

Evaluating the interaction of waste natural fibers and biodegradable polymers

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ABSTRACT

Polymer composites were prepared successfully by combining tea waste, resulting from agricultural product processing, which was used as reinforcement material and biodegradable polymers which was used as matrix material. Chitosan and poly L-lactic acid were used as biodegradable polymers. Sodium tripolyphosphate and borax pentahydrate were chosen as composite additives. Optimization studies were done on the processing parameters and the characterization results obtained from infrared spectra, X-ray diffractograms and thermograms could be used to evaluate the prepared polymer composites for potential applications like food packaging/coating or disposable medical products etc. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses indicated that additives improved the interaction of the tea waste and the polymers. Thermal stability of chitosan was enhanced by preparing a composite with tea waste. The water resistance behavior of the prepared polymer composites increased.

KEYWORDS: tea waste, poly L-lactic acid, chitosan, polymer composites, additive materials, composite characterization.

1. INTRODUCTION

Environmental awareness and legislation in many countries directed the researches in polymer-based technologies to use bio-compliant and biodegradable

polymers and reinforcement materials derived from sustainable sources. So, using green polymers like cellulose, protein, starch and chitosan in traditional polymer applications is a rising trend despite some challenges. Modification of polymers and preparing polymer composites are some of the prominent techniques that are used to overcome these disadvantages of the recyclable polymers. In composite technology, combining reinforcement materials with polymers and sometimes adding specific additives into the polymers may minimize the disadvantages like low resistance to environmental conditions, poor thermal and mechanical properties. Furthermore, obtaining fully green polymer composites is possible by choosing natural inorganic or organic reinforcements as well as choosing bio-sourced polymers. As organic reinforcement, natural fibers have become favorite materials, with them being renewable, cheap, abundant, biodegradable and having low density. Using waste fibers as reinforcements is also attractive not only because valuable bio-based products are gained but also because wastes are removed. In the Black Sea region of Turkey, every year about 40 thousand tons of tea waste after tea production is generated on a dry basis. Although tea waste is rich in organic matter, only a small amount of it is considered for re-use and most of it is disposed of into the environment. Some of the disposal methods lead to environmental pollution. Based on this view, tea waste from the Eastern Black Sea region was used as reinforcement material in this study. Biodegradable poly L-lactic acid and chitosan polymers were used as matrix materials and polymer

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composites were prepared by solvent dispersion method. The objective of this study is to examine the effects of blending polymers and changing the additives, on the interaction of waste natural fibers and biodegradable polymers. Accordingly, composite processing parameters like mixing temperature, time, rate and the solvent type were chosen so as to get the optimal mixtures. The polymer composites were evaluated by tracking the differences observed from FTIR, XRD, thermal analyses and water uptake tests. Although there have been literature on composites prepared by using tea waste [1-4] and tea extract-doped chitosan films [5], the synergistic effect of poly L-lactic acid (PLLA) and chitosan (CT) polymer blend and the additives used in this study with the tea waste have not been examined before as far as we know. In addition to these, the effect of using different solvents for tea waste (TW) was also studied.

2. MATERIALS AND METHODS

Chitosan ((CT), Sigma-Aldrich, middle-viscous) and poly L-lactic acid ((PLLA), Sigma-Aldrich, inherent viscosity ~2.0 dl/g, Mw ~152000) were used as matrix material, sodium tripolyphosphate pentabasic ((TPP), Sigma-Aldrich, ≥ 98.0%, Mw:367.86 g/mol) and borax pentahydrate ((BP, Na₂B₄O₇·5H₂O) supplied from Eti Maden Kirka Boron Plant in Turkey) were used as composite additives, dilute acetic acid ((aa), %100, Merck) and chloroform ((ch), ≥ 99.0%, Merck), sodium hydroxide ((sh, NaOH), Sigma-Aldrich) and ethyl alcohol ((ea), ≥ 99.9%, Merck) were used as solvents for the reinforcement material and polymers. Natural fiber and its dust resulting from agricultural product processing were supplied from a black tea factory in the east Black Sea region of Turkey. The chemical composition analysis of this tea waste (TW) was performed according to the literature [6, 7]. The percentages of raw cellulose, hemicellulose, lignin and extractive material in fiber were found to be 32.95%, 6.26%, 36.80% and 23.99%, respectively.

2.1. Preparation of polymer composites

Polymer composites including 10% TW as reinforcement material were prepared by solvent dispersion method. The composites varied according to the solvents used for TW and the type of the polymer and the additive. The abbreviations and the contents (weight %) of these polymer composites

are given in Table 1. Two composite additives were used in some composites. Tripolyphosphate was chosen for its non-toxic property and quick gelling ability. Such kinds of polyanions have been used to form gels of chitosan [8]. Borax pentahydrate was chosen based on the reports of it being used as a wood preservation chemical against insects and fungi, in wood composites [9] and as a cross-linking agent for water-soluble polymers such as partially hydrolyzed polysaccharides [10]. It was also noted that boron compounds drew attention with their low mammalian toxicity and environmental acceptability [9]. While preparing composites, the processing parameters like the effect of mixing temperature, time, rate and the solvent type were optimized. Briefly, separate beakers and solvents (details are given in Table 1) were used for the reinforcement material and polymer. Next, the mixtures of reinforcement material and those of polymers were stirred separately for 60 minutes at 800 rpm. Then the reinforcement and the polymer mixtures were combined slowly and stirred again at 40 °C for 60 minutes approximately at 800 or 1000 rpm. TPP and BP-added composites were well-mixed at 800 rpm. After that the mixture was agitated in ultrasonic bath for two hours and was dried at room temperature in drying pools. Then the films were kept in desiccators.

