CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2022,
Vol. 16, No. 3, pp. 377–386

Chemistry

WOOD SAWDUST PLUS SILYLATED STYRENE COMPOSITES WITH LOW WATER ABSORPTION

Omari Mukbaniani[1, 2], Witold Brostow[3, ✉], Jimsher Aneli[2], Levan Londaridze[1, 2], Eliza Markarashvili[1,2], Tamara Tatrishvili[1, 2], Osman Gencel[4]

https://doi.org/10.23939/chcht16.03.377

Abstract. Ecologically friendly composites have been made on the basis of wood sawdust and sillylated styrene as the binder. That binder acts simultaneously as a reinforcing agent. The surface structures were studied by a scanning electron microscopy and energy dispersive X-ray microanalysis. The bending strength increases with the increase in temperature from 453 to 493 K at the constant pressure of 15 MPa. Likely we have heterogeneous reactions between active groups of triethoxysilylated styrene and sawdust, which lead to increasing of the spatial (per specific volume) concentration of chemical bonds. Impact viscosity increases in the same temperature range from 14.6 to 25.8 kJ/m^2. Water absorption determined after 3 and 24 h varies over a wide range in the function of the composition. The lowest value is 4.1 wt% water after 24 h.

Keywords*:* sawdust composites, binders, low water absorption, thermogravimetric analysis, differential scanning microscopy.

1. Introduction

There is a significant interest in the development of new composites derived from thermoplastic polymer matrices reinforced with wood fillers due to their environmental and economic benefits.[1,2] The benefits include renewability, biodegradability, low density, high stiffness and relatively low prices.[3] Using wood sawdust involves another important advantage: sawdust does not go as the waste into city dumps. Among thermoplastic matrices used in the manufacture of such composites is polystyrene,[4] which is popular due to its easy processability and ability to provide good electrical insulation.[5]

The use of lignocellulosic fibers has certain disadvantages such as degradation at low temperatures and also poor compatibility between the polar lignocellulosic filler and the non-polar polymer matrix.[6] Due to the strong intermolecular hydrogen bonding between the lignocellulosic fibers, which tend to agglomerate during mixing with the polymer matrix in the compounding process, the resulting composites have relatively poor mechanical and thermal properties.[7]

Improvement of the interface compatibility between thermoplastic polymers and lignocellulosic fillers has attracted significant attention.[8] Several modifications of the fiber surfaces such as by reactions with acid compounds,[9,10] alkali treatment[11,12] and the incorporation of compatibilizer such as a malleated polymer[13,14] or treatment with coupling agents[15,16] have been reported.

Among different coupling agents, organosilanes (R-Si-(OR')$_3$) are often used. These bifunctional molecules with their alkoxysilane groups are used to modify the surfaces of natural fibers. After hydrolysis reactions of the fibers, surfaces rich in OH^- groups can be created. Chemical bonds on the surfaces of the fibers are formed through siloxane bridges; organofunctional groups bond to the polymer matrix. These groups improve the compatibilization between the fibers and the matrix by the formation of covalent bonds. The silane coupling agents provide bridges between the fibers and the matrix.[17-19]

Boussehel[20] prepared composites of polystyrene (PS) with 3-(trimethoxysilyl) propyl methacrylate grafted on the olive pomace flour as a coupling agent to enhance the interfacial bonding between that flour and PS – and thus to improve morphological, thermal and mechanical properties of PS. Composites of PS with fillers such as silica and carbon black were created using coupling agents such as fluorine substituted styrene compounds and styrene compounds containing triethoxy(4-vinylphenylethyl) silane functional groups.[21-23]

[1] Department of Macromolecular Chemistry, Ivane Javakhishvili University,
Ilia Chavchavadze Blvd. 1, Tbilisi 0179, Georgia
[2] Institute of Macromolecular Chemistry and Polymeric Materials, Ivane Javakhishvili University,
Ilia Chavchavadze Blvd. 13, Tbilisi 0179, Georgia
[3] Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas,
3940 North Elm Street, Denton, TX 76207, USA
[4] Department of Civil Engineering, College of Engineering, Bartin University, Bartin 74100, Turkey
✉ *wkbrostow@gmail.com*

We have decided to impregnate lightweight and permeable solid woods by monomers with a low molecular weight, low viscosity and/or high reactivity capable to fill intra- and/or intercellular spaces in wood and/or chemically bond themselves to certain polysaccharides and lignin present in the wood cell walls. We have studied the effects of surface modification on morphological, thermal and mechanical properties of sawdust reinforced triethoxysilylated styrene composites.

2. Experimental

Materials. Following earlier work,[24] we have created composites based on dry pine sawdust with silylated styrene as a binder and a reinforcing agent.

Processing. The composites were prepared by a hot pressing of highly dispersed (50 μm) components under pressures up to 15 MPa and temperatures up to 493 K in molds for 15 min. We have created two types of samples: cylindrical (for investigation of water absorption) and rectangular (for mechanical testing).

Fourier transform infrared spectra were determined with a Varian 660-IR FT-IR Spectrometer. The KBr pellets of samples were prepared by mixing (1.5–2.0) mg of samples, finely grounded, with 200 mg KBr (FTIR grade) in a vibratory ball mixer for 20 s.

SEM and EDS observations were conducted. Measurements were performed under a microscope (Tescan Vega 3, LMU, LaB 6 cathode). Maximum accelerating voltage was 30 kV, resolution 2.0 nm. The microscope was also equipped with an energy dispersive spectrometer of X-ray-induced electron beam specimens (EDS, Oxford Systems). EDS was used to analyze the sample compositions.

