

# Effect of Alkaline Treatment and Pre-impregnation on Mechanical and Water Absorption Properties of Pine Wood Flour Containing Poly (Lactic Acid) Based Green-Composites

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**Abstract** The effect of surface treatments and wood flour (WF) ratio on the mechanical, morphological and water absorption properties of poly (lactic acid) (PLA) based green-composites were studied. WF/PLA interfacial adhesion was promoted by means of alkaline treatment and pre-impregnation with dilute solution of matrix material. The composite materials were manufactured with twin screw extruder and injection molded samples were used for characterization. According to tensile test results, the inclusion of WF without any surface treatment caused high reduction at tensile strength in spite of incremental increase of modulus values. As the amount of alkaline treated WF increased, both modulus and tensile strength increased. Both alkaline treatment and pre-impregnation further increased the mechanical properties including tensile strength, tensile modulus and impact strength. Scanning electron microscopy (SEM) micrographs supported these findings. According to dynamic mechanical analysis (DMA) test results, the glass transition temperature of PLA increased with the addition of WF and the highest increment was obtained when pre-impregnated WF was used. Although alkaline treatment had no effect on water up-take properties of composites, pre-impregnation reduced the water uptake of the composite.

**Keywords** Poly (lactic acid) · Wood flour · Pre-impregnation · Adhesion · Water uptake

## Introduction

Green-composite, a type of composite both matrix and the reinforcing material composed of biodegradable material, gains considerable importance due to increment of environmental consciousness. Poly (lactic acid) (PLA), a well accepted thermoplastic biopolymer for green-composite applications, is derived from agricultural sources like corn starch. It finds a lot of usage such as plastic bags, food packaging and disposable cups but its high cost with respect to commodity plastics and relatively poor impact resistance restrict its wider application. Mixing PLA with low cost and abundant biopolymers like starch and natural fibers gains importance especially both to reduce the cost and to improve the mechanical properties [1–4].

Wood plastic composites (WPC) has considerable importance in a wide range of industries due to their low cost, low density, and certain specific properties. Despite these advantages, some problems exist for wider application of WPC, such as, low thermal stability of lignocellulosics, poor interfacial adhesion between polar lignocellulosics and non-polar matrix material and moisture uptake. The main factors affecting the final mechanical properties of WPC are the degree of filler dispersion and the effective stress transfer at interface between lignocellulosics and matrix material. The better filler dispersion and strong adhesion between matrix and lignocellulosics can be achieved via various physical and chemical methods [5–7]. Alkaline treatment, surface treatment with various types of compatibilizers and pre-impregnation with dilute matrix solution are commonly used methods [8–11].

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The previous studies investigated the effect of WF ratio, surface treatments and the use of compatibilizer on mechanical and morphological properties of PLA based green-composites [9–16]. None of them investigated the effect of pre-impregnation with dilute PLA solution on final properties of PLA based composites. In the current study, it is investigated that the effect of alkaline treatment, WF ratio and pre-impregnation with dilute solution of PLA on the mechanical, morphological and water uptake properties of PLA- WF green-composites produced by melt compounding. Tensile testing, impact and dynamic mechanical analysis (DMA), morphological and water uptake are reported.

## Experimental Procedure

### Materials

PLA under the trade name 6202D were purchased from Cargill-Dow. The density was  $1.24 \text{ g/cm}^3$  (ASTM D792) and the melt flow index was 15–30 g/10 min (2.16 kg, 210 °C) as provided by the supplier. WF from pine (smaller than 20-mesh size) was obtained from local sources. Reagent grade sodium hydroxide (NaOH) and chloroform, were supplied by Sigma Aldrich.

