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PBAT/PLA/HNT filled blends for active food packaging

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Abstract

Bio-compostable films are needed for food packaging to maintain circular economy. Water vapour transmission rate (WVTR) is important factor in these packaging films which can be controlled by blending and incorporation of nano fillers. Polybutylelne adipate terphalate (PBAT)/ Polylactic acid (PLA) blend filled with Halloysite nano tubes (HNT) were successfully solution casted by using doctor blade method. Polyethylene glycol, PEG 400 and TritonX-100 were used as the dispersing agents for incorporation of HNT in the range of 0 to 2 wt%. All the samples were characterized for structure, morphology, mechanical and thermal properties. WVTR, and shelf life studies for green vegetables were carried out in ambient conditions. The results indicated improvement in mechanical properties of 80PBAT/20PLA/HNT filled blends compared to unfilled blends. TritonX-100 gave better dispersion of HNT than PEG400. as evidenced from XRD, SEM and FTIR analysis. Considerable decrease in WVTR was found by the addition of HNT in presence of PEG400 and TritonX-100. The effect was more pronounced in TritonX-100 since it helps to improve chain stiffening effect as reported in earlier studies. The DSC studies indicated increase of crystallinity of HNT filled blends which leads to reduction of WVTR. The evaluation of green vegetables preservation studies by different films showed that there was rapid ripening and deterioration of green vegetables as indicated by red color and shrinkage of the product in the standard low density polyethylene (LDPE) pouches and films without HNT. On the other hand in the presence of HNT the ripening rate was decreased considerably and original green color as well as freshness of green vegetables were maintained over the period of two weeks at ambient temperature conditions.

1. Introduction

Plastic films used in packaging of dry and wet edibles are causing increasing environmental pollution since these are thrown all over after use [1]. Most of these are made from conventional polymers which do not degrade easily. The best possible way to overcome or alter the conventional plastic utilization in food packaging is with the use of bio- based plastics or bio-degradable plastics which can improve shelf life of packed food and also enhance its aroma barrier and thus will lead to less socio- economic impacts on the surrounding environment and living beings [2–5].

There is extensive wastage of agriculture products due to degradation during storage of the vegetables and fruits that are packed in plastic films which have little permeability. In order to extend the storage life it is essential to tailor the permeability of the films and also control the internal atmosphere. In order to achieve this there are efforts reported in literatures to incorporate different nano-materials such as Halloysite, MMT clay, Zinc composites in packaging films [6–11].

Incorporating different types of nano-materials like halloysite in polymeric films leads to better shelf life of the packed food. In order to decrease ripening rate of fresh vegetable and fruits, some researchers used halloysite in polymeric films of packed food for ethylene scavenging which harms the fresh vegetables and fruits [6].

PBAT is one such co-polymer developed by the BASF under the trade name 'Ecoflex' which can be bio-based and can degrade in soil easily. PBAT is tougher bio-based polymer which can enhance mechanical properties when blended with some other bio-based or biodegradable polymers such as PLA [10, 12]. Surface hardness can be increased by addition of nano materials in PBAT due to uniform dispersion of the nano filler [10]. Among the bioplastics, Poly lactic acid (PLA) is mostly preferred due to superior mechanical properties compare to petroleum based polymers. Some studies have shown that, blending PLA with HNT increases the mechanical properties of the polymeric materials due to better interfacial adhesion/bonding between them [11]. Blending PLA with PBAT enhances the mechanical properties such as tensile strength and elongation at break of the resulting blends [11–16].

The present study is aimed at the investigation of the mechanical, thermal, morphological properties of unfilled PBAT/PLA blends and filled with nano material like Halloysite nano tubes (HNT). These films were further used for evaluation of green vegetables preservation studies at ambient temperature conditions.

2. Experimental

2.1. Materials

PBAT (Ecoflex Grade F blend C1200) was purchased from BASF, Mumbai, India. PLA (FKuR grade) was made available by Balson Industries, Pune, Halloysite powder was purchased from Sigma Aldrich and Chloroform was used as a solvent, PEG-400, and TritonX-100 used as dispersing agents for HNT filled blends and supplied by Vijay Chemicals, Pune.

2.2. Preparation of PBAT/PLA blends and incorporation of HNT

The films of neat PLA, neat PBAT and different blends of PBAT/PLA were made via solution blending in chloroform solvent which were cast by doctor blade technique. The casted films were dried at 60 °C–70 °C for 4 h in an air circulating oven and further studied for different mechanical properties such as tensile strength and elongation. From these studies, it was indicated that 80PBAT/20PLA have shown optimum mechanical properties such as elongation and tensile strength.

80PBAT/20PLA blend was modified with HNT by using two dispersing agents via ultrasonication technique. Different nano filled 80PBAT/20PLA blend compositions were prepared without PEG400 and with PEG400 as a dispersing agent. A stock solution of PEG400 and HNT (10 wt%) was made and required amount was used in the PBAT/PLA blends. The concentration of HNT was varied from 0 to 2.0 wt% and dispersed using ultrasonication cycle of 40 min. After ultrasonication, the dispersed solutions were then casted by using doctor blade unit. The thickness was maintained between 30–35 microns. All the prepared 80PBAT/20PLA/HNT filled blends were studied for different properties.

Similarly, 80PBAT/20PLA/HNT filled blend compositions were prepared with TritonX-100 as a dispersing agent. In this case, the desired quantity of HNT was soaked in TritonX-100 (3 ml) for 4 h and then mixed in the PBAT/PLA solutions. The concentration of HNT was varied from 1%, 1.5%, 2%, and 3% and dispersed by ultrasonication cycle of 40 min. Films were cast in the same manner as above.

