

Priscila Ferreira de Oliveira and Maria de Fatima Vieira Marques

CHEMICAL TREATMENT OF NATURAL MALVA FIBERS AND PREPARATION OF GREEN COMPOSITES WITH POLY(3-HYDROXYBUTYRATE)

*Instituto de Macromoleculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro,
RJ, Brazil Cidade Universitaria – Centro de Tecnologia – Bloco J. POBox 68525. CEP: 21945-970
Rio de Janeiro, Brazil; fmarques@ima.ufrj.br*

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Abstract. Malva fiber was submitted to alkali treatments with NaOH aqueous solutions at different concentrations, times and temperatures. Fiber samples were analyzed before and after treatments to study their effects on crystallinity, thermal stability and morphology. The results showed that the crystallinity index and thermal resistance significantly increased when the alkaline treatment was conducted with 7 % NaOH solution. Higher concentrations of NaOH, such as 10, 15 and 20 %, did not considerably increase the fiber crystallinity index. By X-ray diffraction, it was observed that defibrillation occurred in mercerized fibers, which is expected to be advantageous for use as fiber reinforcement in polymer matrices. The same fiber samples were mixed with a poly(3-hydroxybutyrate) matrix in a twin-screw mini-extruder at 453 K. The composites were analyzed by TGA and DMA to evaluate the influence of fiber addition in mechanical and thermal properties of the polymer.

Keywords: malva fiber, alkali treatment, biodegradable polymer.

1. Introduction

The natural fibers of plant origin have been widely investigated for their application as reinforcement in polymeric materials. This interest is due to their properties mentioned in the literature, such as abundant availability, non abrasiveness, low price compared with synthetic fibers, low density, renewability, biodegradability and good mechanical properties [1-4]. However, a disadvantage of the use of natural fibers is the fact that they are polar, hydrophilic and contain amorphous substances in their composition, such as lignin, hemicellulose, pectin and waxes. This causes them to be less compatible with nonpolar polymer matrices [3, 5]. Hence, it is necessary to

apply treatments to plant fibers that modify their surface and chemical composition to improve their adhesion to the polymer.

There are various treatments applied to natural fibers, including acetylation, silanization, mercerization and others [6, 7], to increase their compatibility with polymer matrices. However, the type of compatibilization can be different according to the method employed: it can be achieved by anchoring due to the physical changes caused in the fiber surface or by chemical interactions between the polymer and the groups present in cellulosic fibers after their functionalization. Mercerization, for example, promotes adhesion of the fiber to the polymer matrix by mechanical anchoring, which results in increased physical contact between the two materials [2].

Mercerization, the name for alkaline treatment with sodium hydroxide, is one of the most used methods of natural fiber modification [8], and is capable of removing extractable amorphous cellulosic fibers [9]. Thus, the topography of the fiber surface is modified, causing defibrillation, which is the breaking of hydrogen bonds between the cellulose molecules, forming shorter fibers with increased effective surface area [10].

The literature suggests that the properties of some plant species treated with NaOH solution with the concentration greater than 5 % are dramatically affected [7]. So, many researchers have reported the results of mercerization employing 5 % NaOH solution [2, 7, 9, 10]. According to some authors [11-16], concentrations greater than that can lead to the alkali attack on the cellulose chain.

E. Pires and coworkers [15] studied jute fibers treated with a solution of 5 % sodium hydroxide at room temperature for 48 h. This treatment promoted partial removal of hemicellulose and lignin, which was evidenced by FTIR analysis. The treated jute fiber composites with the epoxy resin showed higher

mechanical properties and storage modulus than those of the neat epoxy resin and untreated fiber composites.

S. Mishra and coworkers [13] studied composites of polyester reinforced with 5 % NaOH treated fibers (pineapple leaf fiber/sisal fiber) and reported higher tensile strength than the material treated with 10 % NaOH [14]. Other authors [12] also concluded that the use of 5 % NaOH solution for 4 h was the most appropriate condition for treatment of coconut shell fibers used as the reinforcement in the polypropylene matrix. 5 % NaOH solution was also utilized for treatment of banana leaf fibers, but the treated fibers showed decreased mechanical properties. Thus, according to several authors, variations in fibers properties are related to the removal of lignin and hemicellulose from the surface of the fibers, possibly causing weakening in the fibers external walls.

However, A. Hay and coworkers [11] observed an improvement in the tensile strength of mercerized palm fiber after applying treatment with 6 % NaOH at 368 K for 3 h. This improvement was considered to be due to the removal of impurities on the fiber surface and to the reduction in the fiber diameter size.

Kim and Netravali [17] observed that mercerization of sisal fibers caused improvement in their fracture stress and Young's modulus. This was due to the increase in the content of cellulose, which is mostly crystalline, resulting in the decrease in fracture strain and toughness of the fibers.

Besides the concentration, other factors can have an influence, such as the reaction time. S. Jayabal *et al.* [18] observed that alkali treatment of coconut shell fiber in 5 % NaOH aqueous solution for 72 h resulted in 31 % increase in tensile strength, while 2 % aqueous solution for 96 h caused 22 % increase in flexural strength and 8 % aqueous solution for 24 h resulted in 30 % increase in impact strength.

Other treatment conditions are found in the literature. A. Correa *et al.* [19] treated curauá fiber with 5 and 17.5 % NaOH solutions and then performed acid hydrolysis aiming to obtain nanocellulose. They noted that mercerization at 17.5 wt % NaOH resulted in the transformation of the majority of cellulose to type II, while 5 wt % NaOH-treatment maintained the original polymorphism of the curauá fiber. The crystallinity index of fiber treated in 17.5 % NaOH was higher than that of raw curauá and fiber treated with 5 % NaOH. The fiber treated with more concentrated solution also showed more resistance to thermal degradation.