### Wood Flour Treatments

#### Alkaline Treatment

The purpose of alkaline treatment is to dissolve partially alkali soluble components from the WF structure like resins, hemicelluloses, lignin and pectin [11]. It is thought that surface cleaning and activation is achieved via NaOH (aq) treatment. The WF was treated with NaOH solution (9 % by wt) for 45 min under continuous mixing. Alkaline treated WF (aWF)

was then washed with water until all NaOH was eliminated. A few drops of acetic acid were added to neutralize the last rinsing solution. The WF was air-dried at 60 °C for 52 h. After the drying process, WF was stored in a desiccators until the extrusion process. SEM images of pristine WF and aWF are shown in Fig. 1. According to SEM images, the surface of WF becomes rougher after NaOH treatment due to the partial removal of alkaline soluble components.

#### Pre-impregnation with PLA Solution

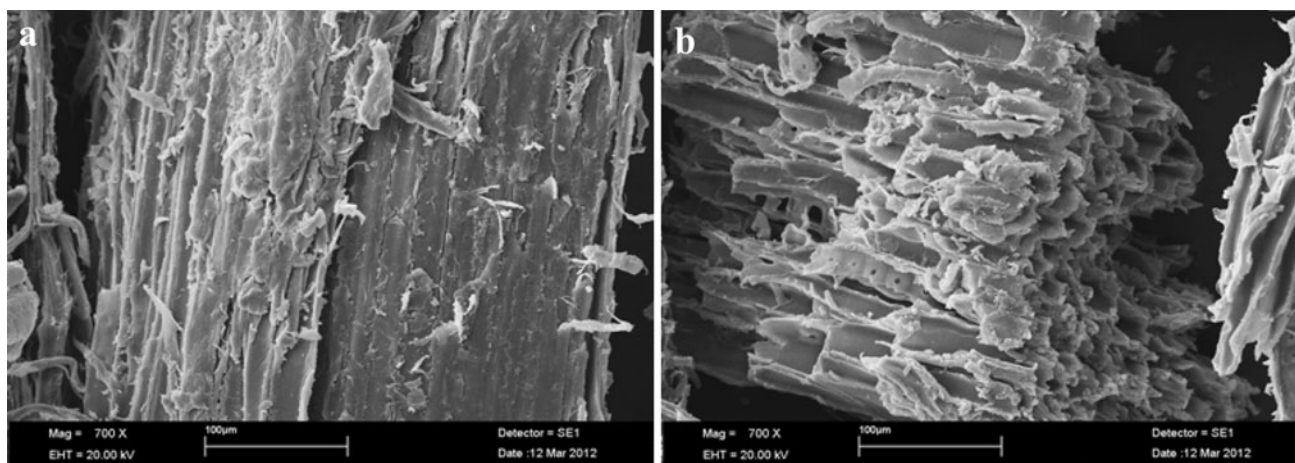
The WF was pre-impregnated with dilute PLA solution. The pre-determined amount of PLA (2.5 g) was dissolved in 200 ml chloroform at 50 °C. After the complete dissolution of PLA, the pre-determined amount of WF (25 g) was added and mixed vigorously for 30 min. After mixing, chloroform was evaporated at 50 °C for 48 h.

#### Preparation of WF-PLA Composites

The mixing of PLA and WF at various composition ratios was carried out with a counter rotating twin screw microextruder (15 ml microcompounder<sup>®</sup>, DSM Xplore, Netherlands) at 100 rpm at 190 °C for 3 min. The extrudate was pelletized and then oven-dried for 48 h at 60 °C and was stored in desiccator for injection molding. The specimens for mechanical tests were molded by a laboratory scale injection -molding machine (Microinjector, Daca Instruments) at a barrel temperature of 200 °C and mold temperature of 30 °C. The compositions, mechanical properties including tensile and impact are listed in Table 1.