Bending testing (also known as a flexural testing) was performed on parallelepipeds with the length of 10 cm and the vertical square cross-section of 1 cm^2. Each specimen was placed on two prisms, with the distance of 8.0 cm between the prisms. The indenter was a metal cylinder with the diameter of 10 mm applied from above to the midpoint of the specimen. Bending strength (or flexural strength) is defined as the stress needed to create a breaking point (a crack) in the outer surface of the test specimen.[25]

Impact viscosity determination, also called *shock viscosity* determination, is a technique applied to soft solids[26,27] and is essentially a drop impact test. The drop height h is the vertical distance between the upper surface of the tested material (h_1) and the bottom surface of the drop hammer at the end of the impact event (h_2). With the sample mass m and the acceleration g, the work W performed by the falling hammer normalized with respect to the horizontal cross-section of the specimen is:

$$W = m\,g(h_1 - h_2) \quad (1)$$

Vicat softening depth consists in the determination of the depth of the indentation with respect to the top surface caused by a flat ended indenter with the cross-section of 1 mm^2. The load applied is 10 or 50 N and the cross-section of the indenter end is circular. The term *Vicat hardness* is also in use – quite confusing since larger values correspond to a lower hardness.

Water absorption is determined simply as the percentage weight change of the sample after submersion in water. We have performed such measurements after 3 h and 24 h exposition to water.

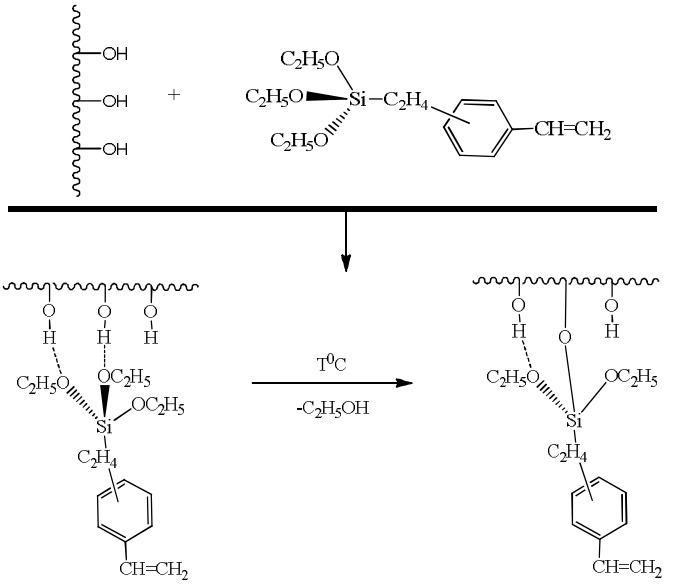
3. Results and Discussion

As noted above, the aim of our work is the creation and development of new composites on the basis of sawdust and ecologically friendly triethoxysilylated styrene.

It is known that the sawdust contains cellulose derivatives and lignin structural rings with hydroxyl groups. In our binder triethoxy(vinylphenethyl) silane we also have ethoxyl groups as well as vinyl groups. Those groups were expected to participate in the etherification reaction with a binder through inter-molecular and intra-molecular reactions, with the possible vinyl group *in-situ* polymerization.

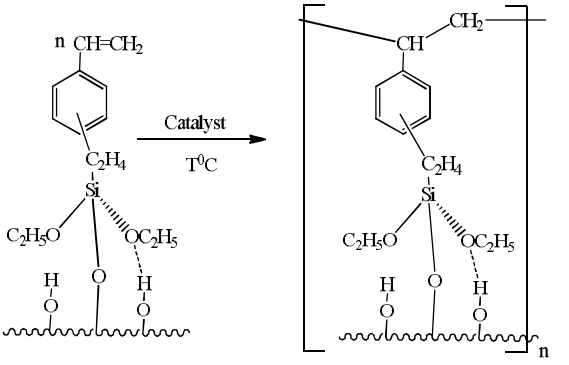
The triethoxysilylated styrene was stirred with benzoyl peroxide (1 wt%) and this homogeneous mixture (3, 5, 10, 15, 20 %) was added to a predefined weight ratio of pine sawdust. Then the mixture was stirred for 5 min until it became homogeneous, placed in a press form and pressed at several temperatures. During hot-pressing, the initiator existing in the mixture may initiate the polymerization reaction of vinyl groups of triethoxysilylated styrene.[28,29] Wood sawdust impregnated with triethoxysilylated styrene, at the moment of hot pressing, forms chemical bonds with the hydroxyl groups of cellulose. Active filler is likely formed, then etherification and polymerization reactions take place. In particular, one expects formation of hydrogen bonds before the onset of the polymerization reaction with triethoxysilylated styrene and also formation of ethyl alcohol.

The monomer triethoxysilylated styrene reacts with the cellulose hydroxyl groups in the filler to form donor-acceptor bonds. The etherification reaction results in creation of new covalent bonds between the filler and the binder – proceeding according to Scheme 1:



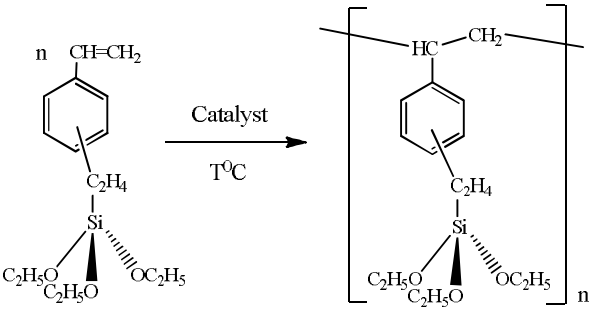
Scheme 1. Interaction and etherification reactions of triethoxysilylated styrene and cellulose

According to the above Scheme, reinforcement processes should take place. Polymerization of the vinyl groups according to Scheme 2 is also possible (Scheme 2).