Several different results show that more studies about the alkaline treatment are necessary for different plant species and applications. The effect of mercerization at different concentrations, times and temperatures has been studied for several types of natural fibers [20]. In the present work, mercerization was performed on malva fibers (*Urena lobata*), which have been mentioned as

potential fibers for use as reinforcement in polymer matrices [21, 22]. These fibers are similar in color and resistance to jute fibers, while their resistance is considered superior to kenaf fibers (a plant native to South Asia), which have been widely studied to obtain polymeric composites. However, there have been few reports about the application of malva fiber as the reinforcement in the polymer matrices.

In this work poly(3-hydroxybutyrate), or PHB, was used as the matrix due to its biodegradability. Moreover, PHB shows better adhesion to natural fibers compared to polyolefins, due to its polar nature. The addition of plant fibers aims to improve the mechanical performance and toughness of PHB, as well as to lower the price of the material obtained with this biodegradable polyester [23, 24].

2. Experimental

Malva fibers were supplied by Pematec Triangel Brasil and used after grinding in a Wiley mill with a sieve of 2 mm; sodium hydroxide was purchased from Vetec Fine Chemicals Ltda., Brazil, and used after preparation of 5, 7, 10, 15 and 20 wt water solutions; PHB was supplied by BASF.

2.1. Chemical Treatment of Fibers

Malva fibers were immersed in 5 % NaOH at 353 K for 1 h under stirring, after which the mixture was filtered. This extraction procedure was repeated three times in succession, completing four extractions, as proposed by I. Grafova *et al.* [9] Samples were named FM1B5, FM2B5, FM3B5 and FM4B5. After last extraction, the fibers were washed with distilled water until neutral pH and dried at room temperature, without any use of other solvents to aid in curing or drying the fibers.

A similar procedure was performed using 7 % NaOH solution. These samples were called FM1B7, FM2B7, FM3B7, and FM4B7. Further treatments were carried out with immersion and stirring during 48 h at room temperature with solutions of 5 and 7 % NaOH, which received, respectively, the codes FM485 and FM487.

Finally, three other experiments at 353 K were carried out with solutions of 10, 15 and 20 % NaOH during 1 h, and named, respectively, FM10, FM15 and FM20. After each treatment, the fibers were washed with distilled water until neutral pH and dried at room temperature.

2.2. Preparation of Composites

The PHB composites with untreated fibers and sample FM487 were obtained by melt compounding using

a counter-rotating twin-screw mini-extruder (Haake MiniLab, Thermo Scientific, Germany) at 453 K for 5 min. The screw was rotating at constant speed to ensure uniform heating and to maintain the melt temperature. Materials were obtained under different rotational speeds (60, 120 and 180 rpm). The composites obtained with untreated malva fibers were called PHBFM 60 rpm, PHBFM 120 rpm and PHBFM 180 rpm. Finally, the composites obtained with FM487 were called PHBFM487 60 rpm, PHBFM487 120 rpm and PHBFM487 180 rpm.

2.3. Materials Characterization

All fiber samples were characterized by X-ray diffractometry (XRD) to determine the crystalline phase content in the samples in order to evaluate the influence of different chemical treatments on fiber properties. X-ray diffractograms (XRD) of the fibers were obtained using a Rigaku Miniflex diffractometer ($\text{CuK}\alpha$, $\lambda = 1.5418 \text{ \AA}$), working with the difference of potential in a tube of 30 kV and electric current of 15 mA. The scanned 2θ range was from 2° to 40° , with a step size of $0.05^\circ/\text{min}$.

The crystallinity indexes (CI) were determined using Eq. (1), where A_c is the area of crystalline peaks determined by Gaussian curves – using the program Fitk for deconvolution of the peaks, and A_t is the total area, *i.e.*, the sum of the areas of the crystalline peaks and amorphous halo.

$$\text{CI} = (A_c/A_t) \cdot 100 \quad (1)$$

The morphology of the untreated and mercerized fibers was studied by scanning electron microscopy (SEM) using FEI Quanta 400 microscope operating in high vacuum, accelerating voltage of 25 kV, using a backscattered electron detector (BSED) and in some samples under acceleration voltage of 15 kV, using a secondary electron detector (ETD).

FTIR spectra of the fibers were recorded with a Varian Excalibur 3100 spectrometer. The removal of amorphous extractables from the plant fiber was characterized in this analysis using the ATR technique (attenuated total reflection) employing a diamond/Zn Se crystal plate, in the wavenumber range of $4000\text{--}600 \text{ cm}^{-1}$, 100 scans and a resolution of 4 cm^{-1} . The content of amorphous cellulose was calculated using the lateral order index (LOI), which is the intensity ratio of the bands near 1421 and 897 cm^{-1} [25].

The thermal stability of the fibers, PHB and composites was calculated in terms of T_{onset} and T_{max} . Thermogravimetric analysis (TGA) was carried out using a TA Instruments model Q500 analyzer, ramped at 10 K/min , from 303 to 973 K under inert atmosphere.

Composite materials were submitted to dynamic mechanical analysis with TA Instruments model Q800 (Q series) dynamic-mechanical analyzer to study their mechanical properties.

3. Results and Discussion

3.1. Mercerization

All treatments carried out on the malva fibers promoted variations in their physical and chemical properties due to effective removal of extractable amorphous components. This can be observed by means of FTIR spectra in Fig. 1.

