*Journal of Chemical Technology and Metallurgy, 54, 2, 2019, 339-347*

# KINETICS OF LONG-TERM WATER ABSORPTION BEHAVIOR OF DIFFERENT ORGANIC WASTE DUST/POLYMETHYLMETHACRYLATE COMPOSITES

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*Received 10 January 2018*
*Accepted 29 June 2018*

## ABSTRACT

*The composites analyzed are prepared by using the shell of hazelnut fruit, chestnut tree and hornbeam dust of a size of 425 μm - 600 μm fixed to PMMA matrix. The kinetics of long composite (13000 h) water absorption behavior of these composites is investigated at 23$^o$C. The results obtained show that PMMA has a high resistance to water absorption due to its hydrophobic character. The water absorption of the composites containing hazelnut tree, chestnut tree and hornbeam dust changes regularly with the dust amount increase because of the latter hydrophilic nature.*

*The water absorption kinetics refers to the Fick diffusion mechanism. The values of the diffusion coefficients (D) and diffusion parameters (k, n) are determined. The increase of the amount of the reinforcing materials added results in regular changes in the absorption (S) and permeability (P) coefficients of the composites.*

*Keywords: organic material dust*, ***polymethylmethacrylate, composite, water absorption, diffusion kinetics.***

## INTRODUCTION

Polymer composites are increasingly used day by day. In particular, reinforced polymer composites are preferred in many structural applications because of their low cost, chemical resistance, good mechanical properties, light weight, easy production and vibration absorption [1 - 3]. Some of the fillers and reinforcing materials used in the production of these composites are natural materials and natural wastes. Wheat and rye bark, various tree dusts [4 - 8] are among the natural materials used.

PMMA is a thermoplastic / thermoset having a wide range of applications due to its defined mechanical, thermal and other physical properties. However, its resistance to water absorption is high because of the limited water uptake [9]. Due to these properties, products made from PMMA have a long aging life in moist environments and even in direct contact with water.

There are many studies in the literature on the water absorption of polymer composites and their aging with moisture. The behavior of composites containing waste materials as organic fillers in respect to water absorption is studied [10-13]. Despite the widespread use of PMMA / organic and inorganic composites in moist environments for extended periods of time, studies on the water absorption behavior of these composites are limited in the literature. For example, Li et al. [14] investigate the water absorption and mechanical properties of PMMA-SBR / brass composites.

Chestnut sawdust and beech saw are seen to be used in part in environmental and furniture research [15 - 18]. There are very few studies on the use of hazelnut shells in composites and their properties. The effect of plasticizer added to Nut Shell / PLA composites is investigated in a study by Balart et al. [19]. It is reported that the plasticizer reduces the fracture sensitivity of the composite and improves its thermal stability.

The present study reports the production of PMMA based composites containing 25 %, 50%, 75 % of two different tree and hazelnut dusts grown in the Black Sea Region. The kinetics of their long-term water absorption behavior is investigated. The absorption and diffusion coefficients (k, n and D, respectively) of all three reinforcement materials are determined according to the Fick's law. In addition, the absorption and permeability coefficients are also calculated.

## EXPERIMENTAL

The trees and the hazelnut used for the dust preparation were selected from the Eastern Black Sea region. The tree dusts were obtained from wood processing factories, while the hazelnut shells gathered were grinded. All cellulosic additives used obtained a size referring to 425 µm - 600 µm using laboratory sieves.

The matrix materials and the peroxide-based chemicals used to construct polymethylmethacrylate composites were obtained from the Turkish representative of Otto Bock Company (Germany).

### Materials and Preparation Technique

All dusts used were dried for 4 h prior to the preparation of the samples to minimize the negative effects attributed to the amount of moisture. PTFE material was used to cast molds of composite test samples from nut shells and other wastes. 2 % peroxide curing agent was added to cure the matrix material. Different dusts (hazelnut dust, chestnut sawdust, hornbeam sawdust) of an amount referring to 25 %, 50 % and 75 % were added to the mixture and stirred with a magnetic stirrer. The product obtained was kept in the 80°C oven for 24 h for final cure.

