEI modified HNTs (m-HNTs) is filled in polymer blends and its composites, which further improves the crystallinity of PVC phase. This is the reason of improvement in mechanical properties (like tensile and impact strength). The tensile strength was observed highest at 1.5 wt. % of m-HNTs. However, thermal stability is also imparted good when branched PEI modified HNTs are incorporated in polymer blends.

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