The Effect of Ultraviolet Light on the “Liquid Wood”

Nedelcu Dumitru¹, Zăgan Sabina², Negreanu-Pirjol Ticuta², Zăgan Remus², Cărausu Constantin¹

¹Technical University “Gheorghe Asachi” of Iasi, Romania, Blvd. Mangeron, No. 59A, 700050 Iasi, Romania
²Constanta Maritime University, Naval Electromechanical Faculty, Mircea cel Batran Street, No. 104, 900663, Constanta, Romania

Corresponding author: Dumitru Nedelcu, nedelcu1967@yahoo.com

Abstract. To preserve resources, the goal is to use biobased materials containing the maximum possible amount of renewable biomass-based derivatives to secure a sustainable future. Bioplastics, biocomposites, biological fibres and related biomaterials will serve as substitutes for materials and products traditionally made from petroleum resources. To support this need, in 1998, Fraunhofer Institute of Chemistry and Tecnaro GmbH Company (founded by Jurgen Pfitzer and Helmut Nagele in Germany) investigated and developed a new compound made of wood components that can be processed as a thermoplastic material. It is well known that bioplastic and biocomposite materials represent another important group of bio-materials that include plastics reinforced with natural fibers and wood-plastic composites (WPCs). The aim of this research is to identify the behavior of “Liquid Wood” after UV irradiation. The materials used were Arbofill Fichte, Arboblend V2 Nature and Arboform L, V3 Nature. The samples were obtained by injection and the experimental study plan followed the Taguchi method with six input parameters and two levels for each of them. Three samples from each material were tested in an ultraviolet environment using different time of exposure in order to establish the material characteristics. After the irradiation process the material did not turn to yellow, which suggests that the composition of the sample liquid timber inhibitors have stability and the number of α-carbonyl (C = O) groups is sufficiently low. After the graphs analyzing can be inferred relatively similar performance of the samples in the first stage both UV and the VIS, indicating that the activity is almost absent. In UV is clearly observed the peak amplitude (maximum absorbance) at different wavelengths (λ). So, in terms of peak intensity the samples follow the order: Arboform L, V3 Nature; Arbofill Fichte and Arboblend V2 Nature.

1. Introduction

Human society has benefited tremendously from the use of plastics, one of the most highly valued materials mainly because of their extraordinary versatility and manufacturability.

Almost all synthetic plastics are made from petroleum and its allied components. In addition, plastics derived from fossil sources are mostly non-biodegradable. The increased use of plastics, along with other materials, over the years has resulted in an increase of plastic waste, which often is dumped as municipal solid waste. [1]. Taking into account the samples properties from “liquid wood”, this biodegradable material [2] is capable of replacing plastic and providing mankind with new materials, [3, 4, 5]. Norbert Eisenreich, a senior researcher at the Fraunhofer Institute for Chemical Technology
in Germany (ICT), said that Arboform, the new material, is made of lignin, which can be derived from soft tissues of wood, [8]. Once mixed with several other ingredients, the substance turns into solid and non-toxic alternative for plastics.

The starting point for a new class of thermoplastic materials from renewable resources is lignin, a natural polymer that is the main constituent of biomass, in trees and other woody plants with an amount of up to 30%, [1]. This growing interest about a green and sustainable chemistry has also contributed to call attention to biomass and specifically on lignocellulosic feedstock as a promising, renewable and vast resource for biopolymers [6]. Lignocellulosic biomass is primarily composed of three biopolymers: cellulose, hemicelluloses and lignin [7]. Lignin plays a major role in woody plants, adding strength and structure to the cell walls, controlling fluid flow and protecting against biochemical stresses by inhibiting enzymatic degradation of other chemical components [6].

The absorption spectra represent the signal dependence by the wavelength $\lambda$. There are many possibilities of obtaining absorption spectra, but the most common used is the representation of absorbance according to wavelength: $A = f (\lambda)$. The other variants, less used - called all absorption spectra - are $T = f (\lambda)$, $\log A = f (\lambda)$, $e = f (\lambda)$ or $\log e = f (\lambda)$. The last two are used mainly to characterize the molecular species because it does not depend on the experimental conditions are the spectra measurements. Each material has a characteristic absorption spectrum, like general form, like spectral domains, like peaks numbers and the ratios between the intensities of the different peaks. The maximum number and the general shape of the curve represent the qualitative characteristic after that can be identifying substances.

2. Technology, Methodology and Research Plan

The samples were obtained using the injection molding process, [10]. “Liquid wood” pellets, (also known under the name of arboform) are mainly composed of lignin discarded during the paper-making process, combined with cellulose and wood waste from industrial plants. These pellets are put in a bunker where are subjected to hot-air drying for two-four hours. After that, they are transferred into the bunker of an injection machine, from where the material enters into an injection cylinder, electrically heated at 160-180° C, being afterwards injected into a mold, which is water cooled at a temperature of 23°C. The main parameters of the “liquid wood” during the injection process, which could be taken into account, are: melting temperature, molding temperature, injection rate, injection and holding pressure, cooling time, holding pressure time inside the mould and injection time.