There was intense absorption in the range of $3500\text{--}3200 \text{ cm}^{-1}$, which is related to stretching of OH bonds; a band at $2900\text{--}2750 \text{ cm}^{-1}$ related to saturated hydrocarbon CH stretching; a band at 1740 cm^{-1} corresponding to stretching of C=O bonds related to carboxylic ester or acetyl groups (hemicellulose) [26], as well as the absorption of angular strain of CH (cellulose and lignin) at 1240 cm^{-1} and also of aromatic CH in lignin at 730 cm^{-1} . Therefore, the original malva fiber has three main components: cellulose, hemicellulose and lignin.

The bands near 2890 cm^{-1} (CH stretching), 1638 cm^{-1} (OH bending of absorbed water), 1200 cm^{-1} (COH bending in the plane at C6), and 897 cm^{-1} are characteristics of cellulose II, while bands such as 2945 cm^{-1} (CH stretching), 1455 cm^{-1} (C–OH bending) and 1282 cm^{-1} (OH bending) are characteristic of cellulose I [27].

In the spectra of natural and treated malva fibers (Fig. 1) of all alkaline treated fibers, the band at around 1730 cm^{-1} disappeared, indicating removal of hemicellulose. According to the literature, this also indicates a change in the chemical composition of the fiber surface, promoted by alkali treatment [28]. We also observed the disappearance of the absorption band around 1230 cm^{-1} , characteristic of the functional group COC, aryl-alkyl ether of lignin, indicating the removal of this component.

The increased intensity of peaks around 1100 and 1050 cm^{-1} can be attributed to increased cellulose content due to removal of other components of the fiber. Moreover, we also observed the presence of cellulose glycosidic COC symmetrical stretching at 1100 cm^{-1} and the stretching of C–OH at $1060\text{--}1050 \text{ cm}^{-1}$ [11, 17].

FTIR analysis also allows the calculation of the lateral order index (LOI), which is calculated by the ratio of the absorbance of the bands around $1420/897 \text{ cm}^{-1}$ [25, 27, 29]. The next band, at 1420 cm^{-1} , corresponds to the symmetric deformation $\delta \text{ CH}_2$ (C6) in cellulose II and amorphous cellulose, while the band at 895 cm^{-1} is characteristic of stretching in the plane (vibration of β -glycosidic bond COC) in cellulose II. Therefore, the LOI represents the variation of the amorphous cellulose fiber and reflects the regions of order perpendicular to the chain direction, which are greatly influenced by the chemical treatments applied to natural fiber. According to

E. Rojo *et al.* [25], the lower the LOI value, the lower the amorphous fraction in the fiber and the higher the fiber crystallinity. However, a direct relationship between LOI and crystallinity of the fiber determined by XRD was not observed in this work. Similarly, in the work [25] there was also no direct relationship between the values of LOI and the crystallinity index obtained by X-ray diffraction analysis.

By means of infrared spectroscopy, the total crystallinity index (TCI) can also be calculated, which represents the total degree of the order in cellulose given by the ratio of the absorption bands at 1372 cm^{-1} (CH deformation of cellulose II) and 2892 cm^{-1} (CH stretching of cellulose II). The LOI and TCI values are shown in Fig. 2. According to the work of J. Siroky and colleagues [29], LOI and TCI exhibit the same trend related to different levels of crystallinity, although with different absolute values. However, in this study, samples FM, FM487 and FM20 showed dissimilar behavior.

Thus, we did not observe behavior that can be directly related to the measured crystallinity index obtained by XRD analysis. Only sample FM487 showed the LOI value lower than that of untreated malva fiber (FM), 0.57 and 0.76, respectively. For total crystallinity index, only samples FM2B5 and FM4B7 had lower values than FM.

The degree of crystallinity of natural fibers is indicative of their potential as reinforcement in Polym. Compos, since the crystallinity of the material is directly related to their thermal and mechanical properties. The values obtained in the X-ray diffraction analysis are shown in Table 1.

The fibers subjected to successive extractions showed crystallinity indices greater than those of the

natural malva fibers. There was an increase in this property with each extraction with a solution of 5 % NaOH, in which the crystallinity index increased from 58.5 % in the untreated fiber to 64.2 % after the first alkaline extraction and to 68.7 % after the third extraction. When 7 % NaOH solution was employed, the crystallinity index was greater than that achieved with the low-concentration solution, and the same behavior of increased CI (%) after successive extractions was observed for the sample FM3B7, achieving 70.6 %. This pattern is related to the removal of extractable amorphous components during the treatments. No significant changes were observed after the fourth treatment.

The highest levels of crystallinity were obtained for the fibers treated with 7 % NaOH, but a small variation occurred from one extraction to another, indicating that for the malva fibers, the number of extractions was not a preponderant factor for the increase in CI, but the alkali concentration was influential. Although the treatments for 48 h were effective, the long interval is a disadvantageous aspect.

On the other hand, treatments with solutions containing 10, 15 and 20 % NaOH during 1 h (FM10, FM15 and FM20) did not produce a significant increase in the crystallinity index. Even though the literature reports that concentrated alkaline solutions can degrade the crystalline phase of cellulosic fibers [2], in the case of malva only the diffraction related to the plane 101 decreased. Malva fibers resisted treatments at high alkali concentrations carried out only for 1 h, with the other crystalline peaks remaining practically unchanged. The XRD patterns indicated a change from cellulose I to cellulose II, which has a thermodynamically more stable crystalline polymorphic structure.