### Characterization of the materials

The density of hazelnut shell, hornbeam and chestnut tree dust was measured by the pycnometer method. Acetone was used as the density measurement liquid. The values obtained are given in Table 1.

### Assessment of the Composite Volume Ratio

Due to the porosity of the natural fibers and the necessity of incorporation of voids in the composite, the following expression was adopted to express the volume fraction ($V_f$) of the composites reinforced with natural fibers [20]:

$$V_f = \left(V_c - \left(M_c - M_f\right)/\rho_r\right)/V_c \qquad (1)$$

Here, $M_f$ was the fiber mass, $M_c$ was the composite mass, $V_c$ was the composite bulk, while $\rho_r$ was the the density of the cured polymer. This relation provides the estimation of $V_c$ whose values are given in Table 2.

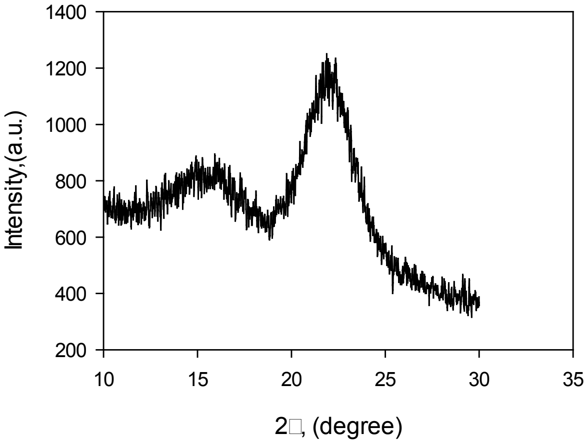

Fig. 1. An X-ray pattern of hazelnut shell dust.

Table 1. Density analysis of the reinforcing materials used.

| Reinforcing materials | Density (gr/cm$^3$) |
|---|---|
| HSD | 1,358 |
| HDB | 0,801 |
| CTD | 0,402 |

### X-Ray Diffraction Analysis

The X-ray diffraction patterns of the typical cellulose crystal cell in the hazelnut shell dust are given in Fig. 2. The two tetra values of the main patterns of the cellulose fiber are 16 and 21.8, respectively. They correspond to (101) and (002) planes. In some studies, the crystal index of various natural fibers, wood and agricultural wastes are determined using the following expression [21]:

$$CrI = (I_{002}-I_{am})x100 /I_{002} \qquad (2)$$

Here $I_{002}$ is the maximum point of the crystal peak, while $I_{am}$ is the lowest point of the amorphous material between the peaks. According to this method, the crystallinity indexes of CTD, HBD, HSD refer to 33 %, 30 %, 28 %, respectively (Fig. 1).

Table 2. Composites mixing ratios and densities.

| Composites<br>(symbol+weight %) | Mixing ratios<br>(volume) | ρ<br>(g cm$^{-3}$) |
|---|---|---|
| PMMA %0 | 100.00/00.00 | 0,920 |
| HSD %12 | 25/75 | 1,029 |
| HSD %36 | 50/50 | 1,139 |
| HSD %60 | 75/25 | 1,248 |
| HDB %22 | 25/75 | 0,890 |
| HDB %47 | 50/50 | 0,860 |
| HDB %72 | 75/25 | 0,830 |
| CTD %13 | 25/75 | 0,790 |
| CTD %30 | 50/50 | 0,661 |
| CTD %57 | 75/25 | 0,531 |

### Water Absorption Tests and Measurements

At least five test specimens of 4 mm thickness (b), 13 mm width (w) and 90 mm length (l) were used for each group in the water absorption experiments. The control samples were dried in an 80 °C oven for 48 h. An analytical scale of XB 220A SCS code and Precisa brand was used. The initial weights ($W_0$) prior to the water absorption test were determined with a precision of 0.1 mg. After the measurement the control samples were placed in glass containers filled with distilled water. The vessels were kept at room temperature and shade environment, while the water baths were renewed at intervals of three months. The samples were taken out at specified time intervals, gently wiped off with a dry napkin, weighed and left again in the water bath. This process was maintained for 13000 h. Due to the completion of the weighing process in about 15 seconds, faults that could occur by evaporation of the absorbed water during the weighing of the control samples were ignored.