The experiments were planned using the Taguchi methodology, [9] and the model proposed by Viger and Sisson was easy to be studied. Each experiment was conducted three times. The proposed matrix model takes into consideration six technological parameters with two levels (table 1). The experimental research determined the coefficients of a type (1) model:

$$Z = M + T_{\text{top}} + t_{\text{inj}} + S_s + P_{\text{inj}} + T_{\text{mat}} + P_{\text{inj}} T_{\text{top}} + P_{\text{inj}} t_{\text{inj}} + P_{\text{inj}} S_s + P_{\text{inj}} T_{\text{mat}}$$  \hspace{1cm} (1)

where: $M$-general average; $T_{\text{top}}$-melting temperature, [°C]; $t_{\text{inj}}$-injection time, [s]; $S_s$-screw displacement, [mm], $P_{\text{inj}}$-injection pressure, [MPa], $T_{\text{mat}}$-matrix temperature, [°C]. The most significant influence on the process is exercised by injection pressure followed by melt temperature and matrix temperature. These are followed by screw speed, injection time and cooling time, which are though less significant. After the orthogonally and number of degrees of freedom conditions were analyzed, there were 16 experimental tests to be made.

In this study were used three samples from each of the three types of “liquid wood”: Arbofill Fichte, Arboblend V2 Nature and Arboform L V3 Nature. All the samples were exposed to different exposure times to UV-VIS radiation, table 2.


**Table 1.** The levels values of input parameters

|        | **T<sub>top</sub>** [°C] | **t<sub>inj</sub>** [s] | **t<sub>r</sub>** [s] | **S<sub>s</sub>** [mm] | **P<sub>inj</sub>** [MPa] | **T<sub>mat</sub>** [°C] |
|--------|-------------------------|----------------------|---------------------|---------------------|-------------------------|------------------------|
| **First level** | 145 | 9 | 18 | 60 | 80 | 50 |
| **Second level** | 160 | 11 | 25 | 80 | 100 | 80 |

**Table 2.** Exposure time to UV-VIS radiation

| Exposure time, [min] | **Arboform L V3 Nature** | **Arbofill Fichte** | **Arboblend V2 Nature** |
|----------------------|--------------------------|---------------------|-------------------------|
| **First Sample**     | 300 | 315 | 315 |
| **Second Sample**    | 300 | 600 | 600 |
| **Third Sample**     | 140 | 760 | 760 |

The samples were irradiated with UV lamp Philips TUV 11W T5 4P-SE in a hermetically sealed steel enclosure. It was used ultraviolet light, with short range UV (UVC) considered that they are also germicidal UV, because UV-C radiation can break down chemical bonds. The value of wavelength used is of 2.537 Angstroms (254 nm). It is known that the exposure to light such as ultraviolet irradiation lignin in phenols are known to produce phenoxy radicals that can be readily oxidized to yellow o-quinones (figure 1).

![Fig. 1. Several lignin structures – formation and subsequent oxidation](image)

Spectrophotometric analysis was performed using CECIL EC -3021 Super Aurius spectrophotometer in order to study the quality of the spectra in the UV -VIS (ultraviolet - visible) domain. Solid samples of each material were brought to fine-grained, homogeneous and then passed in liquid and the testing for homogeneity has been performed. Thus, the samples were subjected to a digestion process (mineralization) to be read by the equipment. For this purpose, there were used different mixtures of acids HNO₃ / H₂SO₄ and HNO₃ / H₂SO₄ / HCl. Second mixture was chosen for more efficient digestion. There have been used high concentrations of pure acids: HNO₃ 65 % GR; H₂SO₄ 96 % GR; HCl 37 %. The proportion was HNO₃: H₂SO₄: HCl = 3ml: 3ml: 3ml. After digestion, the samples were brought to volume in 100 ml volumetric flasks with distilled water as follows: mineralized sample was poured the contents over a quantity of distilled water in 100 ml volumetric flask and then brought the volumetric flask to the mark with distilled water. After calibrating the apparatus, the reference sample (blank sample) was measured. It has been used high quality quartz cuvettes with a path spectral length of 10 mm for both reference and sample.

3. **Results and discussion**

The qualitative spectra of the samples analyzed are shown in Figures 2, 3 and 4.
Fig. 2. The UV-VIS spectrum for Arbofill Fichte: a-UV-VIS full spectrum; b-UV spectrum; c-VIS spectrum
Fig. 3. The UV-VIS spectrum for Arboform L, V3 Nature: a-UV-VIS complete spectrum; b-UV spectrum; c-VIS spectrum
Figure 2 shows the attenuation spectrum on the basis of UV. The spectrum that occur in the absorbance values read at 345, 358, 371, 386, 425, 505, 544, 631, 660, 724 and 747 nm, which is flatten and indicates that the tested material has absorbed UV and thus shows a good performance under the influence of UV irradiation.