2.3. Characterization and testing

2.3.1. FTIR, XRD and SEM analysis

FTIR spectra of all the samples were recorded using a Bruker Alpha spectrometer, USA in the region 4000 to 500 cm^{-1} in transmission mode. The XRD specimens were cut from the casted film with dimensions 2.5 cm by 2.5 cm. Wide angle XRD was recorded using Bruker D8 Advance, USA instrument. This was used for analysis of crystalline phase and fractional crystallinity by standard technique. The phase morphology and dispersion of nano materials in the blends were studied using ZEISS SIGMA FE-SEM as different magnifications.

2.3.2. Mechanical analysis

The tensile sample specimens were cut from the casted films according to the ASTM methods. The tensile strength, elongation at break of the casted films were evaluated at room temperature using a universal Testing Machine (STS 248) according to ASTM D638, method at crosshead speed of 50 mm min^{-1}.

2.3.3. DSC analysis

Differential Scanning calorimeter HITACHI DSC 7000 was used for recording the DSC curves at a heating and cooling rate of 10 °C per minute from 30 °C to 200 °C in nitrogen atmosphere. The melting and cooling curves were analyzed in standard manner for heat of fusion and crystallization.

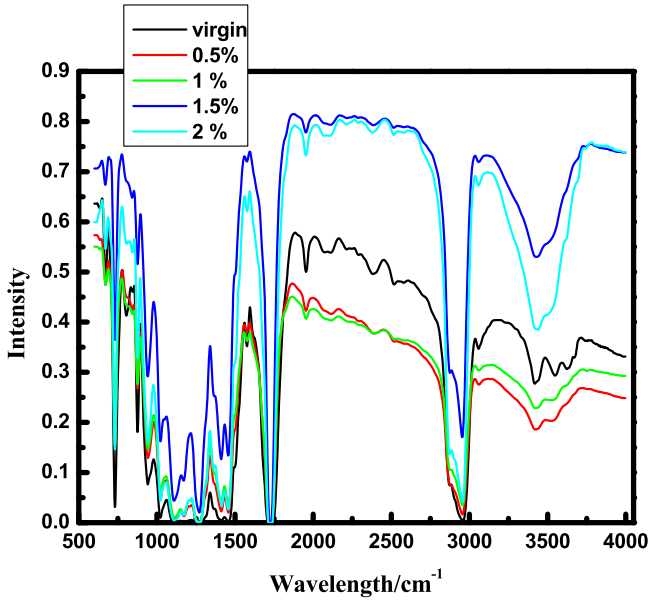

Figure 1. FTIR analysis of 80PBAT/20PLA/HNT filled blends in presence of PEG400 as a dispersing agent.

2.3.4. WVTR analysis

Pouches (50 mm × 50 mm) were made from neat PLA, LDPE, 80PBAT/20PLA and HNT filled 80 PBAT/20PLA blend films by hot sealing the edges. There were filled with known quantity of distilled water and maintained at constant ambient atmosphere. The weight loss was recorded every 24 h for 10 days. Water vapor transmission rate was determined from these data.

2.3.5. Studies on green vegetable preservation

Pouches were made from neat PLA, LDPE, 80PBAT/20PLA and HNT filled 80PBAT/20PLA blend films using PEG-400 as dispersing agent. These were filled with fresh green vegetable (viz. chilli) as per specific dimensions for evaluation preservation studies. The pouches were kept at ambient temperature for two weeks. Samples were visually observed and photographs recorded time to time.

3. Results and discussion

3.1. FTIR analysis

The effect of PEG400 and TritonX-100 as a dispersing agent significantly improves interaction effects of nano-materials in 80PBAT/20PLA filled blends. From the figure 1 it is observed that, there is significant change in the absorption band near 800, 1700, 2980 and 3600 cm^{-1} with the addition of PEG400 as a dispersing agent and nano particles in the 80PBAT/20PLA/HNT filled blends. This is due to strong hydrogen bonding between PEG400 and ester groups of the blend matrix. The broad and strong band near 3600 cm^{-1} especially confirms this. It is seen from figure 2, Triton X-100 as a dispersing agent in nano filled blends intensities of peak at 800, 1100, 1700 and 2980 cm^{-1} are altered significantly. Since TritonX-100 has more hydrophobic nature than PEG, there is little change in the OH– group region i.e. 3600 cm^{-1}. As TritonX-100 dispersing agent gives better dispersion of nano particles in the 80PBAT/20PLA/HNT filled blends, more surface area is available for the interactions and hence, this leads to significant changes in relative intensities of peaks as compared to PEG400. From FTIR figures it indicates that the effect of dispersing agents on the interaction between two polymer matrices and nanofillers.

It is seen from the table 1, that the relative intensities of the FTIR bands in the region below 1740 cm^{-1} change considerably for the Triton X as the dispersing agent while there is little change in the case of PEG400. However, in the latter case there is large change in the intensity of the –OH group i.e. 3450 cm^{-1} which arises due to interaction with PEG 400.

