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THE THERMODYNAMIC BEHAVIOR OF “LIQUID WOOD”

BY

**ELENA PUIU (COSTESCU)^{1*}, LIVIU LEONTIE², MIHAI DUMITRAȘ²,
MIHAI ASANDULESA³, DORIN VĂIDEANU² and
TUDOR-CRISTIAN PETRESCU⁴**

“Gheorghe Asachi” Technical University of Iași, Romania,

¹Faculty of Machine Manufacturing and Industrial Management

⁴Faculty of Civil Engineering and Building Services

²“Alexandru Ioan Cuza” University of Iași, Romania,

Faculty of Physics

³“Petru Poni” Institute of Macromolecular Chemistry of Iași, Romania

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Abstract. Being a material similar to a “thermoplastic”, it is essential to establish the thermodynamic performance of “liquid wood” and its thermal properties. It is intended to study the comportment of “liquid wood” in the heating-cooling process. The study of thermodynamic behavior it was carried out for different ranges of temperature cycles of heating and cooling. These temperature intervals have included negative temperatures up to -400°C and high temperatures up to 800°C . Also, the determinations were made regarding thermal degradation of the “liquid wood”, in the tow presentation forms: Arboform and Arboblend. Considering that it the electrical properties of the “liquid wood” were previously studied, it was intended to see how these properties change with the temperature variation. The results are prone to encourage further research, thermodynamic properties of the “liquid wood” shows that they are suitable for use in many industries successfully replacing

*Corresponding author; *e-mail*: naturaone@gmail.com

other traditional materials (mainly, the plastics materials) that are polluting, having a very low rate of biodegradability.

Keywords: weight loss; crystalline; point of inflection; phase transformations; aggregation state.

1. Introduction

In recent times, the need of so-called “green” materials for various engineering and product applications has increased considerably, in lieu of the adjustments of global environmental statutes and law bills. These aim to impose a cutback on the CO₂ emissions. The gradual exhaustion of raw resources (petroleum, natural gas) has led to much research, with the purpose of evaluating the feasibility of utilizing “green” composite materials. In support of this research, the Fraunhofer Institute, working closely with Helmut Nägele and Jürgen Pfitzer, has created the products known as Arboform and Arbofill following 13 years of effort. The abovementioned products are ordinarily known as “liquid wood”, by virtue of being amorphous at regular temperatures. They present properties similar to plastics, however they are sourced from sustainable resources and are ecological (Rognoli *et al.*, 2010).

2. Technology and Experimental Plan

The trials concerning thermodynamic behavior were carried out using a thermal analyzer F1 Jupiter, Netzsch STA 449, with concurrent registration of TG data (Thermal Gravimetric Analysis, in the mass of the specimen is assessed through temperature fluctuation) and DTA (Differential Thermal Analysis, where it is evaluated the temperature variation among the sample and the source temperature dependent). In order to carry out the data evaluation, Proteus 6.0 software has been utilized (Höhne *et al.*, 2013).

Samples analyzed consisted of Arboform and Arboblend grains, with the mass of approximately 40 mg. The description of the experimental environment is as follows: calefaction pace of 10 K/min, alumina-made melting pots - with confinement agent from the extraneous environment consisting of a stream of N₂ - with the volumetric discharge rate $Q_v = 40$ mL/min.

Non-isothermal investigations were accomplished on a Netzsch STA 449 F1 Jupiter thermal analyzer, employing concurrent registration of TG and DTA data. Once again, Proteus 6.0 software was put to use for data assessment.

The specimens put forward to analysis were constituted of granular Arboform and Arboblend, with a sample mass of roughly 40 mg. Experimental parameters were: calefaction pace of 10 K/min, alumina-made melting pots, under a steady N₂ stream of 40 mL/min. The procedures involving heating and cooling were performed under a primary reference temperature of $t_0 = 200^\circ\text{C}$.