Table 1

Crystallinity index (CI) of malva fiber determined by XRD

Symbol	CI, %	Standard deviation
FM	58.5	1.1
FM1B5	64.2	1.3
FM2B5	64.0	1.5
FM3B5	68.7	0.7
FM4B5	67.3	1.1
FM1B7	67.4	0.9
FM2B7	67.9	0.5
FM3B7	70.6	2.1
FM4B7	65.3	1.2
FM485	64.4	5.4
FM487	68.0	0.3
FM10	63.1	0.6
FM15	63.2	0.5
FM20	60.3	1.3

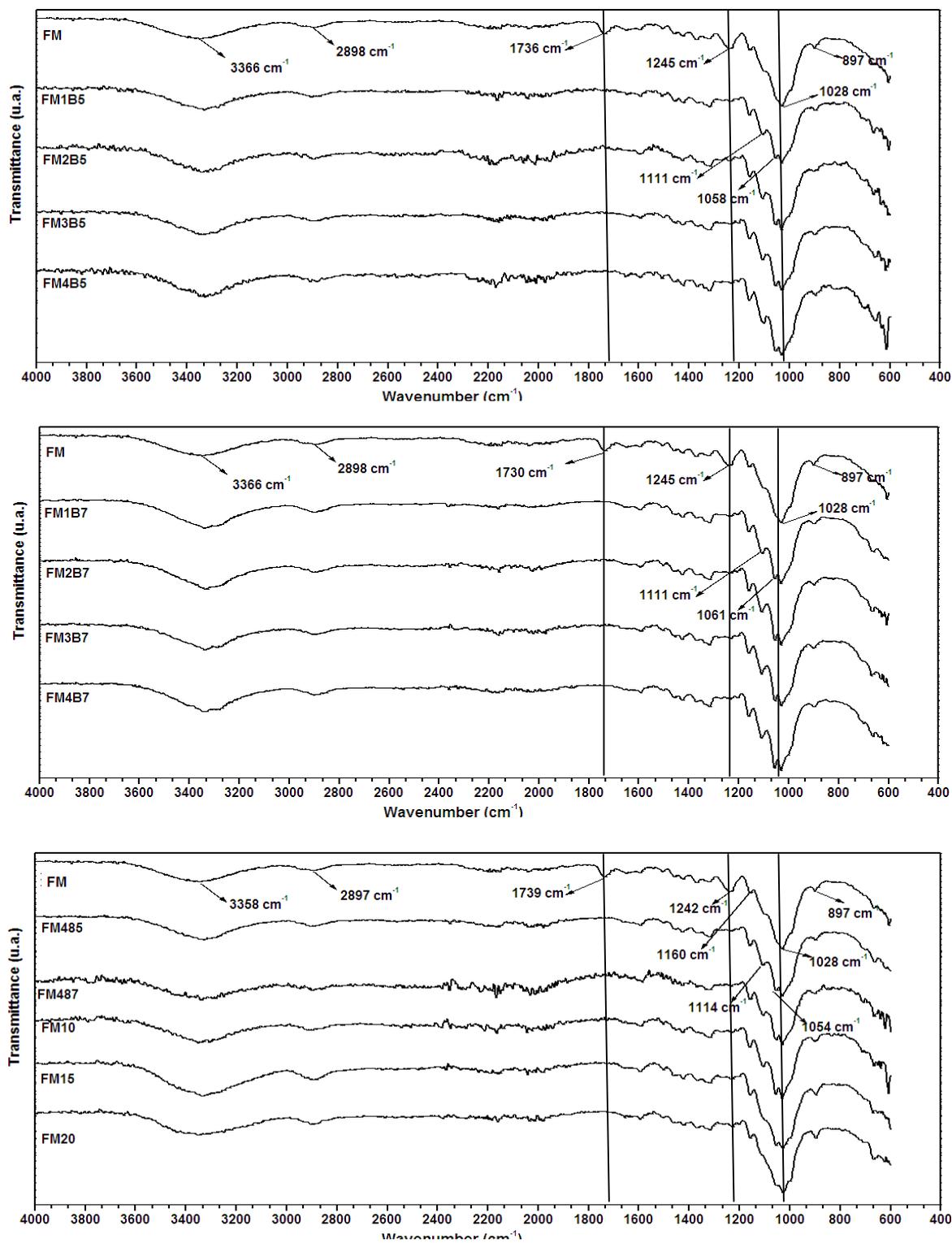


Fig. 1. FTIR spectra of malva fibers

(a): natural malva fibers (FM), FM after 1st extraction with 5 % NaOH (FM1B5), 2nd extraction (FM2B5), 3rd extraction (FM3B5) and 4th extraction (FM4B5); (b): FM after 1st extraction with 7 % NaOH (FM1B7), 2nd extraction (FM2B7), 3rd extraction (FM3B7) and 4th extraction (FM4B7); (c): FM treated with 10 % NaOH (FM10), 15 % (FM15), 20 % (FM20) for 1 h and treated fibers with 5 % NaOH (FM485) and 7 % (FM487) for 48 h