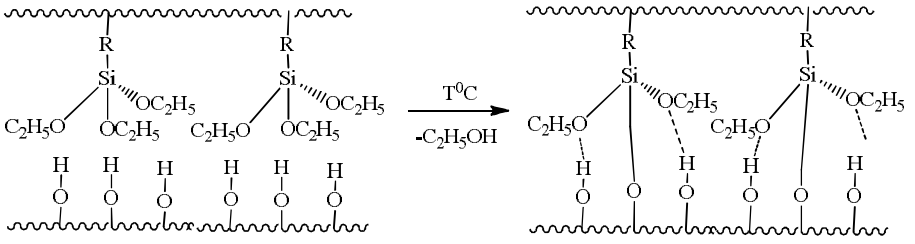
Scheme 2. *In situ* polymerization reaction of triethoxysilylated styrene with fillers

As already mentioned, the use of benzoyl peroxide during hot pressing facilitates the polymerization reaction of triethoxysilylated styrene that should increase the mechanical strength of the composites. We also expect that a polymer that forms during in-situ polymerization according to Scheme 3 will interact with the cellulose surface:



Scheme 3. *In situ* polymerization of triethoxysilylated styrene in a matrix

Then the likely reaction proceeds according to Scheme 4:



Scheme 4. Etherification and intermolecular interaction reactions of triethoxysilylated polystyrene with sawdust; where R = $–C_2H_4C_6H_4–$

The experiments were performed in the following sequence. Triethoxysilylated styrene was taken in the ratio of 3, 5, 10, 15 and 20 % of the sawdust mass at a pressure between 5–15 MPa; we also used benzoyl peroxide which inhibits triethoxysilylated styrene polymerization during hot compression. We have performed experiments in 10 K intervals from 413 to 493 K. The best results were obtained at 493 K, while above that temperature carbonization was visible.

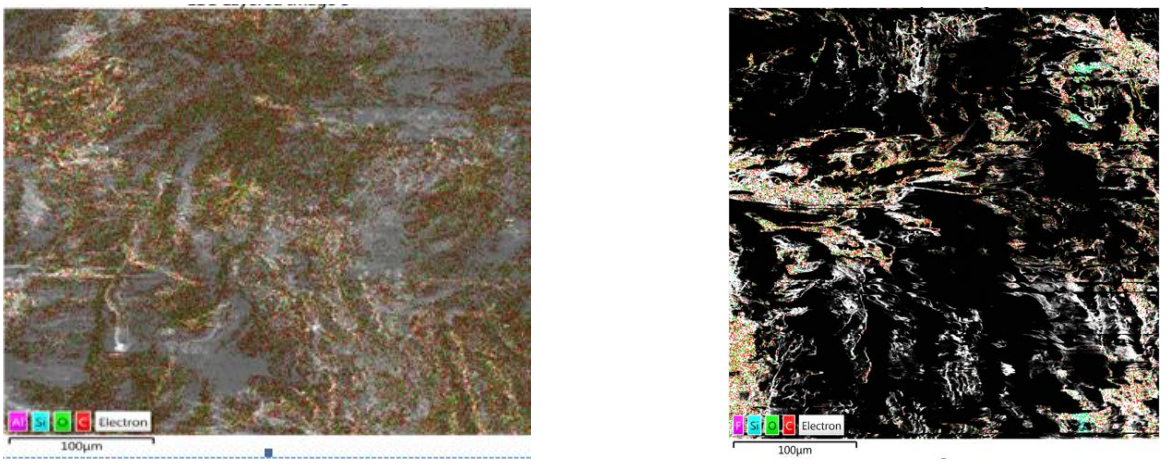
3.1. Fourier Transform Infrared Spectroscopy (FTIR)

For brevity we do not include the spectra here. In the FTIR spectra of composite materials one can see the adsorption bands for the asymmetric valence oscillations characteristic of the ≡Si–O–Si≡ bond, up to a maximum of 1026 cm^{-1}, corresponding to siloxane bonds. The absorption band around 1150 cm^{-1} corresponds to the asymmetric absorption bands characteristic of the Si–O–C and C–O–C bonds – where the absorption bands overlap. Absorption bands at 1262, 1370, 1419, 1507, 1600–1650, 1720, 2800–2950 and 3346 cm^{-1} correspond respectively to the methyl groups, CH bond absorption in (–C / C–/CH_3), CH_2 cellulose – lignin, C=C aromatic, C=C alkene, (C=O ester bond), phenyl groups and –OH groups.

3.2. SEM and EDS investigations

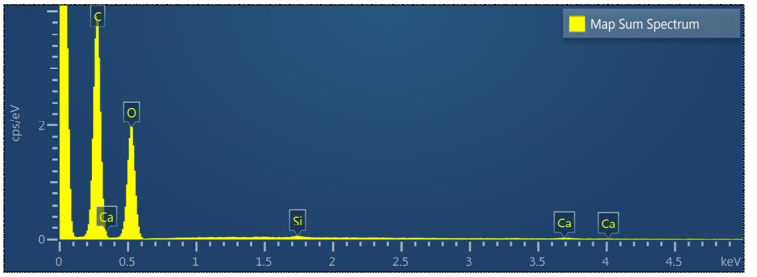
The surface morphology of the composites was studied by a scanning electron microscopy (SEM). In Fig. 1a showing the composite III bright colors indicate pores, indentations and inserts with the sizes in the range of 30–40 μm. Pink spots indicate the presence of aluminum in the composite, blue spots indicate silicon, green spots oxygen, and red spots carbon.

Fig. 2 shows the energy dispersion X-ray microanalysis of composites III and VII. Peaks represent the elements present and their relative concentrations. From the spectra in Fig. 2 we infer that the main elements in the composites are C, O, Si, F and Ca, while C appears in the highest quantities.