#### FTIR Analysis

Attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR) was used to assign peaks involved at



**Fig. 1** SEM images of **a** pristine WF, **b** aWF at a magnification of  $\times 200$

**Table 1** The compositions and the mechanical properties including tensile and impact strength of composites

Sample code	Tensile strength (MPa)	Percentage strain at break (%)	Tensile modulus (GPa)	Impact strength (kJ/m <sup>2</sup> )
PLA	61.2 ± 2.1	3.1 ± 0.1	2.8 ± 0.2	10.0 ± 1.6
PLA-30 WF	33.3 ± 1.1	1.2 ± 0.1	3.7 ± 0.2	5.2 ± 0.3
PLA-30 aWF	56.9 ± 0.3	1.8 ± 0.1	4.1 ± 0.3	6.1 ± 0.9
PLA-40 aWF	59.8 ± 2.0	1.7 ± 0.1	4.4 ± 0.3	5.9 ± 0.4
PLA-50 aWF	66.2 ± 2.0	1.6 ± 0.1	5.4 ± 0.2	6.0 ± 0.2
PLA-40 pre aWF	63.2 ± 2.2	1.7 ± 0.1	4.8 ± 0.2	7.0 ± 0.5

Number shows the WF ratio (wt%)

aWF, alkaline treated WF; pre, pre-impregnated WF

the surface of the fillers after surface treatments with NaOH and PLA solution. IR spectra of aWF, PLA and pre-impregnated WF were obtained with FTIR (Bruker Optics IFS 66/S series FT-IR spectrometer) at an optical resolution of 4 cm<sup>-1</sup> with 32 scans.

#### Scanning Electron Microscopy (SEM)

The morphology of WF, aWF, and fracture surfaces of composites was examined with SEM (LEO 440 computer controlled digital, 20 kV). All specimens were sputter-coated with gold before examination.

#### Mechanical Properties

The specimens were stored in a desiccator for some days before testing. Tension test measurements were performed using Shimadzu AG-X tensile testing machine equipped with 50 kN load cell at room temperature according to ASTM D 638 standard. Tension tests were conducted on dog-bone shaped samples (7.4 × 2.1 × 80 mm<sup>3</sup>) at a crosshead speed of 5 mm/min. Tensile strength, percentage elongation at break and tensile modulus values were recorded. Izod impact strength was measured with Coesfeld-Material impact tester according to ASTM D256 at room temperature. All the results represent an average value of five samples with standard deviations.

#### Dynamic Mechanical Analysis

DMA experiments was carried out using Perkin Elmer DMA 8000 in dual cantilever bending mode at a frequency of 1 Hz to determine elastic modulus and tan δ of the composites. The test was carried out in the temperature sweep mode from 18 to 100 °C at a heating rate of

5 °C/min. The sample with dimensions of 50 × 7.5 × 2.5 mm<sup>3</sup> obtained from injection molded tensile bar.

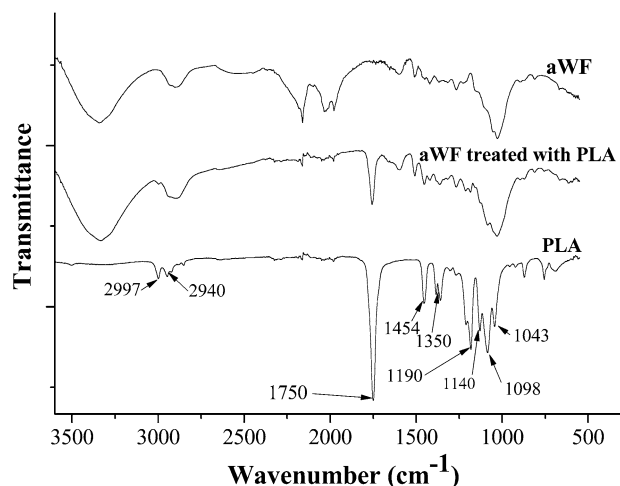
#### Water Absorption

The samples with dimensions (7.4 × 2.1 × 80 mm<sup>3</sup>) were used for the measurement of water absorption. The specimens were periodically taken out of the water, wiped with tissue paper to remove surface water, reweighed and immediately put back into water. The pre-dried (W<sub>0</sub>) was determined and used to calculate the degree of water absorption through the following formula: Water absorption (%) = (W<sub>f</sub> - W<sub>0</sub>)/W<sub>0</sub> × 100, where W<sub>f</sub> is the mass of the sample after immersion.