2.2. Characterization

IR spectra of the composites were recorded using the Perkin Elmer Spectrum 100 model Fourier Transform Infrared spectrometer. Attenuated total reflectance (ATR) accessory in the range of 4000-650 cm⁻¹ was used. Diffuse reflectance infrared fourier transform (DRIFT) accessory in the range of 4000-400 cm⁻¹ was used and 16 scans were taken. KBr was used to dilute the composites (w/w; 3/100) and was used as the reference. The thermal analyses of the composites and the composite components were done by Perkin Elmer Pyris 1 TGA instrument at the Central Laboratory in the Middle East Technical University. Each analysis was performed in the temperature range of 25-700 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The glass transition temperatures of some composites were determined by Perkin Elmer Diamond differential scanning calorimeter (DSC) instrument in the temperature range of 0-170 °C at a heating

Table 1. The abbreviations and the contents of the composites.

Abbreviations (weight %)	Contents (weight % on dry basis.)
10%TW(aa)+90%PLLA(cf)	10% tea waste (acetic acid solvent) and 90% PLLA (chloroform solvent)
10%TW(sh+ea)+90%PLLA(cf)	10% tea waste (sodium hydroxide/ethyl alcohol (1:1, v/v)) and 90% PLLA (chloroform solvent)
10%TW(sh+ea)+90%CT(aa)	10% tea waste (sodium hydroxide/ethyl alcohol (1:1, v/v)) and 90% CT (acetic acid solvent)
10%TW(sh+ea)+10%TPP(cf)+80%PLLA(cf)	10% tea waste (sodium hydroxide/ethyl alcohol (1:1, v/v)), 10% tripolyphosphate and 80% PLLA (chloroform solvent)
10%TW(sh+ea)+45%PLLA(cf)+45%CT(aa)	10% tea waste (sodium hydroxide/ethyl alcohol (1:1, v/v)), 45% PLLA (chloroform solvent) and 45% CT (acetic acid solvent)
10%TW(sh+ea)+10%TPP(cf)+40%PLLA(cf)+40%CT(aa)	10% tea waste (sodium hydroxide/ethyl alcohol (1:1, v/v)), 10% tripolyphosphate (chloroform solvent), 40% PLLA (chloroform solvent) and 40% CT (acetic acid solvent)
10%TW(sh+ea)+10%BP(aa)+40%PLLA(cf)+40%CT(aa)	10% tea waste (sodium hydroxide/ethyl alcohol (1:1, v/v)), 10% borax pentahydrate (acetic acid solvent), 40% PLLA (chloroform solvent) and 40% CT (acetic acid solvent)
PLLA(cf)	PLLA (chloroform solvent)
CT(aa)	CT (acetic acid solvent)
TW	-
TPP	-

rate of 20 °C/min in nitrogen atmosphere. The XRD diffractograms were obtained using Rigaku Ultima-IV XRD at 20 kV, 30 mA, using a Cu incident beam. The analyses were conducted in the 2θ range of 0-80°.

The water uptake amounts of the composites and the composite components were determined by the gravimetric method. Each sample was packed with a tea bag and immersed in a beaker containing 10 mL distilled water for the water uptake analyses and removed at prescribed intervals then gently blotted and weighed. The water uptake value of the sample was calculated according to equation 1. Here m_0 and m_t denote the weights of the sample at the initial time and the time “t”, respectively. The water uptake experiments for each material were repeated at least two times to ensure the reproducibility of the results.

$$\text{Water uptake (\%)} = [(m_t - m_0)/m_0] \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. FTIR spectra

The FTIR spectra of the composite components and composites are given in Figures 1(a) and (b), respectively. In FTIR spectrum of TW, the broad band observed around 3400 cm^{-1} represents the O-H stretching of the inter- and intra-molecular hydrogen bonding of compounds such as alcohols, phenols and carboxylic acids which exist in pectin, cellulose and lignin [11, 12]. Hence, this band shows the presence of “free” hydroxyl groups on the surface. The peaks between 3000 and 2800 cm^{-1} are due to the C-H stretching vibrations of aliphatic groups. The peak at 1732 cm^{-1} is attributed to the C=O stretching of aldehyde, ketone or carboxylic acids in hemicellulose. Asymmetric stretching vibrations of C=O groups in carbonyls of flavonoids and polyphenols [13] are located around 1625 cm^{-1} . Aromatic skeletal vibration of the lignocelluloses is observed around 1520 cm^{-1} . The peak around