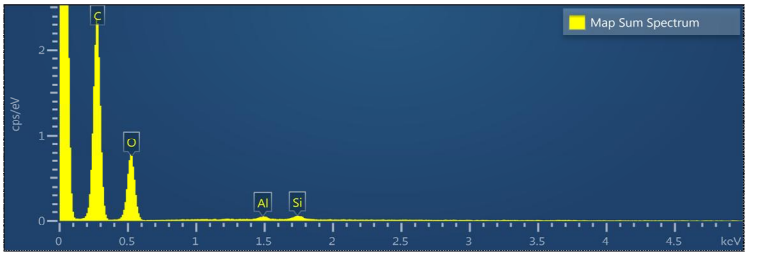


a) b)

Fig. 1. Scanning electron micrograms of the composite III (a) and composite VII (b)



a)



b)

Fig. 2. Energy dispersion micro X-ray spectral analysis of composite III (a) and VII (b)

3.3. Mechanical Testing

Testing was performed at several temperatures and binder concentrations. Bending strength was determined according to a standard for wood + polymer composites.[29] From three-point testing results, the flexural strength σ_f can be calculated as following:

$$\sigma_f = 3F \cdot L/2wd^2 \quad (2)$$

where F is the maximum force applied; L is the length of the sample; w is the width of the sample; d is the depth of the sample.

Thus, to calculate the flexural strength σ_f, we multiply the force by the length of the sample, and then multiply this by three. Impact viscosity was determined with an apparatus of the Charpy type; Table 1 provides the results.

Table 1. Dependence of the values of bending strength and impact viscosity of composites containing sawdust on the conditions (temperature, binder concentration) of sample preparation (exposition time 15 min)

Composite	Binder, %	Pressure, MPa	Temperature, K	Bending strength, MPa	Impact viscosity, kJ/m^2
III	3% TESSt + 1% BP	15	453	17	15
IV		15	463	38	21
V		15	473	40	17
VI		15	483	44	17
VII		15	493	55	20
X	5% TESSt + 1% BP	15	453	19	15
XI		15	463	40	16
XII		15	473	51	20
XIII		15	483	44	19
XIV		15	493	50	21
XVIII	10% TESSt + 1% BP	15	453	31	23
XIX		15	463	36	25
XX		15	473	37	25
XXI		15	483	41	21
XXII		15	493	39	26

Notes: TESSt is the binder, that is triethoxysilylated styrene; BP is a benzoyl peroxide.

Inspection of Table 1 leads us to several conclusions. The bending strength increases with increasing of temperature (453–493 K) at the constant pressure of 15 MPa. Likely we have heterogeneous reactions between active groups of TESSt and sawdust, which lead to increasing the spatial (per specific volume) concentration of chemical bonds. We recall that polymer flexibility Y has been defined[30] as:

$$Y = V_{sp}/\sum_{i}^{n} U_{bi} \quad (3)$$

Here V_{sp} is the specific volume in cm^3/g at a given temperature while the summation is performed over the strengths of bonds in the monomer of a given polymer. Polymer rigidity is defined as $1/Y$.[31] We find that the bending strength values are inversely proportional to the flexibility. If we exceed 5 wt% of the binder, the bending strength decreases; apparently the binder has a relatively high flexibility.

Table 2. Water absorption of sawdust and TESSt composites prepared at different temperatures and the pressure of 15 MPa

Composite	Binder, %	Temperature, K	Weight of composite after 3 h exposition in water, g	Weight of composite after 24 h exposition in water, g	Water absorption after 24 h exposition in water, wt%
I	3%TESSt + 1% BP	433	4.486	Decomposed	-
II		443	3.921	4.145	8.9
III		453	3.953	4.064	7.1
IV		463	3.963	4.062	5.1
V		473	3.746	3.871	5.3
VI		483	3.727	3.850	5.2
VII		493	3.785	3.898	5.1
VIII	5% TESSt + 1% BP	433	3.90	Decomposed	-
IX		443	3.88	Decomposed	-
X		453	3.96	4.307	13.9
XI		463	3.89	4.072	5.7
XII		473	3.85	4.000	4.4
XIII		483	3.81	3.952	4.6
XIV		493	3,80	3.930	4.5
XV	10% TESSt + 1% BP	423	4.252	Decomposed	-
XVI		433	4.049	Decomposed	-
XVII		443	3.779	4.631	28.0
XVIII		453	3.723	3.938	7.7
XIX		463	3.505	3.700	7.9
XX		473	3.503	3.680	7.0
XXI		483	3.522	3.718	78
XXII		493	3.468	3.627	6.5
XXIII	15% TESSt + 1% BP	423	4.079	6.528	92.0
XXIV		433	3.581	5.405	55.9
XXV		443	3.677	5.008	42.8
XXVI		453	3.539	3.754	8.4
XXVII		463	3.475	3.650	6.2
XXVIII		473	3.453	3.619	5.8
XXIX		483	3.449	3.582	4.1
XXX		493	3.503	3.630	5.6
XXXI	20% TESSt + 1% BP	423	3.397	4.522	37.6
XXXII		433	3.367	4.701	45.3
XXXIII		443	3.422	3.855	15.9
XXXIV		453	3.527	3.840	18.1
XXXV		463	3.341	3.548	8.4
XXXVI		473	3.36	3.460	7.5
XXXVII		483	3.237	3.404	6.3
XXXVIII		493	3.157	3.293	5.5

We consider now the impact viscosity at constant pressure. The increase in temperature from 453 to 493 K leads to increasing the impact viscosity from 14.6 to 25.8 kJ/m^2. The explanation provided above for the bending strength may be applied here too. An analogical process takes place at increasing of the technological pressure in the range of 5–15 MPa at the constant temperature, although the effect is less pronounced. Apparently increasing pressure leads to compressing the ingredients and consequently to increasing the interactions between them per unit volume.

3.4. Water Absorption

Water absorption is quite important for wood composites since they are often used under high humidity conditions. The results of water absorption experiments are presented in Table 2. We do *not* imply the accuracy of ±0.001 g.