The results obtained from the water intake tests were evaluated using the Fick diffusion method.

## RESULTS AND DISCUSSION

### Water Absorption Behavior

The characteristic water uptake behaviors of composites formed with pure PMMA and PMMA / chestnut wood shavings are given in Fig. 2. The change of the water uptake amount with the square root of the absorption time is shown in the graph. It is observed that the pure Pmma absorbs very low amounts of water and it takes about 8.000 h to decrease the water absorption rate. It is observed that the rate of water uptake increases with the increase of the supplement ratio in the composites, whereas the saturation time decreases. For example, the latter decreases to 5.625 h in composites containing a filler material of 75 %.

It is found that the water absorption rate of the composite follows an approximately linear character up to the saturation point. Then it decreases remarkably but the linear behavior is preserved. It is seen that the amount of water absorbed to the saturation point in case of a composite containing 75 % CTD is 15 %, while the

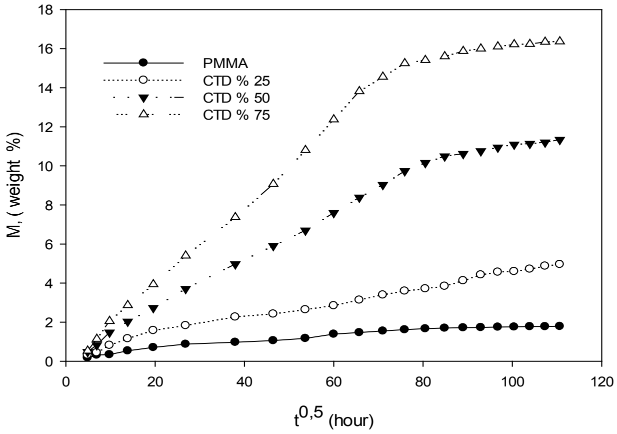

Fig. 2. Water absorption (M-t) graphic of PMMA and PMMA/chestnut dust.

time required amounts to5,625 h. The amount of water absorbed during the following 7.375 h is 1,41 %. For the composite containing 25 % CTD, the amount of water absorbed to the saturation point is 3.70 %, while the saturation time is 8.640 hours. The amount of water absorbed within the following 4.360 h is only 1.25 %. These results show that the amount of water uptake increases proportionally with the added additives amount, and that depending on the amount of the reinforcement, the water absorption after the saturation continues although the water absorption is low.

In their study lasting for more than a decade, Kochetkov et al. [22] report that the tendency of the epoxy/glass sphere composites drawing water at room temperature continues. A similar behavior is observed in other studies referring to composites of a different thickness [23,24]. The continuing water absorption behavior after the point of saturation can be explained with the occurrence of water damage. Some researchers assume that in equilibrium there is a balance between the osmotic pressure of the water and the elastic forces of the polymer and that subsequent water absorption is related to the weakening of the bonds in the polymeric structure [25].

A similar behavior is observed in case of hornbeam and hazelnut shell dust composites as well but the amount of water absorbed after 13,000 h is different. The maximum water uptake rate of HSD composites (25 %, 50 %, 75 %) is 10,13 %, 16,45 % and 24,91 %, respectively, while the water uptake rates of composites formed with HBD refer to 8,11 % , 14.67 %, and 22.81 %, respectively. The water uptake rates of CTD-reinforced composites, having the least amount of water absorptions, are lower than those of the other two composites. They are realized as 4,95 %, 11,34 %, 16,41 %, respectively. As observed in the graph in Fig. 5, the saturation time of HSD composites is shorter than that of CTD. In the 75 % hazelnut dust reinforced composite, the saturation time is 4.225 h.

Fig. 3 shows the images of the samples taken after the water absorption test. The sequence of the samples refers to HSD, CTD, HBD starting from the top to the bottom. The examination of the surfaces shows that the highest degradation is in case of HBD composite, followed by that of HSD. The lowest degradation is observed in CTD composite.