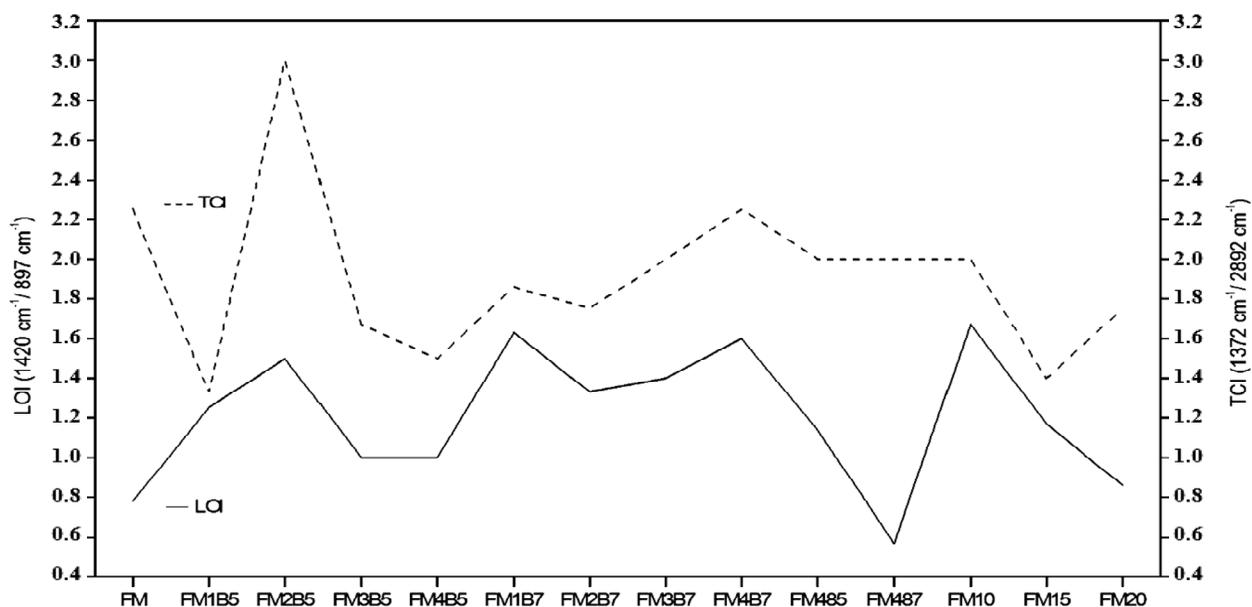


Fig. 2. Lateral order index (LOI) and total crystallinity index (TCI) of the samples from malva fibers obtained after different mercerization methods

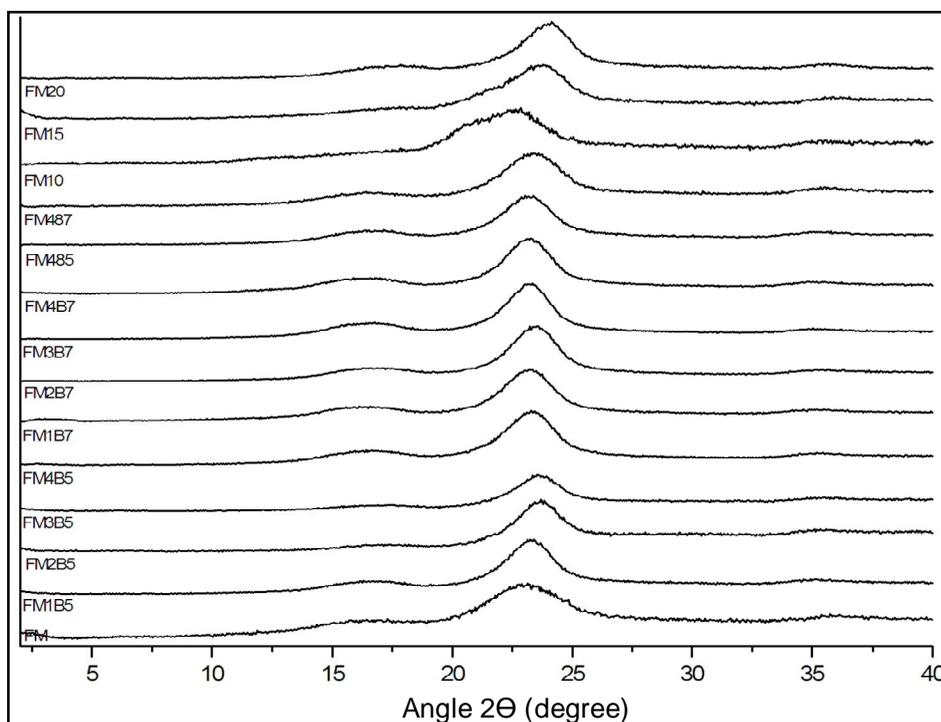


Fig. 3. Diffractograms of all malva fibers (untreated and treated by different methods)

Thermal degradation of a material can be assessed by weight loss with temperature, due to the formation of volatile products from decomposition. The results of thermal analysis of malva fibers confirm there was a change in their properties. The results are presented in Table 2.

According to the values of T_{onset} , all fiber treatments promoted an improvement in thermal degradation resistance, which may also be related to the conversion of the morphological structure from cellulose I to cellulose II, which is thermodynamically more stable than the first structure [30, 31].