## Results and Discussion

#### FTIR Analysis

The FTIR spectra of PLA, aWF and pre-impregnated aWF with dilute solution of PLA are shown in Fig. 2. The spectrum PLA shows a pair of absorption bands at 2,940 and 2,997 cm<sup>-1</sup> due to symmetrical and asymmetrical -CH<sub>2</sub>-stretching vibrations. The absorption bands at 1,140, 1,098 and 1,043 cm<sup>-1</sup> arise from -C-O- stretching. A single absorption band at 1,750 cm<sup>-1</sup> arises from carbonyl stretching in the ester bond. The absorption band at 1,454 cm<sup>-1</sup> results from -CH<sub>3</sub> bending [3]. The presence of PLA absorbed on aWF is confirmed by the characteristic peak of PLA at 1,750 cm<sup>-1</sup> which is not present at FTIR spectrum of aWF and the other characteristic peaks of PLA are masked with those of aWF peaks.



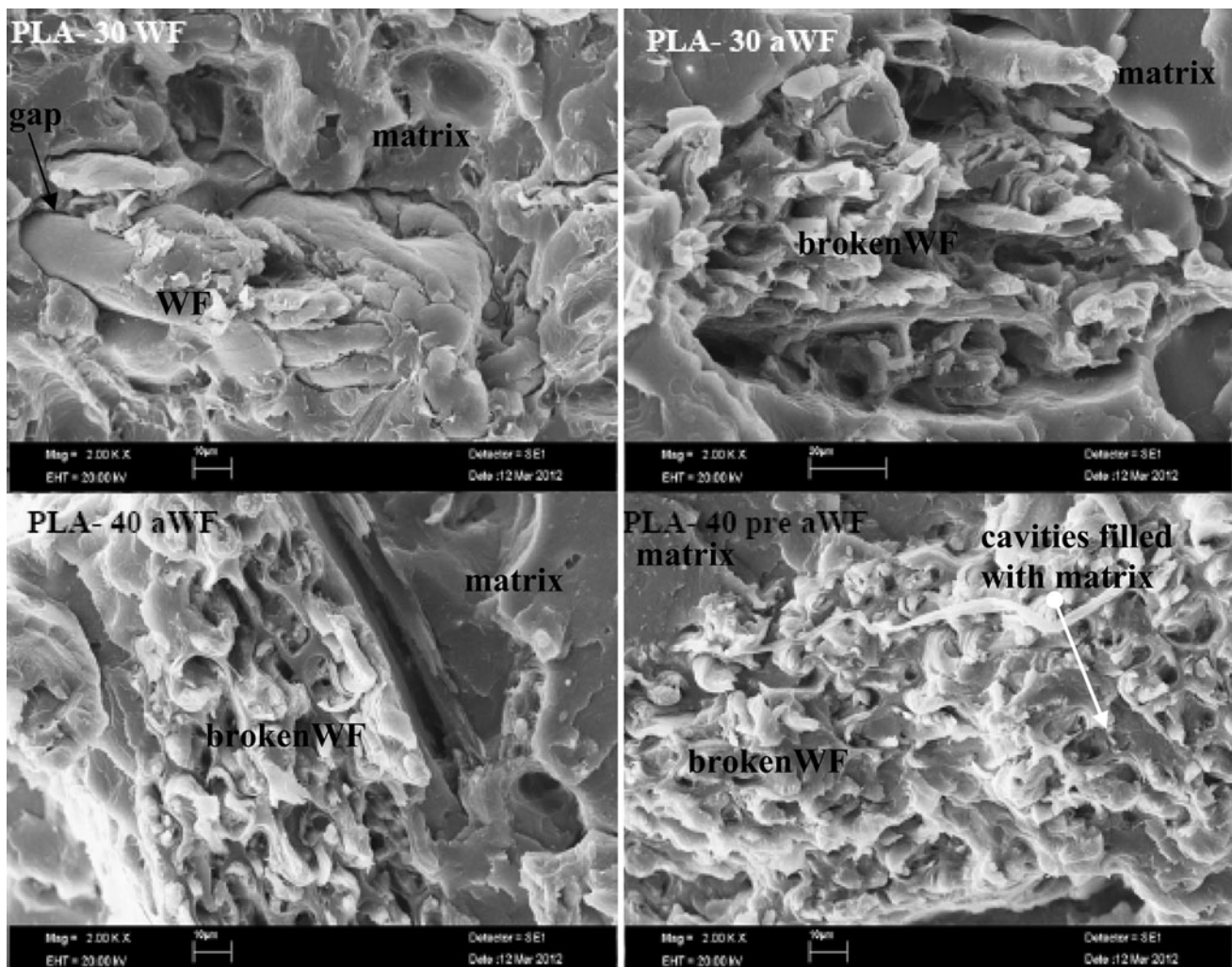
**Fig. 2** FTIR spectra of aWF, PLA and pre-impregnated aWF