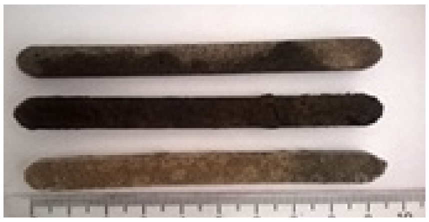

Fig. 3. Samples appearance after the water absorption test.

It is stated that in the literature that a sigmoidal curve may occur in case of the additive's presence increase. This is attributed to the water damage occurring after the saturation point and the increase of the absorption rate [26]. The sigmoidal behavior is not strictly realized in this study because the tests are carried out at room temperature. It can be confirmed from the graph that PMAA has a hydrophobic character in CTD composite and the water damage does not affect the rate too much even though the additive amount is 75 %. However, when the graph is examined again, the sigmoidal behavior is partially outlined in composites formed by adding 75 % HSD (Fig. 4). However, the rapid slope increase is not considered in the literature.

### *Effect of the Added Dust Type on the Water Absorption Behavior*

The water absorption behavior of the composites prepared with three different types of reinforcements differs. One of the main factors affecting the water uptake behavior is the chemical structure of the used reinforcements. Although all three reinforcing materials are of a cellulosic origin, it is suggested that the amount and the structure of the cellulose significantly influences the water uptake behavior. It is estimated that the absorption behavior is affected by the difficulty of the water progress in cellulosic materials where the crystallization in the internal structure is higher. Moreover, the water

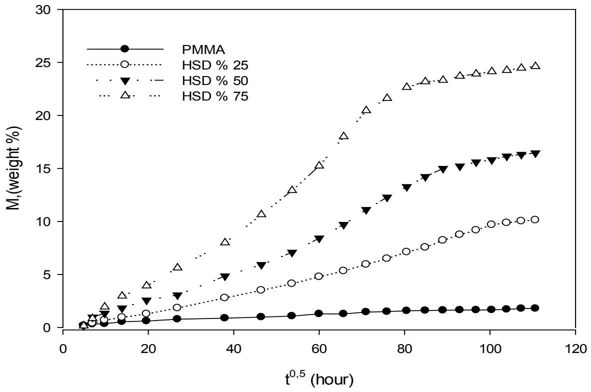

Fig. 4. Water absorption (M-t) graphic of PMMA and PMMA /hazelnut shell dust.

Table 3. Composites maximum water absorption.

| Composites<br>(Symbol +weight %) | $M_{13000}$<br>(weight %) |
|---|---|
| PMMA %0 | 1,79 |
| HSD %12 | 10,13 |
| HSD %36 | 16,45 |
| HSD %60 | 24,91 |
| HDB %22 | 8,11 |
| HDB %47 | 14,67 |
| HDB %72 | 22,81 |
| CTD %13 | 4,95 |
| CTD %30 | 11,34 |
| CTD %57 | 16,41 |

imperfections are not easily formed in the crystalline regions due to the more regular structure and the high intermolecular attraction affecting the water uptake behavior. This provides less water absorption by the composites. As shown, the crystallinity indexes of CTD, HBD, HSD refer to 33 %, 30 %, 26 %, respectively (Fig.1). The relationship between the crystal structure and the water uptake can be clearly seen in view of these values.

**Diffusion**

The water absorption behavior of polymers is classified according to the relative movements of water and polymer chain segments. Some absorption categories are given below [27]. According to this;

(i) In case of Fick's diffusion the water mobility is slower than that of the polymer chain segments, and there is no interaction. The equilibrium state within the polymer is rapidly attained.

(ii) Non-Fick's diffusion is observed when the water mobility and the loosening of the polymer chain segments are comparable.

(iii) In a super state, the water mobility is faster than all other relaxations. There may be strong interactions between the diffuser and the polymer.