3.2. XRD analysis

XRD analysis of prepared 80PBAT/20PLA/HNT filled blend compositions with PEG400 and TritonX-100 as a dispersing agent is shown in figures 3 and 4. XRD peak assignments for XRD of prepared 80PBAT/20PLA/HNT filled blends are shown in figures 3 and 4. From these figures 3 and 4 it is observed that, the addition of nano

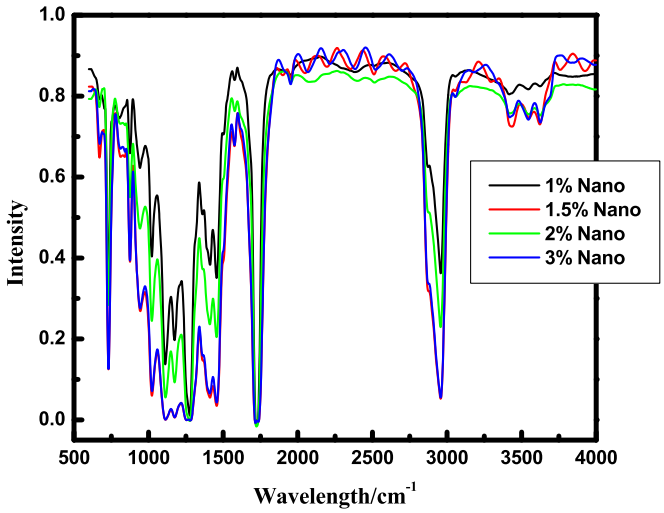

Figure 2. FTIR analysis of 80PBAT/20PLA/HNT filled blends in presence of TritonX-100 as a dispersing agent.

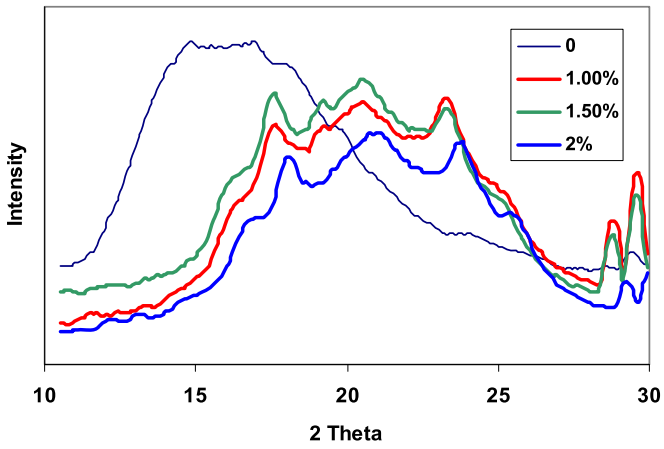

Figure 3. XRD analysis of 80PBAT/20PLA/HNT filled blends in presence of PEG-400 as a dispersing agent.

particles in prepared blends of 80PBAT/20PLA/HNT filled blends increases crystalline peak intensity. The effect of TritonX-100 as a dispersing agent in 80PBAT/20PLA/HNT filled blends helps to improve the distribution of particle in the matrix. The detail analysis of XRD results are tabulated in table 2.

3.3. SEM analysis

SEM micrographs of Halloysite powder and 80PBAT/20PLA/HNT (2 wt%) filled blends with PEG400 and TritonX-100 at lower and higher magnifications are shown in figures 5–8 respectively. It is seen that the particles are very finely dispersed without agglomeration in the films prepared with Triton-X (figures 7 and 8). With the addition of TritonX-100 as a dispersing agent in 80PBAT/20PLA/HNT filled blends, nano materials are finely dispersed than PEG400. Interfacial adhesion between HNT and blends matrix was improved by TritonX-100 which was also supported by FTIR analysis.

3.4. DSC analysis

It is observed that, the addition of nano particles in the 80PBAT/20PLA/HNT filled blends leads to significant changes in ΔH_m and ΔH_c values of each component of the blends and this suggest crystallinity is affected by presence of nanofillers. From the DSC thermal studies it is noted that two melting peaks of PLA at 150 °C and 157 °C are merged into single peak indicating that, α' phase of PLA is suppressed. From ΔH_m values it is observed that PBAT is also preferentially crystallized. This will affect the mechanical properties of films.

The addition of nano particles in the 80PBAT/20PLA/HNT blends leads to enhancement in crystallinity of both PBAT and PLA components as evidenced from the increase of ΔH_m values. There is slight increase of ΔH_c

Table 1. FTIR Relative Intensities of the prominent peaks of 80PBAT/20PLA/HNT filled blends in presence of PEG400 and Triton X-100 as a dispersing agent.

			Dispersant PEG-400		
Peak Intensity Ratio	850 cm^{-1} 1720 cm^{-1}	1100 cm^{-1} 1720 cm^{-1}	1400 cm^{-1} 1720 cm^{-1}	1425 cm^{-1} 1720 cm^{-1}	3450 cm^{-1} 2950 cm^{-1}
T80PBAT/20PLA	0.7	1	1	1	0.266
T80PBAT/20PLA/HNT0.5	0.74	1	0.960	0.96	0.312
T80PBAT/20PLA/HNT1.0	0.680	1	0.893	0.893	0.281
T80PBAT/20PLA/HNT1.5	0.647	0.941	0.847	0.835	0.312
T80PBAT/20PLA/HNT2.0	0.807	1	0.952	0.941	0.519
			Dispersant TRITON X-100		
T'80PBAT/20PLA/HNT1	0.301	0.83	0.563	0.602	0.123
T'80PBAT/20PLA/HNT1.5	0.689	0.99	0.93	0.951	0.208
T'80PBAT/20PLA/HNT2	0.445	0.91	0.713	0.742	0.101
T'80PBAT/20PLA/HNT3	0.679	0.99	0.922	0.941	0.165

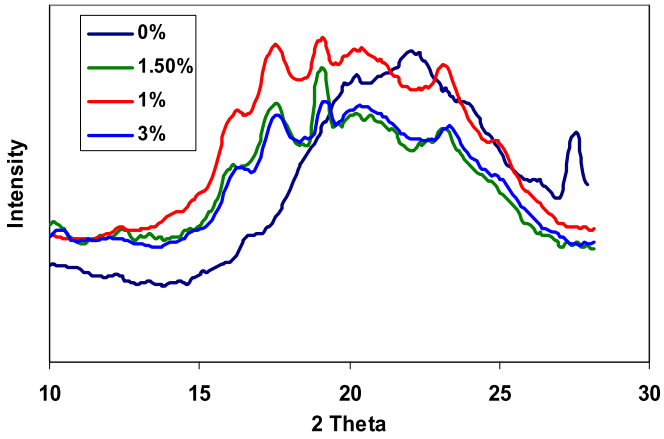

Figure 4. XRD analysis of 80PBAT/20PLA/HNT filled blends in presence of TritonX-100 as a dispersing agent.