From the figure 3, it can be seen a similar behavior as in the case of Arbofill Fichte in the sense of a flattening of the spectrum. In this case, the recorded values range from 345, 358, 371.5, and 386 up to 872 nm. It can also be concluded that this material absorbs UV radiation and has good efficiency under the UV irradiation.

From the graphs shown in Figure 4 is drawn the same conclusion, namely that this material has good performance under the UV radiation.

To achieve prominence between samples made of four materials was done in Figure 5, the spectra overlap, as follows: Figure 5a represents the UV-VIS spectra overlap completely; Figure 5b represents the UV spectra overlap and VIS spectra overlap in Figure 5c.

**Fig. 4.** The UV-VIS spectrum for Arboblend V2 Nature: a-UV-VIS complete spectrum; b-UV spectrum; c-VIS spectrum
4. Conclusions

Digestion of the samples was performed with an array of acids. Was measured the final pH of the solutions prepared (9 ml acid / mineralized sample + 91 ml distilled water) and got the 0.5 value. The analyzing of graphs shows a relatively close performance of the samples in the first stage both for UV and VIS. During the last domain, the activity is almost nonexistent. In
UV was clearly observed the peak amplitude (maximum absorbance) to different wavelengths (\(\lambda\)). So, in terms of peaks intensity the studied materials are in the following order: Arboform L, V3 Nature, Arbofil Fichte and Arboblend V2 Nature. Absorbance peaks were seen in the UV into two groups lengths: first group: 291.5nm - 295.5nm; 297.0nm - 298.5nm; 302.0nm – 303.0nm; 304.0nm; 307.0nm, second group: 345.5nm; 358.0nm; 371.0nm -371.5nm; 385.0nm. If the study object in the next stage will be the acid addition influencing the spectrum of the sample characteristics, research can continue with another solvent matrix to maximize the effect of acids in the next stage, namely pH of samples. Future studies will focus on identifying these types of materials’ resistance to the action of substances highly acidic (pH=1). The first data prove that these materials could play an important role in the manufacture of furniture specifically for areas with high acidity or specific use in chemical laboratories, using acidic substances. Based on actual research, it can be concluded that all materials studied subjected to such treatment will increase resistance to corrosive properties.

References

[1] Srikanth Pilla (2011), Engineering Applications of Bioplastics and Biocomposites- An overview, Handbook of Bioplastics and Biocomposites Engineering Applications,

[2] Björn Winberg, KAM Industries, Albi Plastic Scandinavia AB, Commercial biopolymers Properties and limitations, 2010

[3] Dumitru Nedelcu, Ciprian Ciofu, Nicoleta Monica Lohan, (2013), Microindentation and Differential Scanning Calorimetry of “Liquid Wood”, Composites Part B: Engineering, doi: 10.1016/j.compositesb.2013.05.024 , vol. 55, pp. 11-15.

[4] Dumitru Nedelcu, (2013), Investigation on microstructure and mechanical properties of samples obtained by injection from Arbofill, Composites Part B: Engineering, Volume 47, April 2013, pp. 126–129, doi: 10.1016/j.compositesb.2012.11.023.

[5] Dumitru Nedelcu, Radu Comaneci, (2013), Microstructure, Mechanical Properties and Technology of Samples obtained by Injection from Arboblend, Special Issue on Evolution of Engineering, Technologies and Materials, ModTech2013 International Conference, 27-29 June, Sinaia, Romania, Indian Journal of Engineering & Materials Sciences, manuscript accepted.

[6] Laurichesse S. Av’erous L, Chemical modification of lignins: towards biobased polymers, Progress in Polymer Science (2013),http://dx.doi.org/10.1016/j.progpolymsci.2013.11.004

[7] Patanjali Varanasi, Priyanka Singh, Manfred Auer, Paul D Adams, Blake A Simmons and Seema Singh, Survey of renewable chemicals produced from lignocellulosic biomass during ionic liquid pretreatment,Biotechnology for Biofuels 2013

[8] http://www.tecnaro.de/english/willkommen.htm?section=we, Accesed: 20.11.2011

[9] Nedelcu D.; Pruteanu, O. Aspecte ale formarii canelurilor exterioare prin deformare plastica la rece utilizand metoda Taguchi, Tehnica-Info Publishing House, Chisinau, 2000; pp. 243-261

[10] Ciprian Ciofu, Daniel Mindru, Injection and Micro Injection of Polymeric Plastics Materials, Int. J. of Modern Manufacturing Technologies, Vol. V, No. 1/2013, 49-68