Eq. 3 provides to determine the category of water absorption in a polymer system:

$$\frac{M_{\mathrm{t}}}{M_{\infty}} = k t^{n} , \tag{3}$$

Here $M_t$ is the amount of water absorbed at time t ($M_t = W_t – W_0$), $M_\infty = W_{13000} – W_0$, while the coefficients k and n are diffusion parameters. The coefficient k depends on the structural characteristics of the polymer and shows the interaction between the polymer and the water.

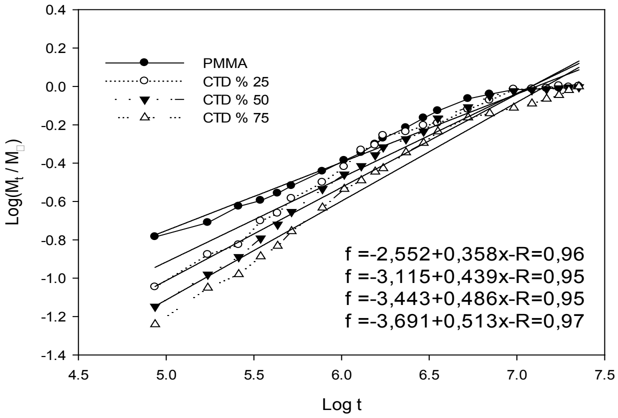

Fig. 5. Diffusion state curves of PMMA/chestnut sawdust composites.

Eq. 1 can be re-organized to calculate the diffusion state parameters (k and n),

$$\log\left(\frac{M_{\mathrm{t}}}{M_{\infty}}\right) = \log k + n \log t . \tag{4}$$

As shown in Fig. 6, log k and n parameters are calculated from the slope of the mean curve and log (Mt / M∞) axis, respectively, and are given in Table 4. Upon addition of hazelnut shell, the composite n value becomes close to 0.5 while the value of k decreases. Because the mass values of the composites are close to 0.5, it is concluded that the water absorption follows the classic Fick diffusion model. For this reason, the data obtained in the study is evaluated according to the classic Fick diffusion.

The second Fick diffusion law for one dimensional diffusion is presented in the form:

$$\frac{\partial C}{\partial t} = D_{\mathrm{x}} \frac{\partial^2 C}{\partial x^2} \tag{5}$$

The boundary conditions are:

$t \leq 0$: $0 \leq x \leq b$, $C = C_{\mathrm{i}}$, (5a)
$t > 0$: $x = 0, x = b$, $C = C_{\infty}$, (5b)

Here C is the local concentration of the diffusing agent (= $M_t$), t is the diffusion time, $D_x$ is the diffusion coefficient in the x-direction perpendicular to the plate surface, *b* is the thickness of the first polymer plate, while i and ∞ sub-indices denote the initial and saturation states, respectively. Although $D_x$ in Eq. 5 is one-dimensional (*x*-direction), the control samples used are three-dimensional and limited in measures. For this reason, it is necessary to incorporate the diffusion from other edges of the control samples into the equation through Eq. 4:

$$D = D_{\mathrm{x}} \left( 1 + \frac{b}{l} + \frac{b}{w} \right)^{-2} , \tag{6}$$

Here *D* is the isotropic diffusion coefficient [28]. For the control samples used in this study, the correction on the right side of Eq. 6 is calculated to be 0.558. The subsequent diffusion coefficients cited in this work are corrected in accordance with Eq.6.

The diffusion coefficient (*D*) is an important kinetic parameter for Fick's diffusion (Case I). As shown in Eq.5, the Fick's diffusion is controlled by the diffusion coefficient *D*. When the polymer sheet concentration is kept constant on the surface, i.e. when the sheet is immersed in a sufficiently large diffusion (water) chamber, the amount of the diffusing water absorbed by the sheet at moment *t* can be expressed as:

$$\frac{M_{\mathrm{t}}}{M_{\infty}} = 1 - \frac{8}{\eth^2} \sum_{\mathrm{i}=0}^{\infty} \frac{1}{(2\mathrm{i}+1)} \exp\left( - \frac{D(2\mathrm{i}+1)^2 \eth^2 t}{b^2} \right) \tag{7}$$