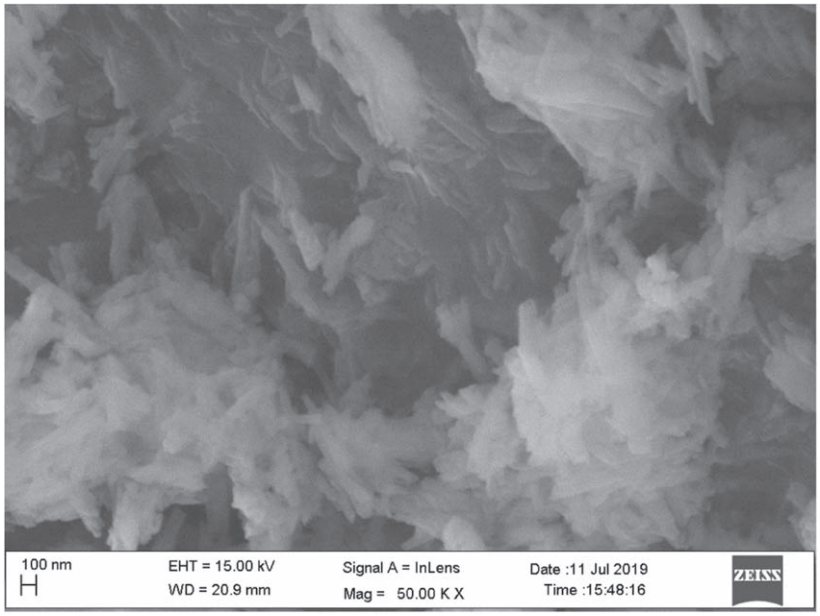

Figure 5. SEM analysis of HNT powder.

Table 2. XRD analysis of 80PBAT/20PLA/HNT filled blends in presence of PEG400 and Triton X-100 as a dispersing agent.

Peak position (2Θ) degrees	Assignment	Remarks
16.32	PBAT	010
17.5	PLA	Main Peak 110/200
19.03	HNT	110
23.23	PLA/PBAT Blend	Second 100
24.9	PBAT + HNT	002 HNT
27.5	Additive in Fkur	Sharp peak occur in base commercial polymer.

for the PLA component in presence of HNT suggesting that there is preferential nucleation of PLA crystals. This supports improvement in mechanical properties of 80PBAT/20PLA/HNT filled blends. The detail DSC analysis is represented in table 3 and figures 9 and 10.

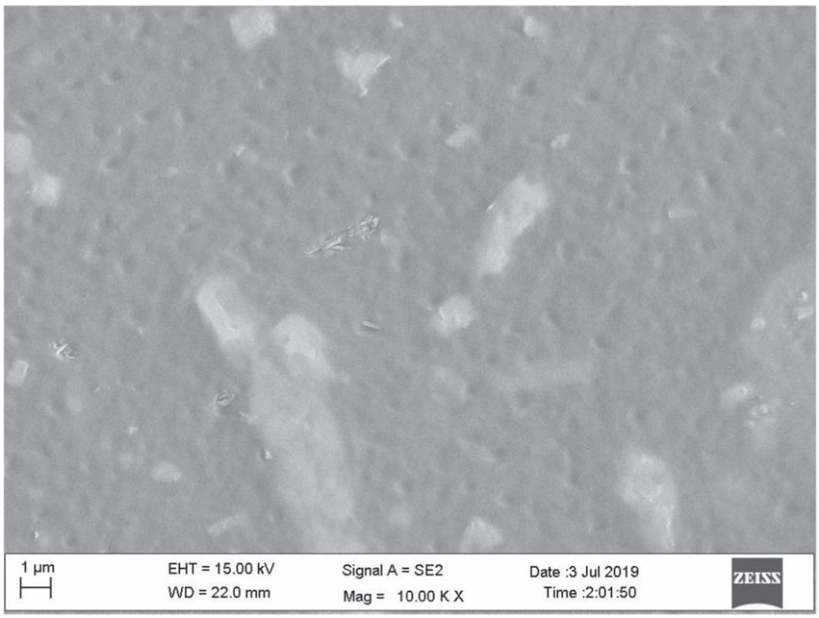

Figure 6. SEM analysis of 2% nano content in 80PBAT/20PLA/HNT filled blend with PEG as dispersing agent.