Regarding the change of electrical characteristics of “liquid wood” following a term of 365 days and its temperature-dependent fluctuation, the electrical conductivity and relative permittivity were evaluated, as well as the difference on two phases, in connection with the temperature.

The dielectric determinations have been executed at room temperature, with the help of a Novocontrol apparatus (Broadband dielectric spectrometer Concept 40, GmbH Germany), using the frequency spectrum of $1 \div 10^6$ Hz, setting up the specimens of homogenous amidst two copper-plated round electrodes, through which an electric current rated at 1V passed (Musteață *et al.*, 2014).

Subsequent to the results achieved to certify the assumptions, analyzes and determinations were made. XRD crystal structure determination performed by means of X-ray specimens in fine grain form. The operating procedure is utilizing X-rays, length $\lambda = 1.54182 \text{ \AA}$, to retrieve an anticathode of Cu Ka.

Through the accomplishment of these analyzes it was attempted to detect if any parallels can be drawn among the structure and the thermal experiments and to ascertain the elements in the indicated materials, which are essential in establishing the thermodynamic performance of the material. In order to portray this, the results were introduced in OriginPro 9 software, which allows plotting graphs, results interpretation and facilitates the drawing of conclusions. Concerning the results obtained, which highlight the thermal properties for the three materials, the subsequent graphs were drawn (Figs. 1 and 2).

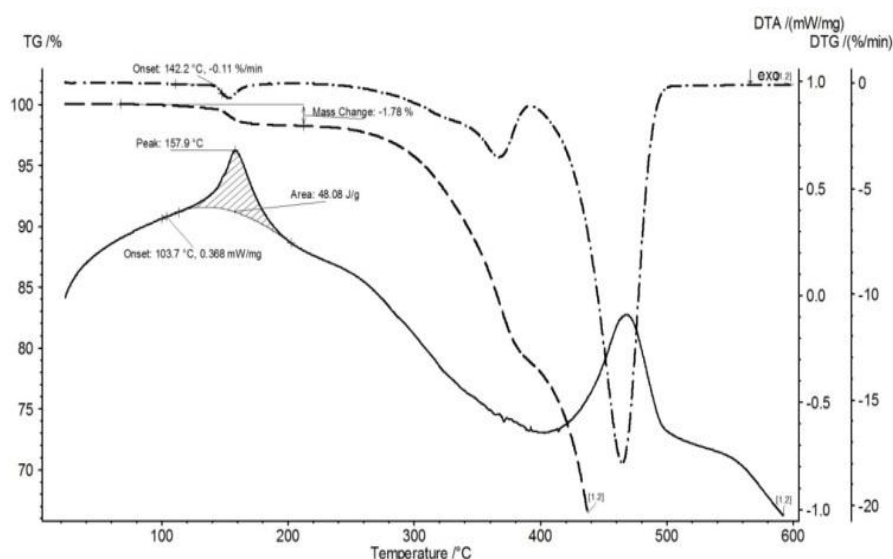


Fig. 1 – Heating curve graph for arboblend sample.