## Morphology

The effect of alkaline treatment and pre-impregnation on the morphology of the composites is studied by SEM. Representative SEM micrographs of fracture surfaces of selected composites are shown in Fig. 3. From SEM image of PLA-30 WF, there is a gap observed around WF after fracture indicating poor adhesion. However, the alkaline treatment greatly improves the interfacial adhesion between aWF and PLA since the PLA still covers on aWF surface after fracture. It is also observed that most of the aWFs are broken during fracturing due to the good stress transfer between matrix and aWF [13]. These findings provide qualitative evidence for the existence of adhesive bonds between surfaces. The pre-impregnation with dilute PLA solution filling the cavities of aWF with matrix material further increases the adhesion between aWF and PLA by promoting mechanical interlocking. The mechanical tests results also support this conclusion.

## Mechanical Properties

The stress–strain curves of WF containing PLA green-composites are shown in Fig. 4 and the relevant mechanical data are reported in Table 1. PLA exhibits necking and undergoes stress whitening arising from crazing during tensile test. With the inclusion of WF, the type of stress–strain curve changes to brittle failure and the toughness of the composites reduces due to WF particles which act as stress concentrators, similar to previous studies [14–16]. The tensile modulus values of all composites containing WF are higher than the pure PLA. As the amount of aWF is increased, the tensile modulus values are further increased. The previous studies show that the filler with higher stiffness than the matrix can increase the tensile modulus of the composites and further increase as the amount increase as a rule of mixture [17–19]. The other factors affecting the tensile modulus of composites are the state of filler dispersion and polymer-particle interfacial area. Alkaline



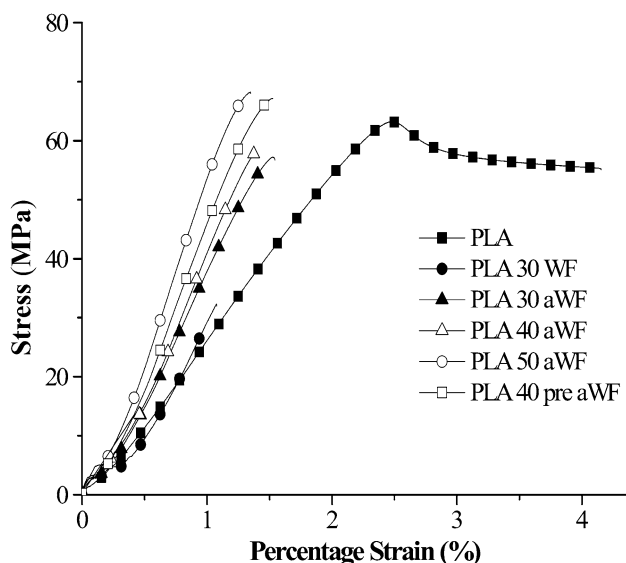
**Fig. 3** SEM micrographs of fracture surfaces of selected composites ( $\times 2,000$  magnification)



treatment further increases the tensile modulus values of the composites due to the higher polymer-particle interfacial area which restricts the inter and intra chain mobility. Pre-impregnation also further increases the tensile modulus values of the composites due to better WF dispersion arising from PLA coating.