The Fick's law is widely used in the form of Eq.7. The latter shows that the weight of the water absorbed by the plate increases linearly with the square root ($\sqrt{t}$) of the duration of the dip. Then it reaches saturation by slowing down [28]. The first-stage of diffusion $D_1$ (0.00 $<M_t / M_\infty$ 0.55) is described by Eq. 8:

$$\frac{M_{\mathrm{t}}}{M_{\infty}} = \frac{4}{h} \sqrt{\frac{D_1 t}{\eth}} . \tag{8}$$

The *D* values of the PMMA / hazelnut shell composite calculated on the ground of the graphs in Fig. 6 and Eq. 8 are presented in Table 4. It is observed that the value of *D* increases with the increase of the amount of hazelnut shells added. According to Crank [29], the diffusing characteristics in a diffusing polymer system may change over time. The author mentions the effects of two possible mechanisms: (i) the polymer structure is slowly changed / relaxed with diffusion; (ii) internal stresses on a portion of the polymer sheet occur while the polymer swells and these stresses affect the neighboring regions. It is concluded that both the polymer relaxation and the internal stresses have the same effect on the diffusion coefficient and mechanical properties of the polymer sheets.

The diffusion coefficients of the polymer composites containing different amounts of wood dust are in agreement with the reported diffusion coefficients ranging from 1.67× $10^{-13}$ to 58 × $10^{-13}$. The latter values are obtained in different climate environments [30]. It is also reported that the water absorption at the saturation point of the polymer composites and the diffusion coefficients increase with the increase of the amount of the filler incorporated.

**Permeability**

The water absorptive regions do not have a homogeneous distribution in a composite product due to

Table 4. Diffusion, k and n parameters of the composites studied.

| Composites (Symbol+weight%) | k ($\mathrm{g\ g^{-1}\ s^{-n}\ 10^{-4}}$) | n | D ($\mathrm{m^2\ s^{-1}\ 10^{-13}}$) |
|---|---|---|---|
| PMMA %0 | 28,05 | 0,358 | 1,85 |
| HSD %12 | 3,74 | 0,459 | 2,96 |
| HSD %36 | 2,46 | 0,504 | 4,27 |
| HSD %60 | 1,08 | 0,548 | 5,08 |
| HBD %22 | 5,19 | 0,457 | 2,41 |
| HBD %47 | 2,25 | 0,506 | 3,12 |
| HBD %72 | 1,27 | 0,537 | 4,59 |
| CTD %13 | 7,67 | 0,439 | 2,05 |
| CTD %30 | 3,60 | 0,486 | 2,46 |
| CTD %57 | 1,27 | 0,537 | 3,22 |

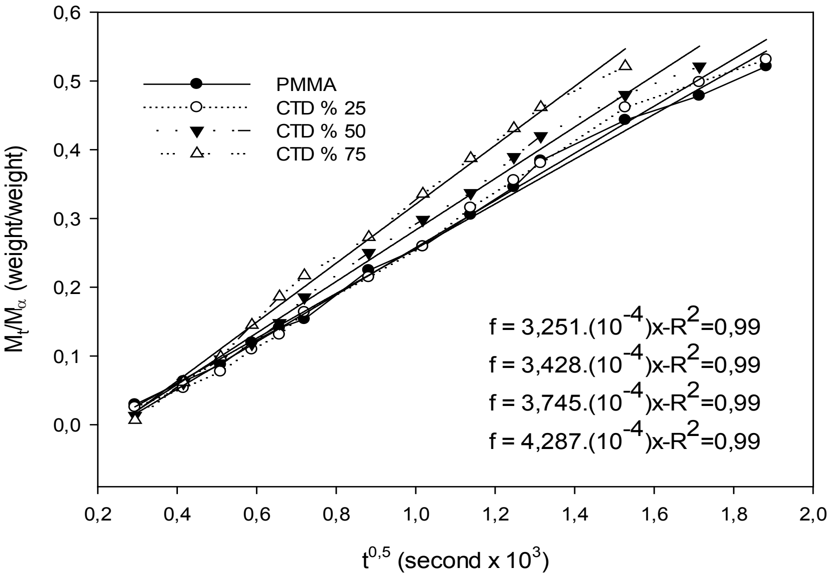

Fig. 6. First-stage of the chestnut tree sawdust composites: Mt / M∞ vs. $t^{0,5}$ graphics.