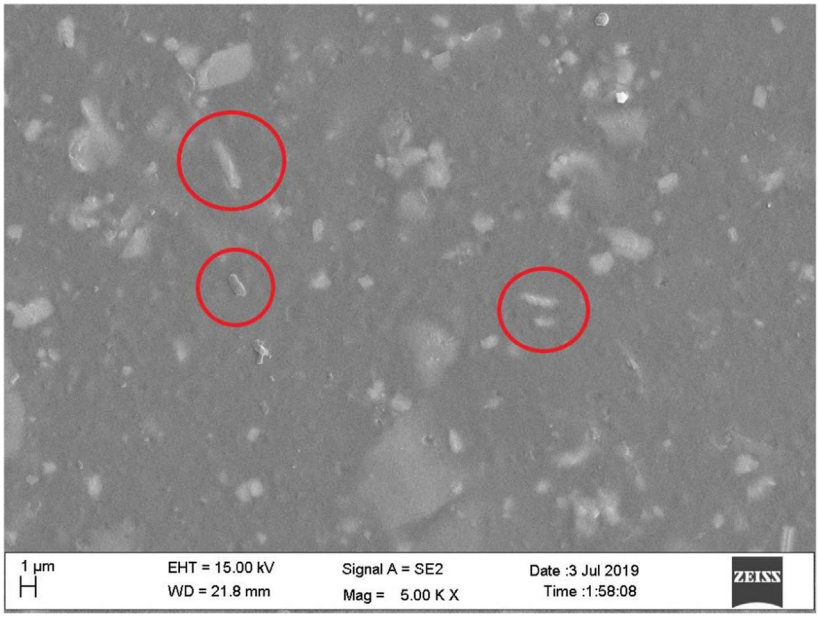

Figure 7. SEM analysis of 2% nano content in 80PBAT/20PLA/HNT filled blend with TritonX-100 as dispersing agent.

3.5. Mechanical properties

Tables 4–6 and figures 11–14 indicate the values of mechanical properties such as tensile strength and elongation of neat PBAT/PLA blends and 80PBAT/20PLA/HNT filled blends composition with PEG400 and TritonX-100 as dispersing agent respectively.

PEG has –OH group so it leads to better plasticization effects in PLA blend compositions which will affect its mechanical properties in terms of % elongation and WVTR. With the addition of nano material in presence of PEG400 in 80PBAT/20PLA/HNT filled blends the plasticization effect was observed. Chain stiffening effect was observed in triton X-100 based 80PBAT/20PLA/HNT filled blends. From these results it may be concluded that, triton X-100 also acts as a coupling agent which helps to improve mechanical performance of 80PBAT/20PLA/HNT filled blends compositions. On the other hand, PEG400 acts as a dispersing agent as well as plasticizer for

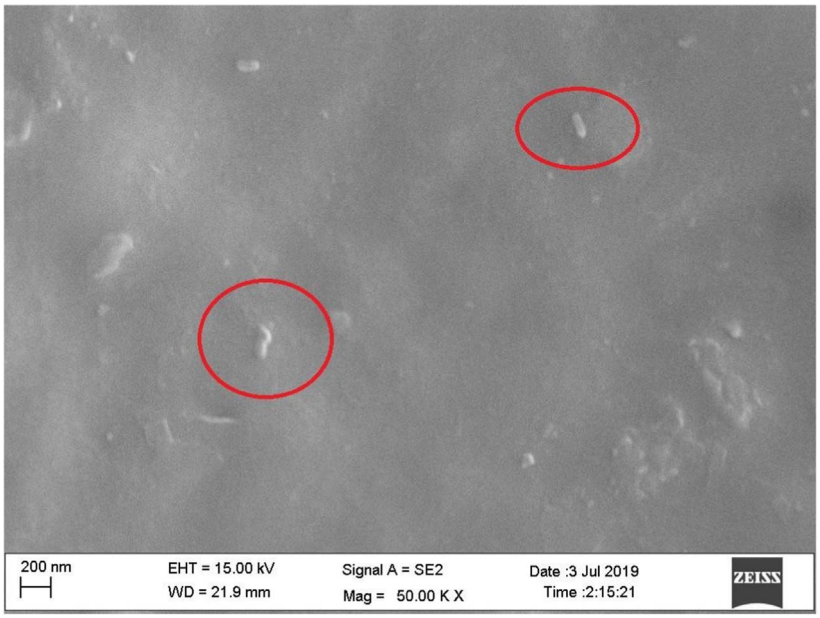

Figure 8. SEM analysis of 2% nano content in 80PBAT/20PLA/HNT filled blend with TritonX-100 as dispersing agent at higher magnification.

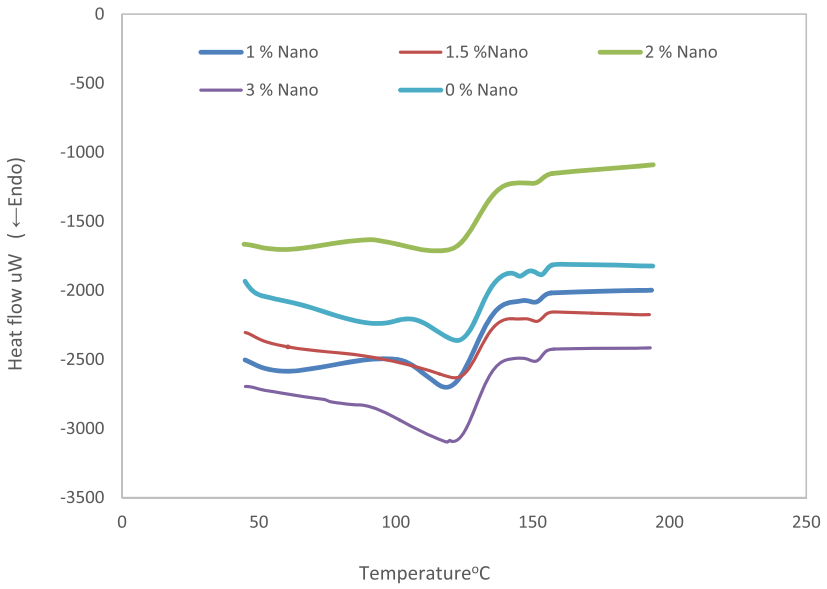

Figure 9. DSC analysis of 80PBAT/20PLA/HNT filled blends in presence of dispersing agent.

Table 3. DSC analysis of 80PBAT/20PLA/HNT filled blends with TritonX-100 as as dispersing agent.