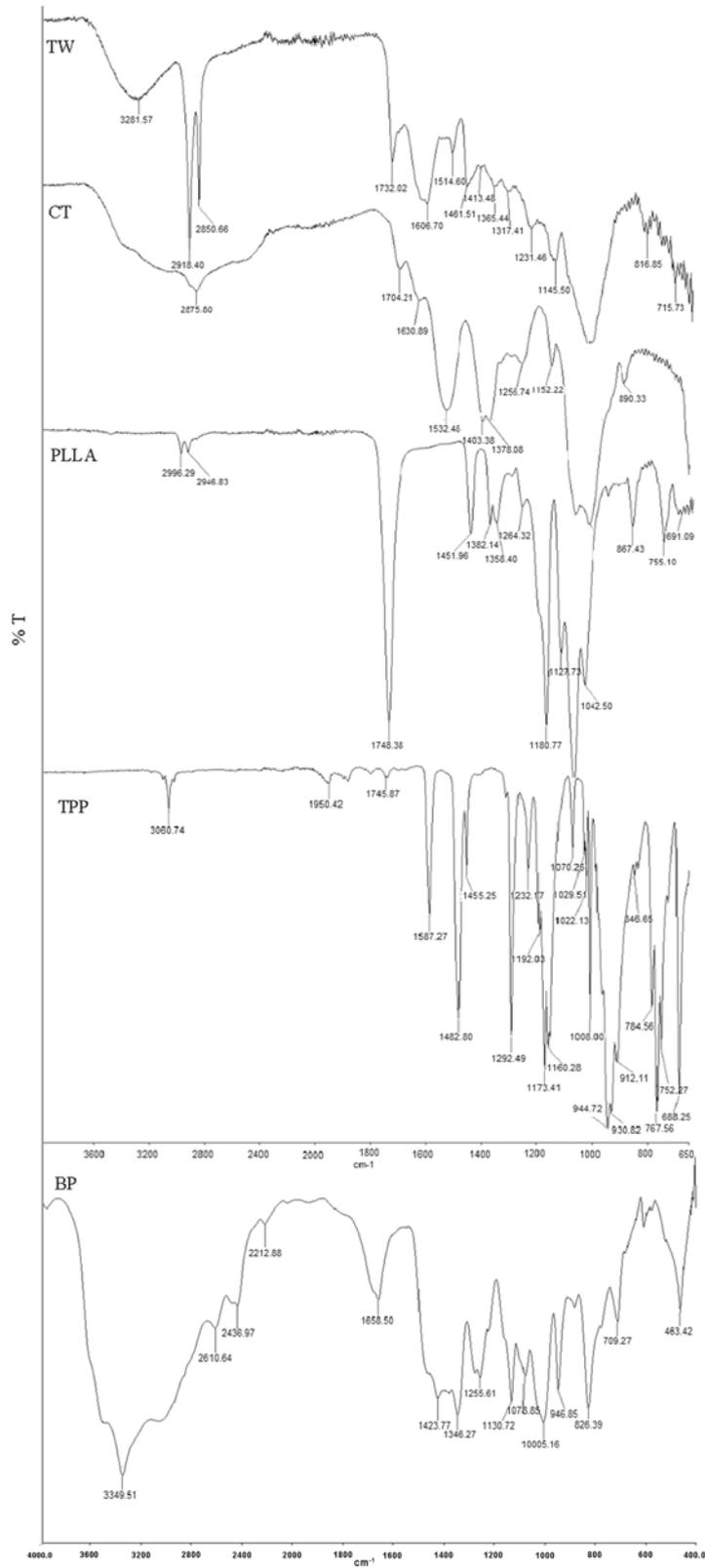


Figure 1(a). The FTIR spectra of the composite components.

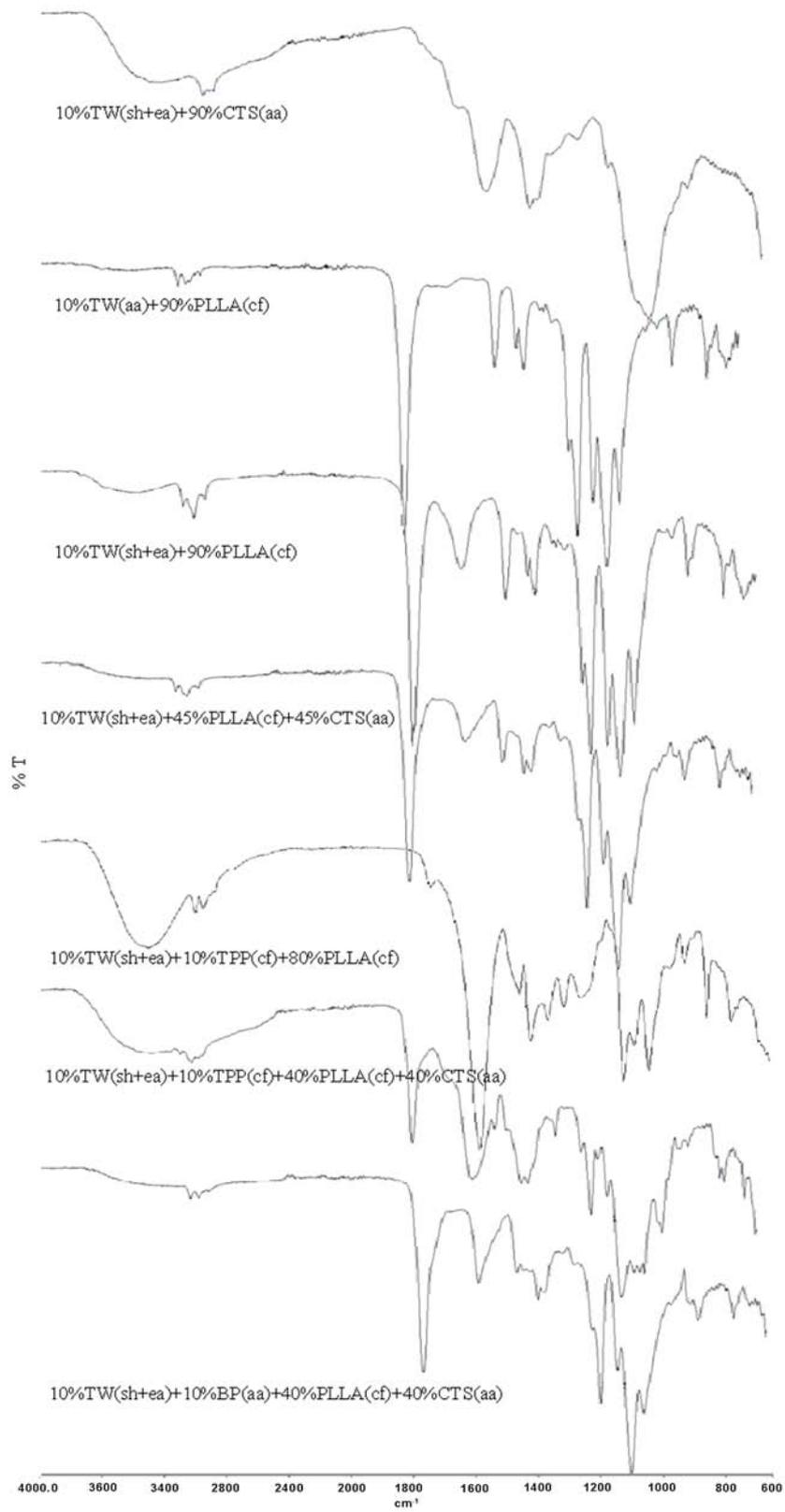


Figure 1(b). The FTIR spectra of the composites.