We see in Table 2 the effects of composition and the temperature of preparation. Relatively low values in the last column reflect low volumes of the empty intermolecular spaces. Exceptions are samples XVII, XXIII, XXIV, XXV, XXXI and XXXII. The common feature of the high values seems to be relatively high concentrations of TESSt and also sample preparation at low temperatures. Apparently at lower temperatures the 'squeezing out' of empty spaces by compression is less successful than at higher temperatures.

Water absorption is also presented graphically in Fig. 3 as a function of the temperature at which pressing was performed. We see that the lowest water absorption is characteristic for composites containing the optimal (5 wt%) of the binder and created at high pressing temperatures – in agreement with some results reported earlier.[28,29]

In Fig. 4 we show the dependence of water absorption on the binder concentration.

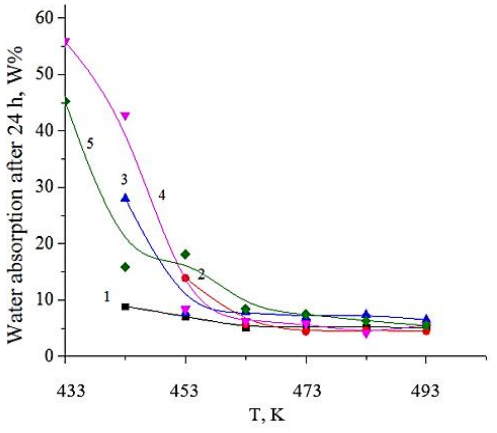


Fig. 3. Dependence of water absorption on the pressing temperature for composites containing 5 wt% (1), 3 wt% (2), 10 wt% (3), 15 wt% (4) and 20 wt% (5) wt% of the binder

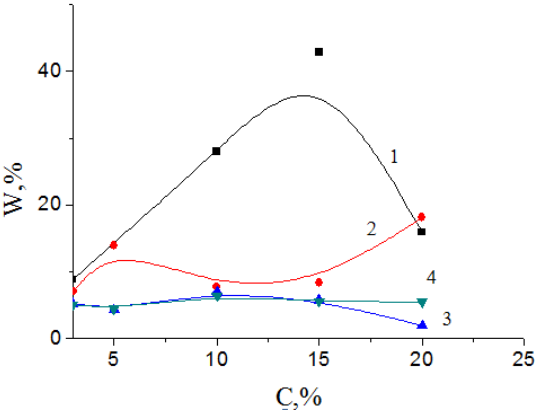


Fig. 4. Dependence of water absorption on the binder concentration, for composites obtaining at 443 K (1), 453 K (2), 473 K (3) and 493 K (4)

The results seen in Fig. 4 might be explained as follows. At low binder concentrations the addition of binder creates some empty spaces between the main components; we recall our discussion above in terms of flexibility. However, at higher binder concentrations the binder might be 'binding to itself' and the free volume decreases. Free volume is discussed by Brostow *et al.*[32]

Table 2 shows the lowest value of water absorption after 24 h of 4.1 wt% for the sample XXIX. For instance, Hashim *et al.*[33] report the water absorption of particle boards made from oil palm biomass in the range from 20 to 130 wt%.

3.5. Vicat Results

The results of determination of the softening temperatures of the composites are shown in Figs. 5-7. Temperature dependence of the softening of composites shows first a monotonic increase and then a maximum or else approaching a horizontal asymptote.

Inspection of the last three figures is instructive. First, increasing the temperature we see higher *h* values, that is more softening. In general, increasing the temperature we get more free volume V^f. The effect is more pronounced at low temperatures since the atoms, molecules and polymer chain segments get more space to move around their equilibrium positions. While we are dealing with amorphous materials, recalling the simple model of Albert Einstein of crystals as harmonic oscillators seems instructive. At higher temperatures, polymer chain segments and other entities present will not need more space; their movements are limited by primary chemical bonds.

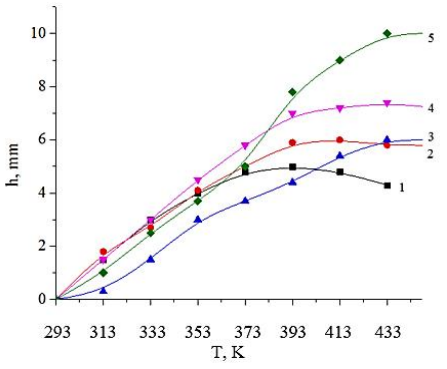


Fig. 5. Dependence of the softening of the sample on temperature for composites with 3 % TESSt + 97 % sawdust obtained at 15 MPa. Curve (1) corresponds to 453 K; (2) to 463 K; (3) to 473 K; (4) to 483 K and (5) to 493 K

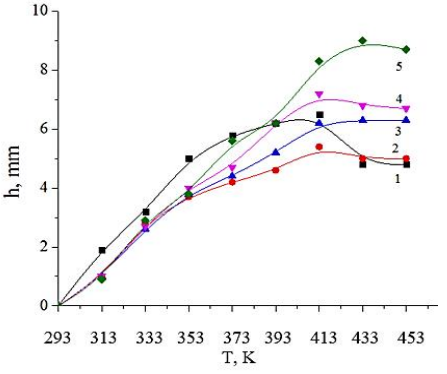


Fig. 6. Dependence of the softening of the sample on temperature for composites with 5 % TESSt (5) + 95 % sawdust obtained at 15 MPa. Curve (1) corresponds to 453 K; (2) to 463 K; (3) to 473 K; (4) to 483 K and (5) to 493 K