Compositions	PBAT		PLA	
	ΔH_m (mJ mg^{-1})	ΔH_c (mJ mg^{-1})	ΔH_m (mJ mg^{-1})	ΔH_c (mJ mg^{-1})
	Fractional		Fractional	
T'80PBAT/20PLA	5.41	—	0.75 (α), 0.1 (α')	12.7
T'80PBAT/20PLA/HNT1	7.61	—	0.65	13.7
T'80PBAT/20PLA/HNT1.5	8.06	—	0.8	13.8
T'80PBAT/20PLA/HNT2	7.66	—	0.9	10.3
T'80PBAT/20PLA/HNT3	11.31	—	1.15	14.8

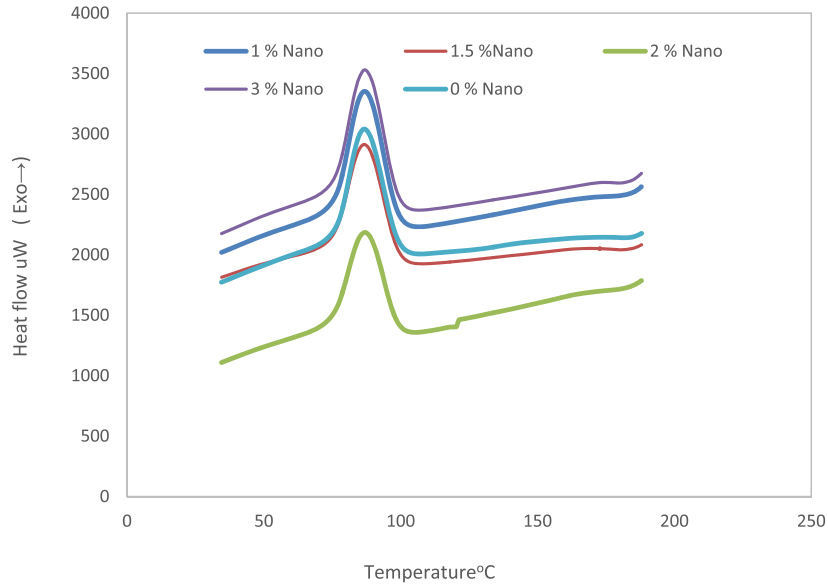

Figure 10. DSC crystallization curve of 80PBAT/20PLA/HNT filled blends in presence of dispersing agent.

Table 4. Mechanical Properties of PBAT/PLA Blends without nano-composites.

Compositions	Tensile strength (MPa)	Elongation (%)
Neat PLA	7.11	102
90PLA/10PBAT	7.00	142
80PLA/20PBAT	6.27	198
70PLA/30PBAT	8.96	422
60PLA/40PBAT	6.66	438
50PLA/50PBAT	7.26	170
80PBAT/20PLA	11.2	878
90PBAT/10PLA	10.54	877
Neat PBAT	10.58	1028

Table 5. 80PBAT/20PLA/HNT blends in presence of PEG 400 as a dispersing agent.

Compositions	Tensile strength (MPa)	Elongation (%)
T80PBAT/20PLA	4.56	258
T80PBAT/20PLA/HNT0.5	6.59	874
T80PBAT/20PLA/HNT1.0	7.34	881
T80PBAT/20PLA/HNT1.5	9.02	1129
T80PBAT/20PLA/HNT2.0	7.53	839

Table 6. 80PBAT/20PLA/HNT blends in presence of Triton X-100 as dispersing agent.

Compositions	Tensile strength (MPa)	Elongation (%)
T'80PBAT/20PLA/HNT1	5.75	489
T'80PBAT/20PLA/HNT1.5	8.90	828
T'80PBAT/20PLA/HNT2	5.99	602
T'80PBAT/20PLA/HNT3	6.10	540

the PLA matrix as is evident from the high elongation values. From the figures 13, 14 it shows that, reinforcing effect in triton X-100 based nano filled system is higher than PEG400 nano filled system which is also supported by higher crystallinity which has been observed from DSC (table no 2) and XRD patterns.

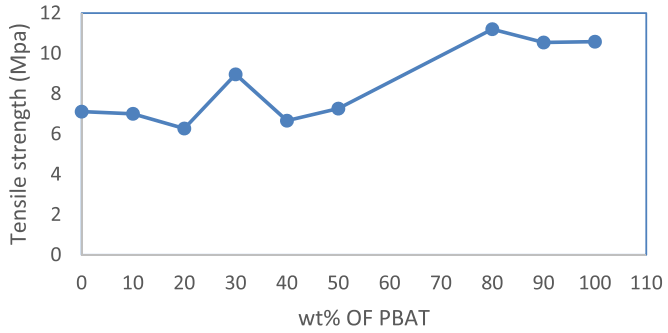

Figure 11. Variation in tensile strength (MPa) of PBAT/PLA blends against the content of PBAT.

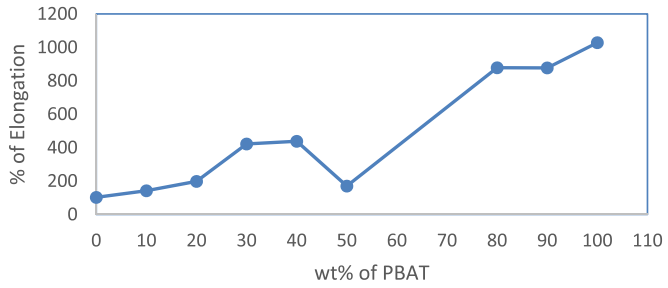

Figure 12. Variation in elongation (%) of PBAT/PLA blends against the content of PBAT.