1320 cm^{-1} is attributed to the C-N stretching vibrations of aromatic primary and secondary amines [14]. The other prominent peaks at 1231, 1145 and 1028 cm^{-1} are due to C-H bending. The peak at 715 cm^{-1} corresponds to N-H group. In FTIR spectrum of PLLA, the peaks between the regions of 1720–1800 cm^{-1} and 1300–1450 cm^{-1} are assigned to the C=O and C-H groups, respectively [15]. C-O-C asymmetrical and symmetrical stretching vibrations are found around 1250 and 1175 cm^{-1} , respectively [16]. The peaks at 1082 and 1042 cm^{-1} are assigned to the C-C stretchings [17]. The spectrum of the chitosan shows the C-H vibrations of the carbohydrate ring at 2925 and 2875 cm^{-1} . The peak around 1700 cm^{-1} is related to the C=O stretching. The peaks around 1630 cm^{-1} are attributed to the N-H bending and those at 1532 cm^{-1} are assigned to the secondary amide groups [18]. CH_3 symmetric bending at 1410 cm^{-1} is due to the C-H rocking, and that at 1295 cm^{-1} is related to the stretching vibrations of N-C in the structure. Those peaks at 1153 and 1085 cm^{-1} are indicative of C-O stretching vibrations of chitosan [19]. In BP spectrum, a broad band observed between 3700 and 2700 cm^{-1} wave numbers is assigned to the O-H stretching vibration [20]. The peak around 1658 cm^{-1} is due to the chemically bounded water [21]. H-O-H bending is located at 1661 cm^{-1} [22]. The peaks between 1300 and 1100 cm^{-1} are due to the boron bonds in triangular geometry [23]. The absorption bands of the structure of B_4O_7 can be observed between the wave numbers of 1375–1340 cm^{-1} and 1000–990 cm^{-1} [24]. TPP spectrum indicates that absorption bands between 1325–1180 cm^{-1} and 950–875 cm^{-1} are attributed, respectively, to P=O and P-O groups present in phosphate.

The spectrum of 10%TW(aa)+90%PLLA(cf) composite is very similar to the spectrum of PLLA. Merely the wave numbers of the main peaks shifted to the right slightly and the intensity of the C-H groups increased in the spectrum of the composite. The reason may be the existence of the tea waste. Although the spectra of the composites 10%TW(aa)+90%PLLA(cf) and 10%TW(sh+ea)+90%PLLA(cf) are very similar to each other, the peaks of 10%TW(sh+ea)+90%PLLA(cf) composite around 2920 and 2850 cm^{-1} are more notable and a characteristic absorption band of aromatic ring is displayed at 1597 cm^{-1} indicating the existence

of tea waste. This result suggests that the mixture of the sodium hydroxide and ethyl alcohol solvents used for tea waste seems to improve the interaction of the composite compounds. The polymer may not only have covered the tea waste surface but also penetrated into the tea waste. Alkali treatment, already is known as the most effective surface modification technique to improve the compatibility between the polymer and the fiber [25]. The spectrum of 10%TW(sh+ea)+90%CT(aa) shows the main characteristic peaks of CT. Besides, the peak intensities of the composite are lower than that of CT and the peaks of the composite shifted to the right slightly. C=O stretching of CT disappeared and the C-H stretchings between 3000 cm^{-1} and 2800 cm^{-1} are more clear, indicating that the C-H bonding was enhanced. Although the band intensities of the spectrum of 10%TW(sh+ea)+45%PLLA(cf)+45%CT(aa) are lower than that of the 10%TW(sh+ea)+90%PLLA(cf) composite, the peak profiles of the composites are similar. In the spectrum of the first composite, it is difficult to detect the effect of chitosan. This may be because of the location of the polymers. The tea waste and the chitosan may be enveloped by PLLA. Furthermore, addition of TPP significantly changed the spectrum. The peaks of P=O and P-O groups observed in the spectra of the TPP-including composites (10%TW(sh+ea)+10%TPP(cf)+80%PLLA(cf) and 10%TW(sh+ea)+10%TPP(cf)+40%PLLA(cf)+40%CT(aa)) indicate the existence of TPP in these polymer composites. Besides, the band around 3280 cm^{-1} is assigned to the OH stretching of flavonoids and phenolic compounds and can be observed for TW, 10%TW(sh+ea)+90%PLLA(cf) and 10%TW(sh+ea)+10%TPP(cf)+80%PLLA(cf). Addition of BP to the composite did not change the general view of the spectrum except the peak around 1570 cm^{-1} . PLLA is the dominant compound in the spectrum of this composite.

3.2. Thermal characterization

The thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) curves of composite components and some selected composites are given in Figure 2.

In Figure 2, the TG curve of tea waste showed three degradation steps. An initial weight loss of 7% occurs between the range of 50–150 $^{\circ}\text{C}$, which may be due to evaporation of the chemically