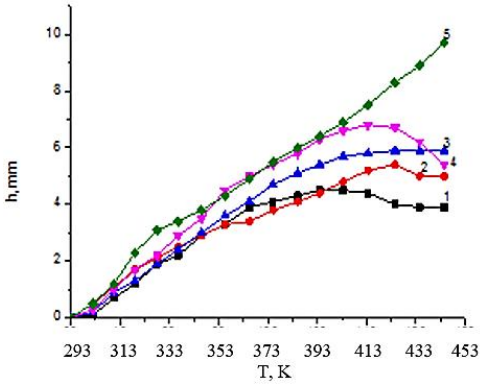


Fig. 7. Dependence of the softening of the sample on temperature for composites with 10 % TESSt + 90 % sawdust obtained at 15 MPa. Curve (1) corresponds to 453 K; (2) to 463 K; (3) to 473 K; (4) to 483 K and (5) to 493 K

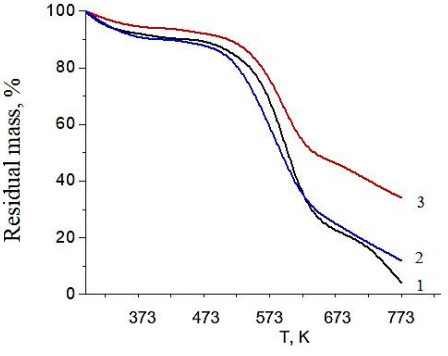


Fig. 8. Thermogravimetric curves of composite materials: composite III (1); composite IV (2) and composite VII (3)

We now turn to the TGA results presented in Fig. 8. The TGA technique is described in detail in some studies.[31,32] At 373 K we see 5–7 % mass losses – likely due to elimination of moisture and ethyl alcohol. The main degradation processes proceed in the temperature range of 523–623 K. The composite VII is characterized by the high thermal stability if compared with composites III and IV. This can be explained by the fact that in the composite created at 493 K the esterification reactions between sawdust hydroxyl and ethoxyl groups of binders proceed more extensively, with the formation of more chemical bonds.

Differential scanning calorimetry (DSC) examinations were also performed for our composites. We do not include the curves for brevity. In some composites the so-called glass transition temperature $T_g \approx 192$ K. As discussed by Kalogeras and Hagg Lobland,[34] representing a glass transition region, for instance 30 K wide, by a single number is not only an uphill battle, but provides a confusing image of the situation. The softening temperatures are in the range from 243 to 313 K.

We would like to mention other approaches to creation of wood + polymer composites. Iulianelli *et al.*[35] have created wood flour + PVC composites by compression molding using sapwood and heartwood from *Angelin Pedra* as a filler. The composites specimens were subjected to water immersion and impact tests. A sapwood composite containing 10 phr of wood flour exhibited the water absorption in 63 days of 0.58 % weight gain. The impact property was affected by a wood content and less by a wood type. Composites containing 10 phr of wood showed the higher impact strength than those prepared with 25 and 40 phr of wood flour. We also note the work by one of us and coworkers[36] of combustion of wood studied by thermogravimetry. *Pinus monticola, Acer saccharum, Quercus rubra, Diospyrus spp., Tabebuia spp.* and *Guaiacum spp*. were chosen to provide a wide range of hardness values and densities. *Quercus*

rubra burned to the hottest temperature of the samples, and also left the least amount of ash behind. There seems to be no connection between the wood density and the parameters characterizing the burning process. Finally, we note the work of Pyshyev *et al*.[37] on creation of charcoal from wood and also from agricultural wastes.

It is pertinent to note the importance of wetting[38] – in this case between sawdust and the polymer.

4. Conclusions

We have created composites on the basis of sawdust and triethoxysilylated styrene as a new binder at several temperatures *via* hot pressing method. Good properties are achieved at relatively low concentrations of the binder and at thermal treatment temperatures up to 473 K.

As expected, changes of pressure and temperature affect the microstructures of our composites. The largest effects are seen in the water absorption.

Acknowledgements

The financial support of the Georgian National Science Foundation, Tbilisi (Grant ##FR-19-795) is gratefully acknowledged.

References

[1] Ichazo, M.N.; Albano, C.; Gonzalez, J.; Perera, R.; Candal, M.V. Polypropylene/Wood Flour Composites: Treatments and Properties. *Compos. Struct*. **2001**, *54*, 207-214. https://doi.org/10.1016/S0263-8223(01)00089-7

[2] Seung-Hwan, L.; Tsutomu, O. Mechanical and Thermal Flow Properties of Wood Flour–Biodegradable Polymer Composites. *J. Appl. Polymer Sci*. **2003**, *90*, 1900-1905. https://doi.org/10.1002/app.12864

[3] Torres, F.G.; Cubillas, M.L. Study of the Interfacial Properties of Natural Fibre Reinforced Polyethylene. *Polym. Test*. **2005**, *24*, 694-698. https://doi.org/10.1016/j.polymertesting.2005.05.004

[4] Arrakhiz, F.Z.; Elachaby, M.; Bouhfid, R.; Vaudreuil, S.; Essassi, M.; Qaiss, A. Mechanical and Thermal Properties of Polypropylene Reinforced with Alfa Fiber Under Different Chemical Treatment. *Mater. Des*. **2012**, *35*, 318-322. https://doi.org/10.1016/j.matdes.2011.09.023.