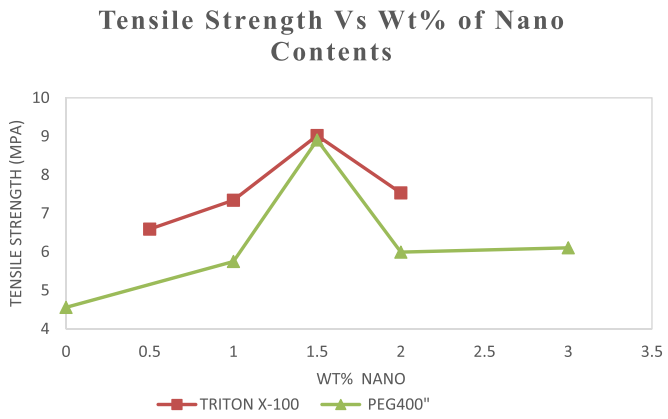

Figure 13. Variation in tensile strength (MPa) of 80PBAT/20PLA/HNT filled blends against % of Nano –Contents in presence of dispersing agents.

3.6. Water vapor transmission rate analysis

From the table 7 and figure 15 it is seen that, in presence of PEG400 as a dispersing agent in 80PBAT/20PLA/HNT filled blends water vapor transmission rate increases considerably as compared to blends prepared with Triton X-100. It has gone to lower limiting values with addition of nano filler and remained more or less constant with addition of higher % of nanofiller and dispersing agent concentration. This is due to plasticization effect of PEG400 as a dispersing agent which is reported by others ([13–16]). This has also been observed by us in the present studies which is evident from high elongation values. Due to addition of HNT as a nano-fillers in 80PBAT/20PLA filled blends there is considerable reduction in water vapor transmission rate even in presence

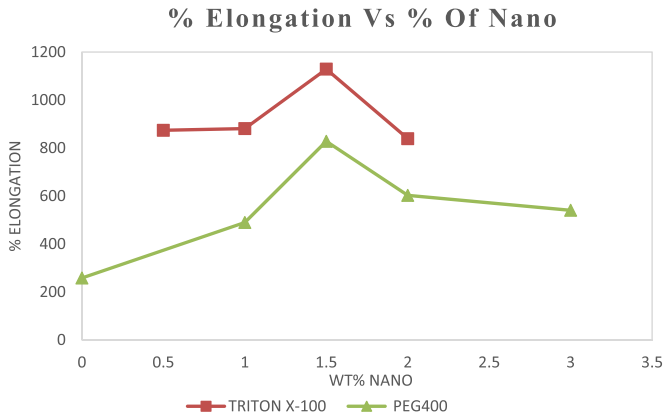

Figure 14. Variation in tensile strength (MPa) of 80PBAT/20PLA/HNT filled blends against % of Nano –Contents in presence of dispersing agents.

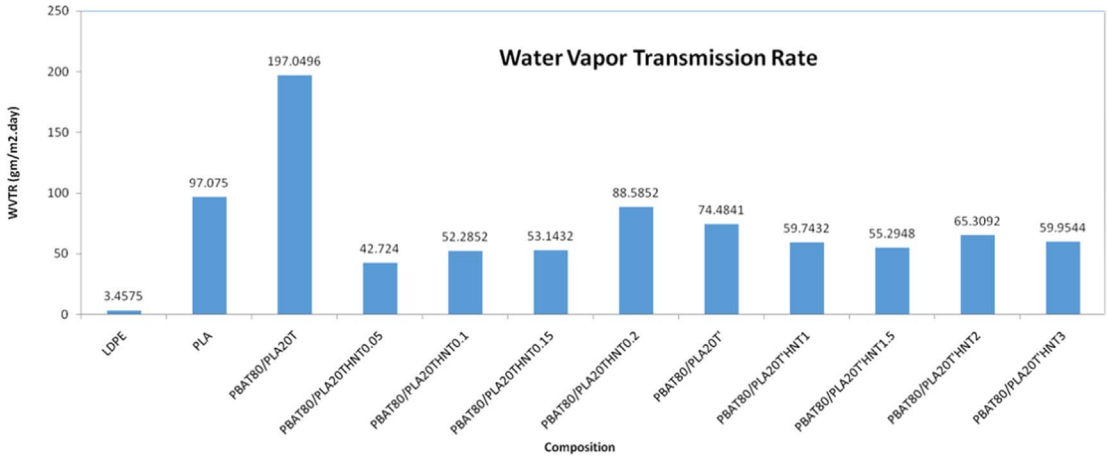

Figure 15. Variation in water vapor transmission rate of LDPE, PLA, PBAT/PLA blends and 80PBAT/20PLA/HNT filled blend in presence of dispersing agents.

Table 7. Values of water vapor transmission rate of LDPE, PLA, PBAT/PLA blends and 80PBAT/20PLA/HNT filled blend in presence of dispersing agents.

Material compositions	Water vapor transmission rate(gm m^{-2}.day^{-1})
LDPE	3.45
PLA	97.07
T80PBAT/20PLA	197.04
T80PBAT/20PLA/0.05HNT	42.72
T80PBAT/20PLA/0.10HNT	52.28
T80PBAT/20PLA/0.15HNT	53.14
T80PBAT/20PLA/0.20HNT	88.58
T′80PBAT/20PLA/	74.48
T′80PBAT/20PLA/1%HNT	59.74
T′80PBAT/20PLA/1.5%HNT	55.29
T′80PBAT/20PLA/2%HNT	65.30
T′80PBAT/20PLA/3%HNT	59.95

of PEG400. On other hand, TritonX-100 does not give plasticization effect. TritonX-100 improves the dispersion of HNT in blends which leads to significant reduction water vapor transmission rate filled blends. Additionally, the increase in crystallinity in presence of HNT also helps to reduce WVTR as compared to unfilled blends.