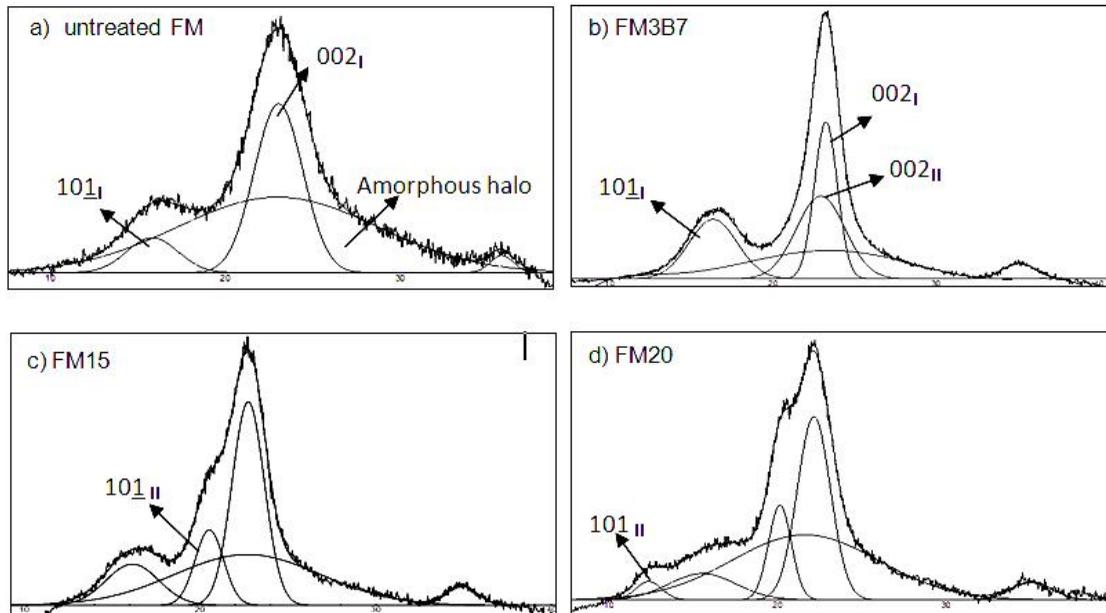


Fig. 4. Diffractograms of malva fibers: untreated FM (a); after 3rd extraction with 7 % NaOH (b); 15 % NaOH treated fiber (c) and 20 % NaOH treated fiber (d)

Table 2

Results obtained from thermogravimetric analysis of malva fibers

Sample	1 st step		2 nd step	
	T_{onset} , K	T_{max} , K	T_{onset} , K	T_{max} , K
FM	535	564	604	620
FM1B5	565	604	696	723
FM2B5	559	601	728	733
FM3B5	561	598	700	727
FM4B5	560	609	697	737
FM1B7	584	623	770	772
FM2B7	584	624	790	798
FM3B7	585	624	–	–
FM4B7	581	620	–	–
FM485	578	619	–	–
FM487	584	626	–	–
FM10	573	623	738	753
FM15	585	626	–	–
FM20	579	623	735	773

Furthermore, according to the values of T_{onset} obtained after successive extractions with 5 % NaOH solution, all initial degradation temperatures were lower than 573 K, while for other treatments they were higher. Therefore, extractions with 5 % NaOH appear to be less efficient for the removal of amorphous extractables than with other methods. This result is unlike many others, in which NaOH concentration of 5 % is considered ideal, since higher concentrations can lead to excessive delignification, weakening or damaging the fiber [9, 7].

Moreover, no significant improvement in properties was observed with increasing number of

extractions, both for fibers treated with 5 and 7 % NaOH solutions, indicating that the concentration of the alkaline solution was more important than the number of extractions for these two procedures. This did not occur in the work of I. Grafova *et al.* [9], in which the authors found a considerable difference in the values of T_{onset} and T_{max} by successive extractions.

In the case of treatments with solutions of 5 and 7 % NaOH for a longer period of time (48 h at room temperature), the longer interval compensated the elevated temperature of the successive extractions. T_{onset} was 578 K for sample FM485 and 584 K for FM487, although the

time of treatment was a disadvantageous aspect, considering that other treatments with more concentrated solutions also provided very similar values. Also, some thermograms showed two mass loss events. The first can be attributed to the pyrolysis of cellulose and hemicellulose, which completely degrade in the range of 588–673 K, respectively, and the second event is related to pyrolysis of lignin, which resists up to 973 K in an inert atmosphere [28].

The surface treatment aims to remove amorphous extractables, impurities and waxes on the surface of the fibers, in order to improve their adhesion with the polymer matrix. Fig. 5(a-n) shows the SEM images of the fibers subjected to different treatments with NaOH. Fig. 5a shows that the surface of the fiber contains impurities, which are removed after successive extractions for longer periods of time or higher alkali concentrations.

The micrographs show there was an increase in the defibrillation after successive extractions and the most defibrillated samples were FM4B7 and FM487, the first one was obtained after the fourth extraction with 7 % alkali and the second one – by the reaction at room temperature for 48 h.

Another effect of the alkali treatment is to increase the surface roughness of fibers [32, 33]. This is regarded as an improvement in morphology and is intended to promote anchoring of the fibers in a polymeric matrix [10, 18].

Samples FM10, FM15 and FM20 did not show high defibrillation, but higher NaOH concentration could have cleaned the fiber even more thoroughly. This is explained by the high resistance to thermal degradation despite the indices of crystallinity.

The degree of defibrillation depends on many factors besides the concentration of the alkaline solution, such as reaction time and temperature. For the same reaction condition, successive extractions promote longer contact with the impurity-free solution; since each extraction solution is renewed, so the degree of defibrillation is increased.

This was observed in the SEM images for both samples subjected to successive extractions at 353 K with 5 % NaOH and 7 % NaOH. However, a long contact with the alkaline solution can compensate the effect of higher temperature, because sample FM487 (Fig. 5k) shows similar defibrillation as the sample FM4B7 (Fig. 5l).

Samples FM3B7 and FM487 showed better results for crystallinity index and thermal properties as well as greater defibrillation. It is expected that more defibrillated fibers disperse better in the polymeric matrix, so composite materials were prepared by mixing sample FM487 in a commercial PHB matrix.

3.2. Composites

The composite materials were obtained from a preliminary experiment on the influence of the mercerized fiber on the mechanical and thermal properties of PHB. The results of the TG analysis (Table 3) showed a small improvement in the thermal properties of the matrix.

It is possible to observe that the composites reinforced with untreated malva fibers show slightly superior thermal degradation resistance to materials obtained from treated fibers (FM487). This may be related to the higher lignin content in raw fibers, acting as an antioxidant. All composites showed higher thermal degradation resistance than pure PHB, although this increase was not very great. Nevertheless, the results were acceptable compared to other studies, such as those of J. Macedo *et al.* [34] where the PHB composites reinforced with coconut fibers had a lower thermal resistance than pure PHB.