[5] Rosa, S.M.L.R.; Santos, E.F.; Ferreira, C.A.; Nachtigall, S.M.B. Studies on the Properties of Rice-Husk Filled PP Composites: Effect of Maleated PP. *Mater. Res*. **2009**, *12*, 333-338. https://doi.org/10.1590/S1516-14392009000300014

[6] Poletto, M.; Dettenborn, J.; Pistor, V.; Zeni, M.; Zattera, A.J. Materials Produced from Plant Biomass. Part I: Evaluation of Thermal Stability and Pyrolysis of Wood. *Mater. Res*. **2010**, *13*, 375-379. https://doi.org/10.1590/S1516-14392010000300016

[7] Kim, H.S.; Lee, B.H.; Choi, S.W.; Kim, S.; Kim, H.J. The Effect of Types of Maleic Anhydride Grafted Polypropylene (MAPP) on the Interfacial Adhesion Properties of Bio-Flour Filled Polypropylene Composites. *Compos. Part A-Appl. Sci. Manuf*. **2007**, *38*, 1473-1482. https://doi.org/10.1016/j.compositesa.2007.01.004

[8] Sain, M.; Suhara, P.; Law, S.; Bouilloux, A. Interface Modification and Mechanical Properties of Natural Fiber Polyolef in Composite Products. *J. Reinf. Plast. Compos*. **2005**, *24*, 121-130. https://doi.org/10.1177/0731684405041717

[9] Özmen, N. A Study of the Effect of Acetylation on Hemp Fibres with Vinyl Acetate. *BioResources* **2012**, *7*, 3800-3809.

[10] Manikandan Nair, K.C.; Sabu, T.; Groeninckx, G. Thermal and Dynamic Mechanical Analysis of Polystyrene Composites Reinforced with Short Sisal Fibres. *Compos. Sci. Technol*. **2001**, *61*, 2519-2529. https://doi.org/10.1016/S0266-3538(01)00170-1

[11] Bachtiar, D.; Sapuan, S.M.; Khalina, A.; Zainudin, E.S.; Dahlan, K.Z.M. Flexural and Impact Properties of Chemically Treated Sugar Palm Fiber Reinforced High Impact Polystyrene Composites. *Fibers Polym*. **2012**, *13*, 894-898. https://doi.org/10.1007/s12221-012-0894-1

[12] Venkateshwaran, N.; Peruma, A.E.; Arunsundaranayagam, D. Fiber Surface Treatment and Its Effect on Mechanical and Visco-Elastic Behavior of Banana/Epoxy Composite. *Mater. Des.* **2013**, *47*, 151-159. https://doi.org/10.1016/j.matdes.2012.12.001

[13] Kakou, C.A.; Arrakhiz, F.Z.; Trokourey, A.; Bouhfid, R.; Qaiss, A.; Rodrigue, D. Influence of Coupling Agent Content on the Properties of High Density Polyethylene Composites Reinforced with Oil Palm Fibers. *Mater. Des.* **2014**, *63*, 641-649. https://doi.org/10.1016/j.matdes.2014.06.044

[14] Singha, A.S.; Raj, R.K. Natural Fiber Reinforced Polystyrene Composites: Effect of Fiber Loading, Fiber Dimensions and Surface Modification on Mechanical Properties. *Mater. Des.* **2012**, *41*, 289-297. https://doi.org/10.1016/j.matdes.2012.05.001

[15] Asumani, O.M.L.; Reid, R.G.; Paskaramoorthy, R. The Effects of Alkali Silane Treatment on the Tensile and Flexural Properties of Short Fibre Non-Woven Kenaf Reinforced Polypropylene Composites. *Compos. Part A-Appl. Sci. Manuf*. **2012**, *43*, 1431-1440. https://doi.org/10.1016/j.compositesa.2012.04.007

[16] Merkel, K.; Rydarowski, H.; Kazimierczak, J.; Bloda, A. Processing and Characterization of Reinforced Polyethylene Composites Made with Lignocellulosic Fibres Isolated from Waste Plant Biomass such as Hemp. *Compos. Part B-Eng*. **2014**, *67*, 138-144. https://doi.org/10.1016/j.compositesb.2014.06.007

[17] Nekkaa, S.; Guessoum, M.; Benamara, R.; Haddaoui, N. Influence of Surface Flour Treatment on the Thermal, Structural and Morphological Properties of Polypropylene/Spartium Junceum Flour Composites. *Polym. Plast. Technol. Eng*. **2013**, *52*, 175-181. https://doi.org/10.1080/03602559.2012.734363

[18] Xie, Y.; Callum, A.S.H.; Xiao, Z.; Holger, M.; Carsten, M. Silane Coupling Agents Used for Natural Fiber/Polymer Composites: A Review. *Compos. Part A-Appl. Sci. Manuf*. **2010**, *41*, 806-819. https://doi.org/10.1016/j.compositesa.2010.03.005

[19] Abdelmouleh, M.; Boufi, S.; Belgacem, M.N.; Dufresne, A. Short Natural Fibre Reinforced Polyethylene and Natural Rubber Composites: Effect of Silane Coupling Agents and Fibres Loading. *Compos. Sci. Technol*., **2007**, *67*, 1627-1639. https://doi.org/10.1016/j.compscitech.2006.07.003

[20] Boussehel, H. Influence of 3-(Trimethoxysilyl) Propyl Methacrylate Coupling Agent Treatment of Olive Pomace Flour Reinforced Polystyrene Composites. *Rev. Compos. Mater. Av*. **2019**, *29*, 375-380. https://doi.org/10.18280/rcma.290606

[21] Pugh, C.; Jana, S.C.; Swanson, N.; Raut, P.; Albehaijan H. Polybutadiene Graft Copolymers as Coupling Agents for Carbon Black and Silica Dispersion in Rubber Compounds. U.S. Patent US 2017/0298166 A1, Oct. 19, 2017.

[22] Guy, L.; Pevere, V.; Vidal, T. Use of a Specific Functionalised Organosilicon Compound as a Coupling Agent in an Isoprene Elastomer Composition Including a Reinforcing Inorganic Filler. U.S. Patent US20120225233A1, March 17, 2015.