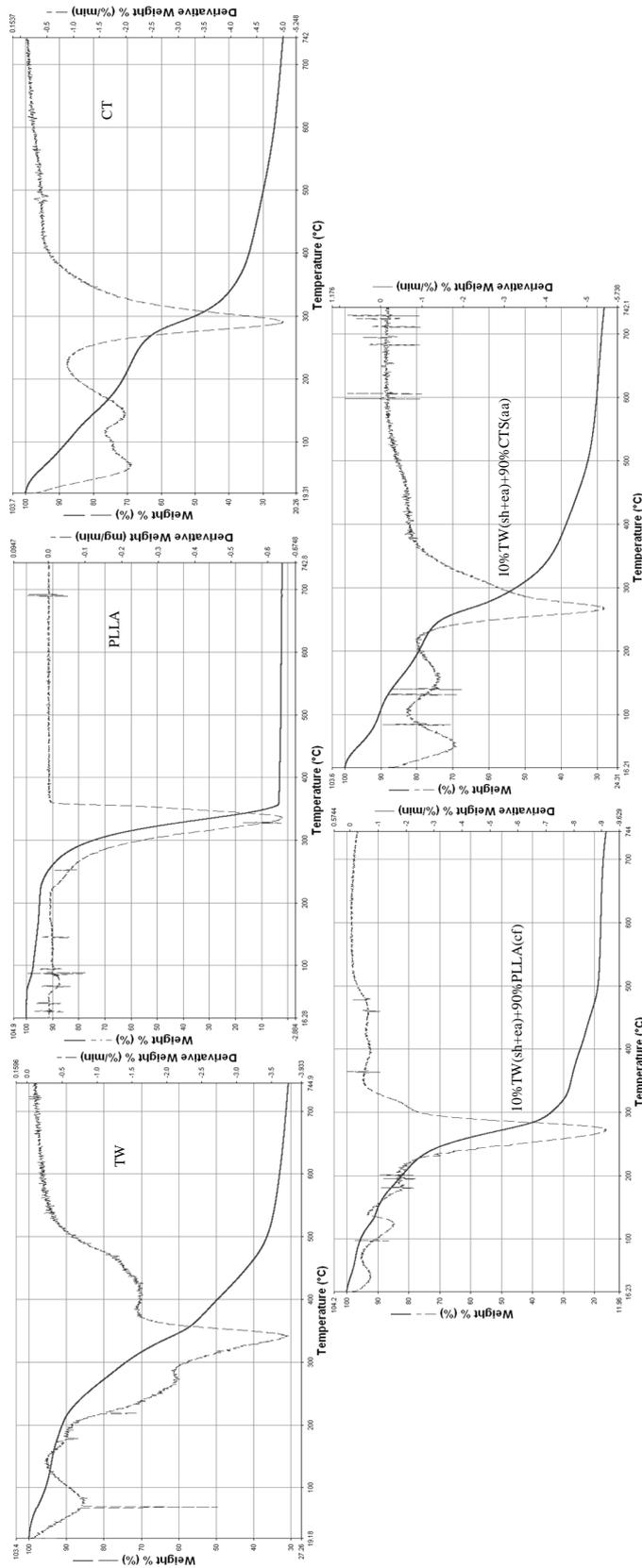


Figure 2. The TGA and DTA curves of the composite components and some selected composites.

strong and physically weak bound moisture in the structure [26]. Volatile components and light gases such as CO and CO₂ may also be released during this step [27]. It is known that the degradation of hemicelluloses occurs at 150–350 °C, cellulose at 248–350 °C, and lignin at 200–700 °C [3]. The total weight loss of the tea waste is about 70%, due to the devolatilization and the degradation of the chemical components. The TG curve of PLLA shows a one-stage degradation process. PLLA began to degrade at about 250 °C, and its maximum degradation temperature was around 342 °C. Two weight losses are observed in the thermogram of CT. The first degradation is due to dehydration. The continuing weight loss of water above 100 °C is owing to the presence of hydrogen bonding. The second weight loss is assigned to the degradation of chitosan main chains, as was reported in the literature [28]. The thermogram exhibits a maximum degradation temperature around 300 °C. Multi degradation behaviors were observed for the 10%TW(sh+ea)+90%PLLA(cf) and 10%TW(sh+ea)+90%CT(aa) composites. In order to compare the differences, the weight loss percents of the composites and the components at different temperatures are given in Table 2. The 10%TW(sh+ea)+90%PLLA(cf) composite showed higher weight loss than the composite components. Besides this, the weight losses of the 10%TW(sh+ea)+90%CT(aa) composite are lower than that of the pure polymer at constant temperatures and the thermal degradation temperatures of the composite are higher than that of the pure polymer. This result confirmed that the thermal stability of chitosan was improved slightly by preparing the composite with tea waste. This improvement is attributed to the interfacial interaction and chemical bonding between chitosan and the polyphenols present in TW [26].

The DSC curves of some selected composites are given in Figure 3. In the heating curve of the 10%TW(sh+ea)+90%PLLA(cf) composite, an exothermic peak can be observed at 129.51 °C. This peak is attributed to the crystallization of PLLA [29]. The cold crystallization temperature was found as 129.2 °C for PLLA in a study [30]. Furthermore, the glass transition temperature (T_g) of the 10%TW(sh+ea)+10%BP(aa)+40%PLLA(cf)+40%CT(aa) composite was obtained as 53.87 °C. On the other hand, the 10%TW(sh+ea)+90%CT(aa), 10%TW(sh+ea)+45%PLLA(cf)+45%CT(aa) and 10%TW(sh+ea)+10%TPP(cf)+40%PLLA(cf)+40%CT(aa) composites exhibited no significant peaks. The main reason of this result may be the limited analyzing temperature range. Some processes may be occurring out of this range. All of the three composites contain chitosan and the T_g of the chitosan was reported in a study [31] as a subject of controversy because, this value ranged from 23 to 203 °C according to the source, water content and deacetylation degree of the polymer etc. It was reported [31] that no evidence was found for T_g even at higher temperatures, suggesting that the degradation prevents T_g determination.

3.3. Morphological characterization

The XRD diffractograms of tea waste and the composites are presented in Figure 4. The tea waste has one intensive peak at the 2θ value around 21.5°, reflecting the crystalline state of cellulosic waste [32] that was almost similar for all the composites. The diffractograms of 10%TW(aa)+90%PLLA(cf) and 10%TW(sh+ea)+90%PLLA(cf) composites were apparently the same but the intensity of the peak around 22° was slightly higher for the latter. This may be due to the better integration of polymer into the waste. The 10%TW(sh+ea)+90%CT(aa) composite and TW showed similar diffractograms, but the peak intensity of the composite around 22°

Table 2. The weight loss percents of the composites and the components at different temperatures.