reasons caused by the polymer and the fillers. Thus, during water absorption, nonuniform swelling deformation and stress zones may occur depending on the nature and the additive amount. However, as polymer composites containing hydrophilic fillers absorb more water, the water caused stresses may also increase. As a result of this, considerable water damage such as cracks and discrete surfaces can occur throughout the entire composite structure. Consequently, the presence of hydrophilic fillers and water-borne damage in the polymer structure affects the water absorption kinetics. The water permeability of a composite is given by:

$$P = D.S \tag{9}$$

where *P* is the permeability coefficient, D is the Fick's diffusion coefficient, while S is the sorption coefficient [31]. The permeability coefficient (P) is equal to the steady rate of permeation of water molecules through a layer of a limited thickness. The diffusion coefficient (D) expresses how fast the water molecule moves through a polymer mass. The sorption coefficient (S) amounts to the mass of the water absorbed per polymer mass at the saturation point. As shown in Table 5, this value increases significantly with the increase of the amount of cellulosic reinforcing materials added, while P value of PMMA is low. This can be explained by the fact that PMMA/cellulosic impregnated composite interfaces play the role of water channels which regularly form along the entire composite.

Table 5. Diffusion (D) coefficient, sorption coefficient (S) and permeability (P) values of the composites studied.

| Composites (Symbol+weight%) | D ($m^2\ s^{-1}\ 10^{-13}$) | S ($g\ g^{-1} 10^{-2}$ ) | P ($m^2\ s^{-1}\ 10^{-15}$) |
|---|---|---|---|
| PMMA %0 | 1,85 | 1,02 | 1,88 |
| HSD %12 | 2,96 | 1,63 | 4,82 |
| HSD %36 | 4,27 | 2,08 | 8,88 |
| HSD %60 | 5,08 | 2,49 | 12,64 |
| HBD %22 | 2,41 | 1,39 | 3,34 |
| HBD %47 | 3,12 | 1,92 | 5,99 |
| HBD %72 | 4,59 | 2,33 | 10,69 |
| CTD %13 | 2,05 | 1,14 | 2,33 |
| CTD %30 | 2,46 | 1,78 | 4,37 |
| CTD %57 | 3,22 | 2,33 | 7,26 |

## SYMBOLS

| | |
|---|---|
| HSD | hazelnut shell dust |
| HBD | hornbeam dust |
| CTD | chestnut tree dust |
| PMMA | Polymethylmethacrylate |
| SBR | Styrene-butadiene rubber |
| D | Diffusion coefficient |
| k, n | Diffusion parameters |
| S | Absorption coefficient |
| PLA | Polylactic acid |
| P | Permeability coefficient |
| PTFE | Polytetrafluoroethylene |
| WPC | Wood-plastic-composite |
| MDF | medium density fiber board |
| CRI | Crystalline index |
| M | Mass |
| W | Weight |

## CONCLUSIONS

The present communication studies the maximum humid gathering behavior of HSD, HBD, and CTD reinforcing materials with maximum addition amount of 75 %. It is found that CTD is the reinforcing material which holds the least moisture. The composites formed with these three reinforcements show that HSD is more sensitive to gathering humidity than the other composites. This behavior can be disadvantageous (in terms of life) in terms of the use of composites containing HSD in humid environments. From the environmental point of view, it is known that wastes absorbing more water will shorten the deterioration period of the composite. The composite formed from thermoplastic waste and HSD may be an alternative of this thermoplastic waste re-use. In these composites, HSD is thought to have a positive effect on environmental stress decrease through acceleration of thermoplastics aging.

It is hoped that the composites produced will be used instead of wood in some structural applications regaining wastes to the economy. Thus they will provide significant environmental benefits. The support of this composite, which is an environmental friendly product, means support of this subject sensitivity.

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