[23] Swanson, N. Polybutadiene Graft Copolymers as Coupling Agents in Rubber Compounding. PhD Thesis, Akron University, USA, 2016.
[24] Titvinidze, G.; Tatrishvili, T.; Mukbaniani, O. Chemical Modification of Styrene with Vinyl Containing Organosiloxane via Friedel-Crafts Reactions. *Abstracts of Communications of International Conference Enikolopov's Readings*, Erevan, Armenia, 4-7 October, 2006; p. 74.
[25] Grigoriev, A.P.; Fedotova O. Ya. *Laboratornyi Praktikum po Tekhnologii Plasticheskikh Mass, v dvuh chastyakh. Chast 2. Polikondensatsionnyie i Khimicheski Modifitsirovannyie Plasticheskie Massy*; Vysshaya shkola: Moskva, 1977.
[26] Mineev, V.N.; Mineev, A.V. Viscosity of Metals Under Shock-Loading Conditions. *J. Phys. IV France* 1997, **7**, C3-583 – C3-585; https://doi.org/10.1051/jp4:19973100
[27] Liu, C.; Tanaka, Y.; Fujimoto Y. Viscosity Transient Phenomenon During Drop Impact Testing and its Simple Dynamics Model. *World J. Mech*. **2015**, *5*(3), 33-41. https://doi.org/10.4236/wjm.2015.53004
[28] Mukbaniani, O.; Brostow, W.; Hagg Lobland, H.E.; Aneli, J.; Tatrishvili, T.; Markarashvili, E.; Dzidziguri, D.; Buzaladze, G. Composites Containing Bamboo with Different Binders. *Pure & Appl. Chem*. **2018**, *90*, 1001-1009. https://doi.org/10.1515/pac-2017-0804
[29] Mukbaniani, O.; Brostow, W.; Aneli, J.; Markarashvili, E.; Tatrishvili, T.; Buzaladze, G.; Parulava, G. Sawdust Based Composites. *Polym. Adv. Technol*. **2020**, *31*, 1-8. https://doi.org/10.1002/pat.4965
[30] Brostow, W.; Hagg Lobland, H.E.; Hong, H.J.; Lohse, S.; Osmanson, A.T. Flexibility of Polymers Defined and Related to Dynamic Friction. *J. Mater. Sci. Res*. **2019**, *8* (3), 31-35. https://doi.org/10.5539/jmsr.v8n3p31
[31] Brostow, W.; Fałtynowicz, H.; Gencel, O.; Grigoriev, A.; Hagg Lobland, H.E.; Zhang, D. Mechanical and Tribological Properties of Polymers and Polymer-Based Composites. *Chem. Chem. Technol*. **2020**, *14*, 514-520. https://doi.org/10.23939/chcht14.04.514
[32] Brostow, W.; Hagg Lobland, H.E. *Materials: Introduction and Applications*. John Wiley & Sons, 2017.
[33] Hashim, R.; Nadhari, W.N.A.W.; Sulaiman, O.; Kawamura, F.; Hiziroglu, S.; Sato, M.; Sugimoto, T.; Seng, T.G.; Tanaka, R. Characterization of Raw Materials and Manufactured Binderless Particleboard from Oil Palm Biomass. *Mater. Des*. **2011**, *32*, 246-254. https://doi.org/10.1016/j.matdes.2010.05.059
[34] Kalogeras, I.M.; Hagg Lobland, H.E. The Nature of the Glassy State: Structure and Transitions. *J. Mater. Educ*. **2012**, *34*, 69-94.
[35] Iulianelli, G.; Bruno Tavares, M.; Luetkmeyer, L. Water Absorption Behavior and Impact Strength of PVC/Wood Flour Composites. *Chem. Chem. Technol.* **2010**, *4*, 225. https://doi.org/10.23939/chcht04.03.225
[36] Brostow, W.; Menard, K.P.; Menard, N. Combustion Properties of Several Species of Wood. *Chem. Chem. Technol.* **2009**, *3*, 173. https://doi.org/10.23939/chcht03.03.173
[37] Pyshev, S.; Miroshnichenko, D.; Malik, I.; Bautista Contreras, A.; Hassan, N.; Abd ElRasoul, A. State of the Art in the Production of Charcoal: a Review. *Chem. Chem. Technol*. **2021**, *15*, 61-73. https://doi.org/10.23939/chcht15.01.061
[38] Brostow, W.; Gonçalez, V.; Perez, J.M.; Shipley, S.C. Wetting Angles of Molten Polymers on Thermoelectric Solid Metal Surfaces. *J. Adhes. Sci. Technol*. **2020**, *34*, 1163-1171. https://doi.org/10.1080/01694243.2019.1701893

Received: April 23, 2021 / Revised: June 01, 2021 / Accepted: July 22, 2021

ДЕРЕВНА ТИРСА ПЛЮС СИЛІЛЬОВАНІ СТИРОЛЬНІ КОМПОЗИТИ З НИЗЬКИМ ВОДОПОГЛИНАННЯМ

Анотація. *На основі деревної тирси та силільованого стирену як в'яжучого, що діє одночасно і як зміцнюючий агент, виготовлені екологічно чисті композити. Досліджено структуру поверхні композитів за допомогою скануючої електронної мікроскопії та енергодисперсійного рентгенівського мікроаналізу. Встановлено, що міцність на згин збільшується з підвищенням температури від 453 до 493 К при постійному тиску 15 МПа. Показана можливість перебігу гетерогенних реакцій між активними групами триетоксисилільованого стирену та тирсою, які призводять до збільшення просторової (на питомий об'єм) концентрації хімічних зв'язків. Ударна в'язкість збільшується в тому ж діапазоні температур від 14,6 до 25,8 кДж/м^2. Поглинання води, визначене через 3 і 24 години, змінюється в широкому діапазоні. Найнижче значення становить 4,1 мас.% води через 24 години.*

Ключові слова: *тирсові композити, в'яжучі, низьке водопоглинання, термогравіметричний аналіз, диференціальна скануюча мікроскопія.*