The tensile strength and percentage elongation at break are sharply reduced with the addition of 30 wt% WF due to the weak interfacial adhesion [20]. Both the tensile strength and percentage strain at break values increase with alkaline treatment with respect to non-alkaline treated one but still lower than the pure PLA. The increase in tensile strength is an indication of good stress transfer between PLA matrix and WF particle. As the filler loading is increased, the percentage strain at break values are reduced owing to reduced the deformability of the matrix material arising from the rigid WF particles. The tensile strength of the composite increases as the amount of aWF increases and exceeds that of PLA when the amount of aWF reaches 50 wt%. The pre-impregnation further increases the tensile strength of the composites due to the penetration of PLA into the cavities of aWF enabling better mechanical interlocking.

Izod impact strengths of the composites are listed in Table 1. The impact strength of unnotched samples is governed by crack initiation and crack propagation [13]. There is a relationship observed between the area under the stress strain curve (toughness) and the impact strength of composites. The impact strength of PLA is highly reduced with the inclusion of WF regardless of its amount and surface treatment. The alkaline treatment increases the impact strength with respect to untreated one due to the good adhesion between PLA and WF. Previous studies show that

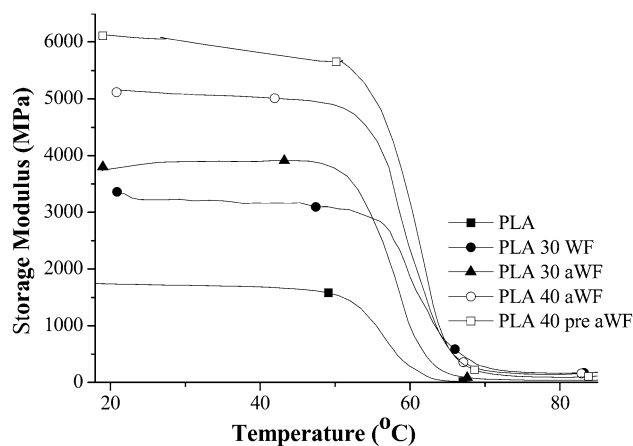


**Fig. 4** The stress–strain curves of WF containing PLA composites

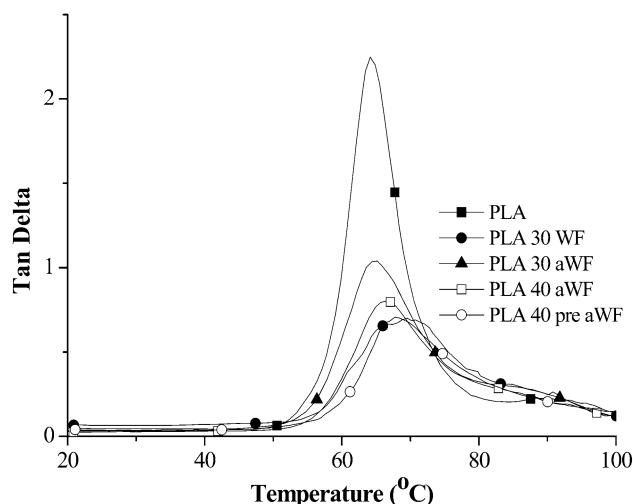
poor adhesion between WF and matrix results in the formation of micro voids that reduce efficient stress transfer from continuous polymer matrix to the dispersed WF and cause the material to absorb less energy [13, 17, 21]. There is no significant difference observed in impact strength of the composites with the increasing amount of aWF. The pre-impregnation of aWF with dilute PLA solution further increased the impact strength of the composite due to the improved WF dispersion and good adhesion between matrix and WF by mechanical interlocking.