The TGA results were in line with those from dynamic-mechanical analysis in relation to most appropriate speed for processing the materials. The materials with improved properties were those processed at 120 rpm. At this rotation speed, the shear appears to have been sufficient to promote better dispersion of the fibers in the matrix.

Dynamic-mechanical analysis (DMA) is a technique used to study the performance of Polym. Compos.s that can provide information about mechanical properties of these materials as a function of temperature. This analysis allows the assessment of morphological and structural changes caused by the addition of fillers to the polymer. Among the composites studied in this work, the best properties were expected from the sample FM487 because the treated fibers should have better adhesion to the PHB matrix.

Table 3

Results obtained from thermogravimetric analysis of biodegradable composite materials

Samples	Screw speed, rmp	T_{onset} , K	T_{max} , K
PHB	–	255	268
PHB FM	60	264	279
PHB FM	120	271	287
PHB FM	180	268	283
PHB FM487	60	265	278
PHB FM487	120	266	281
PHB FM487	180	262	276

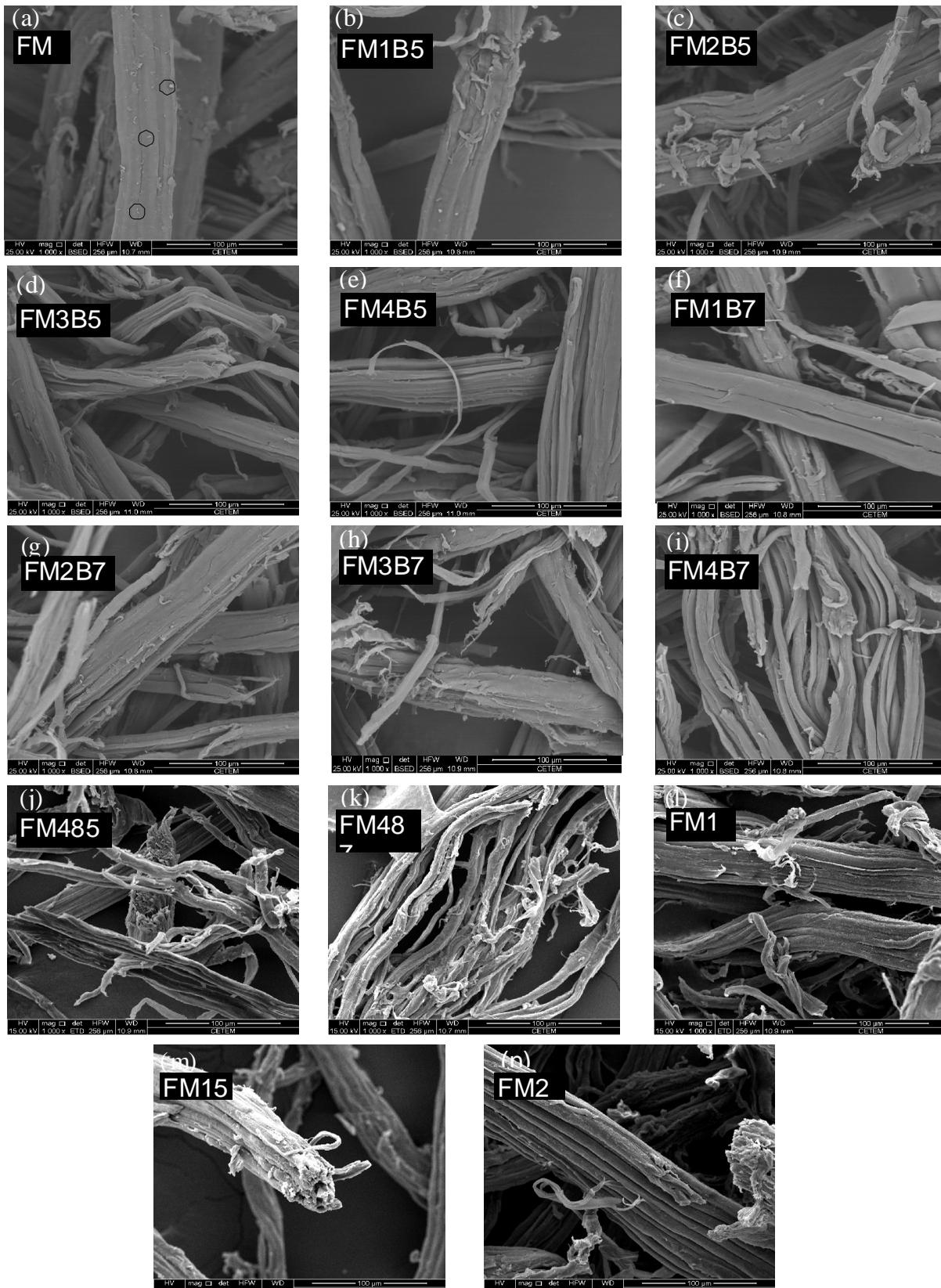


Fig. 5. SEM micrographs of untreated and treated malva fibers

Table 3

Results of DMA analyses of the composites

Samples	278 K		298 K		$T_{g(\tan\delta)}$, K	$T_{g(E'')}$, K	$\tan\delta_{\max}$
	E' , MPa	E'' , MPa	E' , MPa	E'' , MPa			
PHB	2945	174.2	2054	157.6	18.97	13.77	0.0768
PHB FM 60 rpm	1726	310.2	1327	250.5	18.26	12.99	0.1920
PHB FM 120 rpm	3565	460.3	2340	305.6	16.59	7.31	0.1393
PHB FM 180 rpm	2031	517.5	1626	324.6	8.61	-2.32	0.2567
PHBFM487 60 rpm	3121	685.9	2409	455.5	12.63	2.00	0.2334
PHBFM487 120 rpm	5398	449.1	3533	357.3	22.97	8.79	0.1020
PHBFM487 180 rpm	1481	290.9	1097	254.6	29.21	1.42	0.2349