Material	100 °C	200 °C	300 °C	400 °C	500 °C	700 °C
TW	5	9	26	50	64	69
CT	12	29	50	66	70	75
PLLA	3	5	26	97	97	98
TW + PLLA	5	18	66	76	81	83
TW + CT	10	21	47	61	68	71

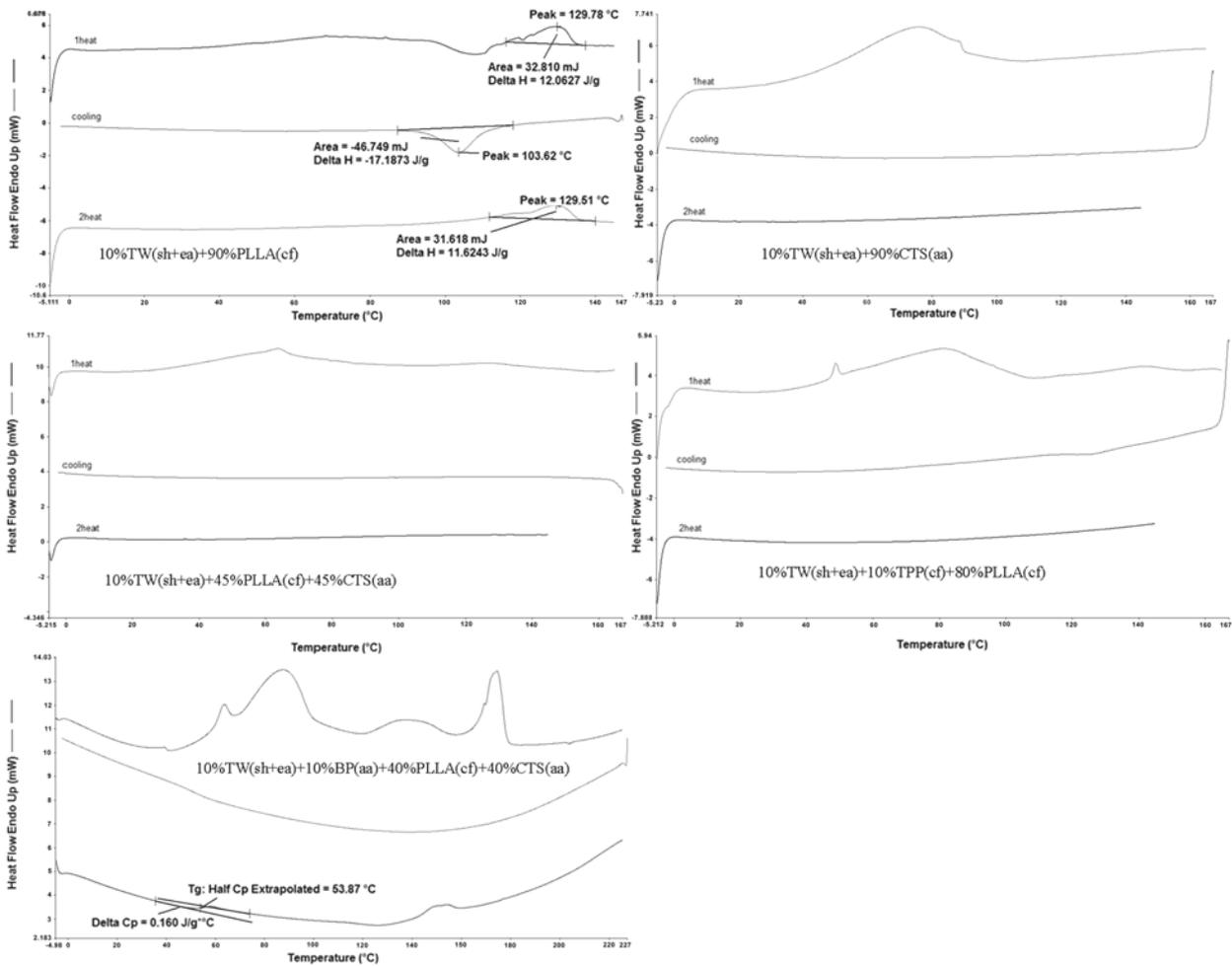


Figure 3. The DSC curves of some selected composites.

was lower, which may be indicative of the decrement of the cellulose in the structure. Different from the TW diffractogram, a weak, broad peak of chitosan structure was observed around 8° . Furthermore, the difference in the diffraction peaks of the 10% TW(sh+ea)+90% PLLA(cf) composite from the 10% TW(sh+ea)+10% TPP(cf)+80% PLLA(cf) composite could be attributed to difference in molecular arrangement of polymer chains in the presence of TPP molecules [33]. Although there are variations in the peak intensities of 10% TW(sh+ea)+45% PLLA(cf)+45% CT(aa) and 10% TW(sh+ea)+90% PLLA(cf) composites, they show the most intense diffraction peaks of PLLA at 2θ values of 16.6° and 18.96° [34]. Besides the main peaks of PLLA, the characteristic peaks of CT at 2θ values of 8.6° and 20.6° [35] were

observed for the CT-including composites. The diffraction peak of TW can also be observed at the same angle value in the diffractograms of 10% TW(sh+ea)+90% CT(aa), 10% TW(sh+ea)+10% TPP(cf)+80% PLLA(cf) and 10% TW(sh+ea)+10% TPP(cf)+40% PLLA(cf)+40% CT(aa) composites. New peaks were observed at 2θ values around 11° and 42° for the 10% TW(sh+ea)+10% BP(aa)+40% PLLA(cf)+40% CT(aa) composite, reflecting the presence of BP, which is in agreement with the literature [36].

3.4. Water uptake results

The water uptake property may affect the mechanical properties and the dimensional stability of the composites detrimentally. So, the water absorption characteristic plays an important role in evaluating