#### Dynamic Mechanical Analysis

The dynamic storage modulus and  $\tan \delta$  values of PLA composites as a function of temperature are shown in Figs. 5 and 6, respectively. As seen in Fig. 5, a general declining trend is observed as the temperature increases and sharp reduction is observed when composites reach



**Fig. 5** The dynamic storage modulus of PLA composites as a function of temperature



**Fig. 6**  $\tan \delta$  values of PLA composites as a function of temperature

their glass transition temperature, corresponding to 60–64 °C depending on composition. The  $T_g$  of the composites shifts to a bit higher temperatures due to the restricted molecular motion arising from strong interaction between the matrix and WF [22]. The highest increase obtained in the case of pre-impregnated WF since the dilute PLA solution fills the cavities of WF and PLA gets absorbed on WF surface, increases the effective volume of the filler. The study of Huda et.al [10] showed that the glass transition temperature increases with increasing amount of WF. It is found that the addition of WF into PLA increases storage modulus. The alkaline treatment and the pre-impregnation have further improved the storage modulus of composites at same amount of WF loading level. The results are in accordance with the tensile modulus results. The peak  $\tan \delta$  decreases and the curve gets broadened with the addition of WF regardless of its amount and the surface treatment.  $\tan \delta$  broadens and the peak position shifts if there is an interaction between the matrix polymer and the filler/reinforcement [22–24]. The highest reduction at  $\tan \delta$  value is obtained when pre-impregnated aWF is used due to the restriction of the movement of PLA polymer chains adsorbed on WF [13].

#### Water Absorption

Water absorption in WPCs is partly related to hydrogen bonding of water molecules to the hydroxyl groups present on wood surface [21, 25, 26]. The second factor in water uptake is the pore volume of the WF. The water absorption behavior of the composites are shown in Fig. 7. It becomes clear that alkaline treatment has no effect on water absorption values of composites and they absorb approximately the same amount of water at the end of 40 days. The water absorption increases as the amount of WF

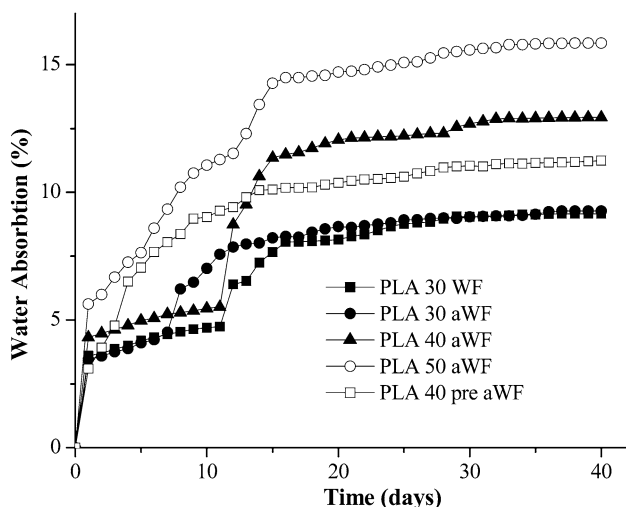


Fig. 7 The water absorption behavior of the composites

increases due to high hydrophilic character. The pre-impregnation made with dilute solution of PLA enables the penetration of PLA into the WF structure and reduces number of capillaries (pores) and water uptake (suction).

#### Conclusion

In the current study, the effect of alkaline treatment, WF ratio and pre-impregnation on mechanical including tensile, impact and DMA and water absorption properties of WF containing PLA based composites are investigated. It is concluded that alkaline treatment and pre-impregnation are effective methods to increase the mechanical properties including tensile modulus, tensile and impact strength of PLA-WF composites. Alkaline treatment one can speculate increases the interfacial interactions between WF and PLA by creating functional groups at the interface. Apparently porosity remains unchanged so the water uptake remains constant. Pretreatment of WF with PLA on the other hand reduces porosity by impregnating WF. DMA analysis reveals that the  $T_g$  of the composites shifts to a bit higher temperatures with the addition of WF and the highest increase is obtained in the case of pre-impregnated WF. This observation can be explained by the hinderance of polymer chain motions due to increased interaction with adhered polymer segments. Alkaline treatment has no effect on water uptake properties but pre-impregnation is effective by reducing the pore volume and the water sensitivity of the composite.

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