The loss factor, also called mechanical damping factor, is directly related to the impact resistance of a material. $\tan\delta$ is equal to the ratio of the loss (E'') and the storage (E') moduli. In turn, E'' is related to molecular motions that dissipate the energy applied to the material. In the case of composites reported in the literature [35-37], the smaller the $\tan\delta$, the better the adhesion between matrix and load. When better interfacial adhesion occurs, the impact resistance of the material is higher, which seems to contradict the relationship of $\tan\delta$ with energy dissipation. If there is good adhesion between fiber and polymer, molecular motion will be less when the composite is subjected to a mechanical stress. However, one must consider that the energy transfer between the dispersed and continuous phases results in higher impact resistance. Therefore, the relationship between $\tan\delta$ and impact resistance is indirect in the case of composites.

Table 3 shows the results of storage (E') and loss (E'') modulus at 278 and 298 K, and T_g (calculated using the temperature of maximum $\tan\delta$ and maximum E''), and the value of the damping factor ($\tan\delta_{\max}$).

In general, E' decreased at higher temperature, which is associated with the fact that the chains have better mobility at higher temperatures, promoting greater softness, in other words, making the composite less rigid.

There was an increase in storage modulus at both temperatures (278 and 298 K) with the addition of the untreated malva fibers in the composites obtained using screw speed 120 rpm. This means there was an increase in the rigidity of PHB in this composite. The same occurred in the composites obtained with FM487, but when this

sample was used, the modulus increased in the experiments at 60 and 120 rpm. Regarding the T_g , it decreased in most composites compared to the neat matrix, except composites PHBFM487 120 and PHBFM487 180. The increase in T_g values is due to the formation of larger free volume, which is proportional to the volume of the interface, showing that the adherence is not perfect.

The increase of $\tan\delta$ in the composites indicates worsening of the impact resistance due to the weak fiber-matrix interfacial adhesion. According to the literature [24, 38], the reduction of $\tan\delta$ is associated with an improvement in the interfacial bonding between PHB and fibers, as well as the good dispersion of the load in the polymer matrix. Hence, an increase in $\tan\delta$ values indicates a poor compliance, which occurred in most materials. However, a less significant increase was observed in the composite PHB FM487, from 0.0768 (in pure PHB) to 0.1020 (in the composite). Poor compatibilization between PHB and natural fiber was also observed by N. Graupner and J. Mussig [39].

Moreover, the extrusion at 180 rpm led to a drastic decrease of the mechanical and thermal properties, showing that high shear, though it may contribute to dispersion and compatibility of the fibers with the polymer, also leads to degradation of the polymer.

The increase in storage modulus in the composite PHBFM 487, from 2945 (in pure PHB) to 5398 MPa (an increase of 183 %) at 278 K shows that the treated plant fibers can act as reinforcement in PHB matrices, but

further studies are necessary compatibilization between the matrix and that kind of load.

4. Conclusions

Although the alkaline treatment with 5 % NaOH solution is the most frequently reported in the literature, it is not the best for all kinds of fiber. In the present study, we observed that malva fibers subjected to treatments with solutions of the same concentration have different properties if other reaction conditions are not identical.

The use of malva fiber as the reinforcement in the polymer has not yet been fully explored, and we observed that treatment with 7 % NaOH solutions was effective in removing amorphous extractables. Also, an increase in the thermal degradation resistance of these samples occurred. It is very interesting to observe that malva fiber apparently endured the treatments at high concentrations of NaOH without suffering drastic degradation.

Comparing the composite of PHB with untreated malva fiber (FM) and that with alkali fiber (sample FM487) processed at 120 rpm, the latter showed higher mechanical and thermal properties than the former one, although the $\tan\delta$ values indicated the weak compatibility between the composites components. This problem can be resolved using a compatibilizer agent.

Improvement of PHB properties with addition of natural fibers broadens the perspectives for application in industrial sectors such as the automotive, without decreasing the polymer biodegradability.

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**ХІМІЧНЕ ОБРОБЛЕННЯ НАТУРАЛЬНИХ
МАЛЬВА ВОЛОКОН І ПРИГОТУВАННЯ
ЗЕЛЕНИХ КОМПЗИТІВ З ПОЛІ(3-
ГІДРОКСИБУТИРАТОМ)**

***Анотація.** Проведені дослідження лужного оброблення мальва волокон водними розчинами NaOH при різних концентраціях, часі та температурах. Визначено кристалічність, термічну стабільність та морфологію волокон до і після оброблення. Показано, що індекс кристалічності та тепловий опір значно зростають при лужному обробленні 7%-ним розчином NaOH. Вищі концентрації NaOH (10, 15 і 20%)*

несуттєво підвищують індекс кристалічності. За допомогою методу рентгенівської дифракції доведено виникнення дефібриляції в мерсеризованих волокнах, що дає можливість використовувати їх як армуючі в полімерних матрицях. Проведено дослідження змішування волокна з полі(3-гідроксибутиратною) матрицею в двухшнековому міні-екструдері при 453 К. Композити проаналізовано з використанням методів ТГА і ДМА. Показано вплив додавання волокон на механічні та теплові властивості полімеру.

***Ключові слова:** мальва волокно, оброблення лугом, біодеградабельний полімер.*