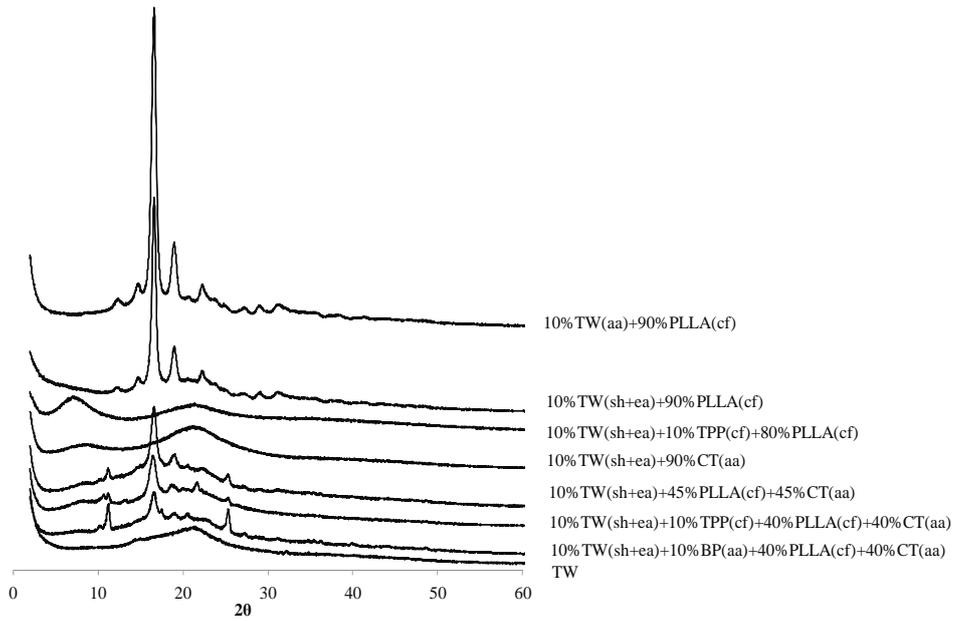


Figure 4. The XRD diffractograms of tea waste and the composites.

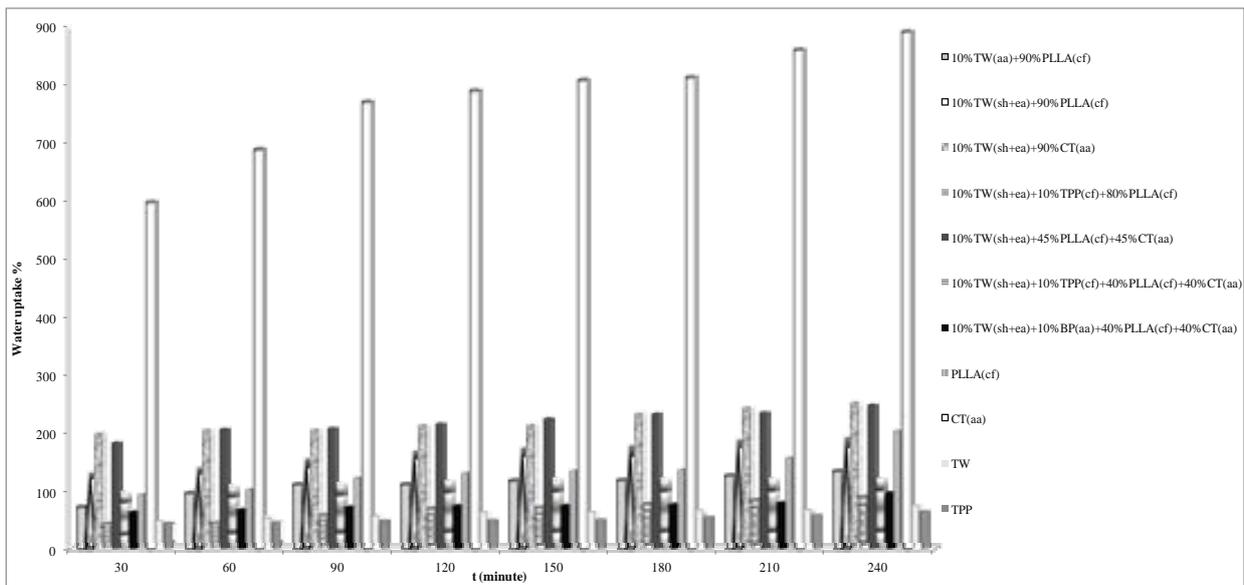


Figure 5. The water uptake percents of the composite components and the composites.

the quality of the composites. In this study, water uptake analyses of the composites and composite components were carried out at 23 °C and repeated at least two times. The calculated water uptake percent results are given in Figure 5. It can be seen that, most of the tested materials absorbed a large amount of water in the first 30 minutes, then

the absorption continued slowly and almost stopped at 210 minutes. The water uptake percents of the composites and the composite components generally decreased in the following order: CT > 10% TW(sh+ea)+90% CT(aa) > 10% TW(sh+ea)+45% PLLA(cf)+45% CT(aa) > 10% TW(sh+ea)+90% PLLA(cf) > PLLA > 10% TW(sh+ea)+

10% TPP(cf)+40% PLLA(cf)+40% CT(aa) > 10% TW(aa)+90% PLLA(cf) > 10% TW(sh+ea) +10% BP(aa)+40% PLLA(cf)+ 40% CT(aa) > 10% TW(sh+ea)+10% TPP(cf)+ 80% PLLA(cf) > TW > TPP. It was observed that the BP and TPP-added composites had lower values of water uptake percents. This result showed that TPP and BP enhanced the water resistance property of the polymers. Containing chitosan which has the highest water uptake percent did not affect the lower water uptake characteristics of those composites. Perhaps the strong interaction of the additives and the composite components affected the result. Additives may also have increased the adhesion between the interface of the reinforcement and the matrix. So the water molecules were restricted to diffuse or penetrate into the gaps or channels. Moreover, the presence of borax was reported as providing a better effect on either intercalated or exfoliated morphology of the composites [10]. On the other hand, among all composites, the composites without additives had higher water uptake percentages.

4. CONCLUSION

Solvent dispersion method was successfully applied for preparing waste fiber-included bio-sourced polymer composites. This method allowed the incorporation of the composite additives of borax pentahydrate and sodium tripolyphosphate effectively. Polymer composite processing method was evaluated based on the parameters like mixing temperature, time, rate and the solvent type. Better composite mixtures were obtained by using 800 rpm for TPP and BP-added composites and 1000 rpm for others, at 40 °C. The additives provided easy mixing. The solvents of sodium hydroxide and ethyl alcohol were chosen for TW processing according to the FTIR spectrum and XRD diffractogram results indicating better interaction of TW and the polymer. Additionally, lower water uptake results of acetic acid-treated TW-including composites showed that the TW surface was covered by the PLLA polymer. Furthermore, approximately four hours were spent preparing each composite. Notably the diffractograms of the composites displayed a shift of diffraction angles and variations in the peak intensities, indicating the changes in the structure and the interactions between composite components. Thermal gravimetric analysis indicated

that TW increased the thermal stability of chitosan slightly. Optimizing the processing parameters and characterization of the prepared composites provided an insight for potential evaluation of huge amounts of the waste from tea-producing factories.

CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest.

REFERENCES

1. Awadallah-F., A. and Naguib, H. F. 2017, *Polym. Bull.*, 74, 4659.
2. Rathod, Y., Bari, P., Hansora, D. P. and Mishra, S. 2017, *J. Appl. Polym. Sci.*, 134, 44750.
3. Donmez Cavdar, A., Kalaycioglu, H. and Mengeloglu, F. 2011, *Journal of Reinforced Plastics and Composites*, 30, 833.
4. Riyajan, S. and Sukhlaaied, W. 2012, *KGK Rubberpoint*, 65(3), 20.
5. Souza, V. G. L., Fernando, A. L., Pires, J. R. A., Rodrigues, P. F., Lopes, A. A. S. and Fernandes, F. M. B. 2017, *Industrial Crops & Products*, 107, 565.
6. Li, S., Xu, S., Liu, S., Yang, C. and Lu, Q. 2004, *Fuel Processing Technology*, 85, 1013.
7. Demiral, I. and Sensoz, S. 2008, *Bioresource Technology*, 99, 8002.
8. De Moura, M. R., Aouada, F. A., Avena-Bustillos, R. J., McHugh, T. H., Krochta, J. M. and Mattoso, L. H. C. 2009, *Journal of Food Engineering*, 92, 448.
9. Kurt, R. and Mengeloglu, F. 2011, *Turk J. Agric. For.*, 35, 155.
10. Benli, B. 2013, *J. Appl. Polym. Sci.*, 128, 4172.
11. Pirbazari, A. E., Pargami, N. R., Ashja, N. and Emami, M. S. 2015, *J. Environ. Anal. Toxicol.*, 5, 5.
12. Gnanasambandam, R. and Protor, A. 2000, *Food Chem.*, 68, 327.
13. Senthilkumar, S. R., Sivakumar, T., Arulmozhi, K. T. and Mythili, N. 2017, *Int. Res. J. Biological Sci.*, 6(3), 1.
14. Szymczycha-Madeja, A., Welna, M. and Zyrnicki, W. 2013, *J. Braz. Chem. Soc.*, 24(5), 777.

15. Tan, H. Y., Widjaja, E., Boey, F. and Loo, S. C. J. 2009, *J. Biomed. Mater Res. Part B: Appl. Biomater*, 91B, 433.
16. Lasprilla, A. J. R., Martinez, G. A. R., Lunelli, B. H., Figueroa, J. E. J., Jardini, A. L. and Filho, R. M. 2011, *Chemical Engineering Transactions*, 24, 985.
17. Stuart, B. 2004, *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley & Sons Ltd., England.
18. Austero, M. S., Donius, A. E., Wegst, U. G. K. and Schauer, C. L. 2012, *J. R. Soc. Interface*, 9, 2551.
19. Yuan, Q., Hein, S. and Misra, R. D. K. 2010, *Acta Biomater.*, 6, 2732.
20. Ferdous, D., Dalai A. K. and Adjaye J. 2004, *Appl. Catal. A: General*, 260, 137.
21. Frost, R. L., Kristof, J., Paroz, G. N. and Kloprogge, J. T. 1998, *Journal of Colloid and Interface Science*, 208, 216.
22. Kanturk, A., Sari, M. and Piskin, S. 2008, *Korean J. Chem. Eng.*, 25(6), 1331.
23. Weir, C. E. 1966, *Journal of Research of the National Bureau of Standards-A. Physics and Chemistry*, 70A(2), 153.
24. Khan, J. I., Kennedy, T. J. and Christian, D. R. Jr. 2011, *Basic Principles of Forensic Chemistry*, Springer Science & Business Media, New York.
25. Rokbi, M., Osmani, H., Imad, A. and Benseddiq, N. 2011, *Procedia Engineering*, 10, 2092.
26. Xia, G., Obi Reddy, K., Uma Maheswari, C., Jayaramudu, J., Zhang, J., Zhang, J. and Varada Rajulu, A. 2015, *International Journal of Polymer Analy. and Charact.*, 20, 377.
27. Gurten, I. I., Ozmak, M., Yagmur, E. and Aktas, Z. 2012, *Biomass and Bioenergy*, 37, 73.
28. El-Hefian, E. A., Nasef, M. M. and Yahaya, A. H. 2012, *E-Journal of Chemistry*, 9(2), 510.
29. Marras, S. I., Zuburtikudis, I. and Panayiotou, C. 2007, *European Polymer Journal*, 43, 2191.
30. Elangovan, D., Yuzay, I. E., Selke, S. E. M. and Auras, R. 2012, *Polym Int.*, 61, 30.
31. Altınışık, A., Seki, Y. and Yurdakoç, K. 2009, *Polym. Compos.*, 30,1035.
32. Pandey, J. K., Chu, W. S., Kim, C. S. and Lee, S. H. A. 2009, *Composites: Part B*, 40, 676.
33. Pati, F., Adhikari, B. and Dhara, S. 2012, *J. Mater. Sci.: Mater. Med.*, 23,1085.
34. Huang, J., Xiong, J., Liu, J., Zhu, W. and Wang, D. 2013, *Journal of Nanomaterials*, Article ID 515741, 10.
35. Rotta, J., Minatti, E. and Barreto, P. L. M. 2011, *Ciência e Tecnologia de Alimentos*, 31(2), 450.
36. Yunus Gumus, O., Unal, H. I., Erol, O. and Sari, B. 2011, *Polym. Compos.*, 32, 418.