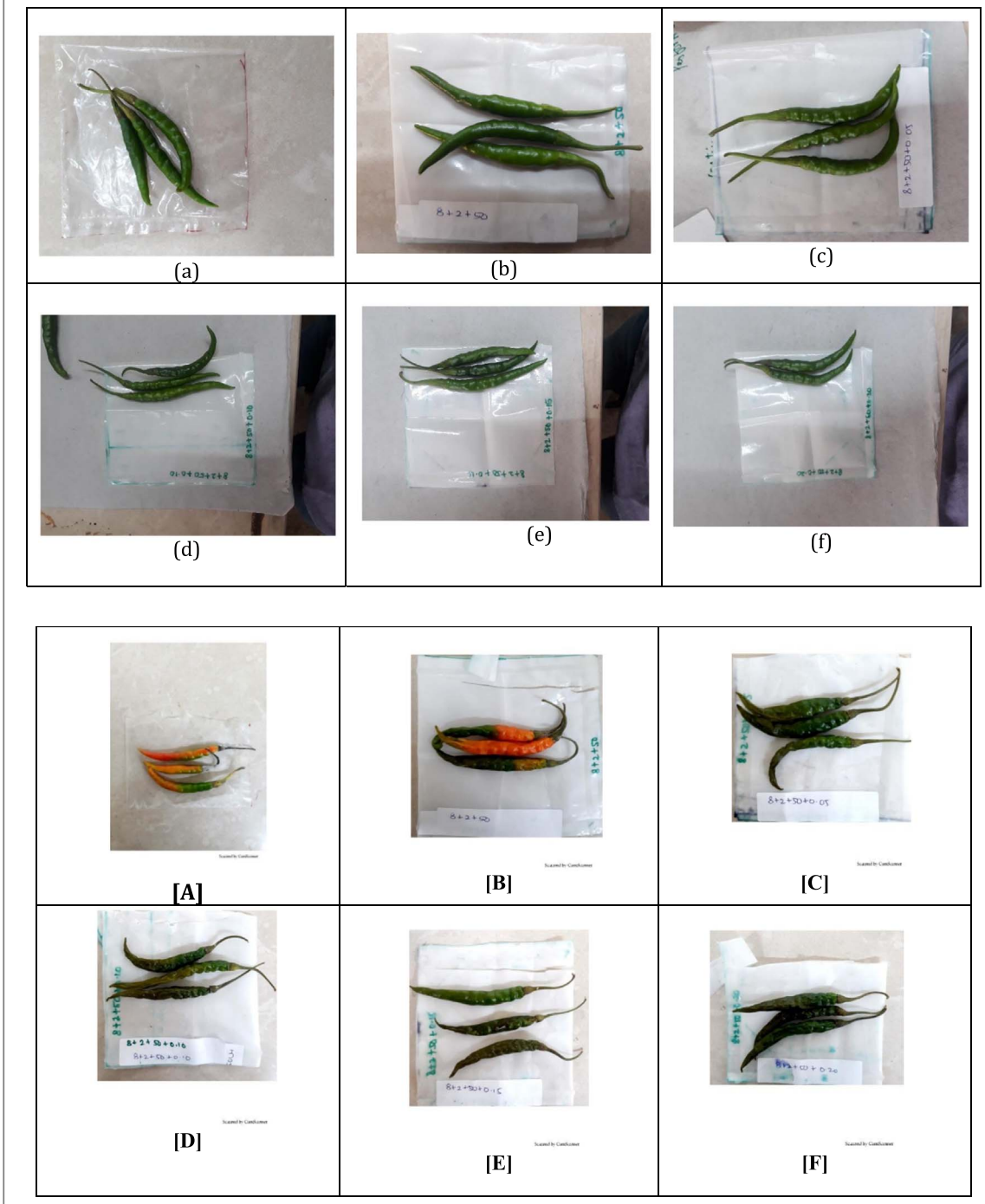

Figure 16. Photographs of Preservation analysis of Green Vegetables after 1st day (a)–(f) and after 16th day [A–F] in LDPE, 80PBAT/20PLA unfilled blend, T80PBAT/20PLA/HNT0.5, T80PBAT/20PLA/HNT1, T80PBAT/20PLA/HNT1.5 and T80PBAT/20PLA/HNT2 filled blend Pouches.

3.7. Preservation analysis

From the photographs indicated in figure 16, it is observed that, the green vegetables turn into ripened red state for the pouches made from LDPE as well unfilled blends. On the other hand, the addition of HNT in the 80PBAT/20PLA/HNT blends, the product in these pouches remains green even after 15 days under ambient conditions of temperature (30 °C). This indicates that there is considerable decrease of the ripening rate of the green vegetables due to the presence of HNT. Food ripening depends on moisture accumulation within packaging and gases generated during ripening effect (particularly ethylene gas) so WVTR has to be optimum to prevent moisture accumulation and gas evolved has to scavenge to prevent ripening. This can be due to two reasons viz. (a) scavenging effect of HNT as reported earlier ([6]) and (b) the control of permeability due to increase of crystallinity as observed above.

4. Conclusion

From the above studies following conclusions can be made. PBAT/PLA blends give optimum properties at 80 PBAT/20PLA composition. The addition of nano materials in 80PBAT/20PLA prepared with PEG400 as dispersing agent leads to plasticization effect but still there is increase mechanical properties like tensile strength and elongation of which is due to increase of overall crystallinity. The water vapor transmission rate of 80PBAT/20PLA/HNT filled blends is considerably lower than the unfilled blend. All these factors lead to extension of the shelf life of fresh green vegetable. Thus, these materials can be used to develop sustainable active packaging for fresh green vegetables.

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