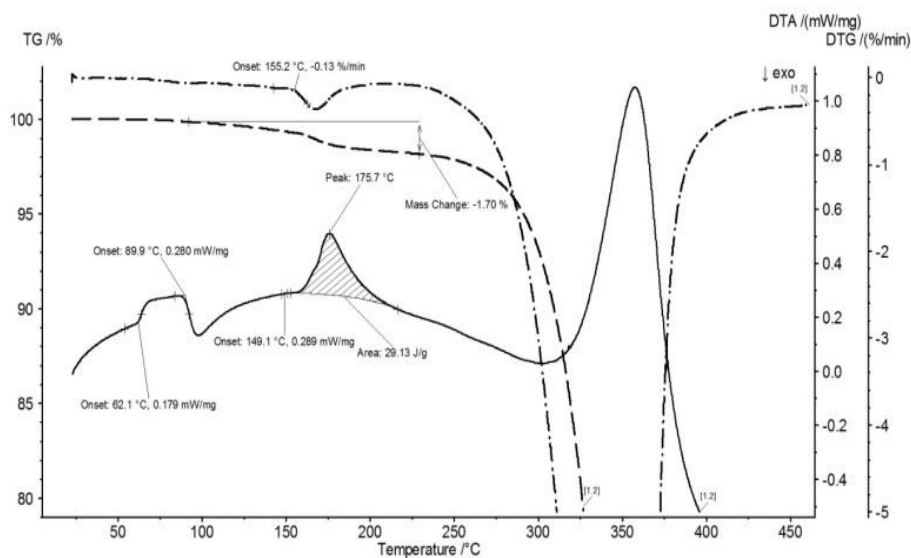


Fig. 2 – Heating curve graph for arboform sample.

Following the investigation of the three graphs several important aspects may be noticed: the melting point of arboblend begins at about $t = 103.7^{\circ}\text{C}$, at $t = 142.2^{\circ}\text{C}$, temperature the entire mass of material is almost melted, only a small amount of 0.11% remains unmelted, at temperature $t = 157.9^{\circ}\text{C}$ the entire mass of the material is melted, it can be seen that at $t = 142.2^{\circ}\text{C}$ the material begins to lose mass (1.78%) until it melts completely. Continued warming is observed as the material gradually loses mass, culminating at temperatures above 400°C which is seen a steep drop from the table, and around 460°C a second phase transformation occurs, that is most likely a vaporization. Same phase transition for Arboform is observed, with a second order glass transition material showing a crystalline phase. The melting temperature is higher than in the case of the other two materials. In the process of melting arboform loses mass (1.7%).

Resting on these remarks and attempting to seek out probable explanations for the thermodynamic performance of the three materials, a series of experiments have been conducted, analyzing the X-ray diffraction (XRD) and spectral infrared (FTIR).

Following XRD analyzes, a series of charts were obtained that endorse the presence of a second type of transformations, analogous to a vitreous shift from a crystalline state to an amorphous one. It was in these states of the two materials that phase shifts of second type have been spotted (Fig. 3a, b).

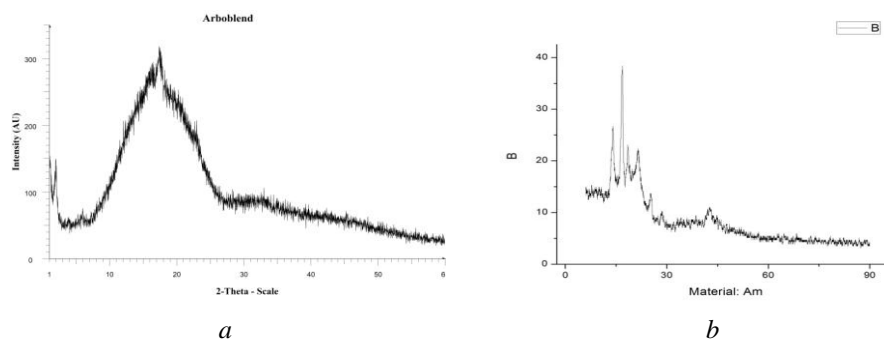


Fig. 3 – a) XRD arboblend; b) XRD arboform.

Arboblend shows no crystalline state (Fig. 3a) while Arboform shows crystalline state (Fig. 3b).

Following XRD analyzes, a series of charts were obtained that uphold the presence of a second type of transformations, analogous to a vitreous shift from a crystalline state to an amorphous one. It was in these states of the two materials that phase shifts of second type have been spotted (Fig. 3a, b) (Nägele *et al.*, 2005).

Lignin behaves as a forming agent for the biodegradable composite and promotes crystallization. The extent of the lignin substance (amorphous in itself) takes part in the polymer crystallization process (Madden *et al.*, 1971).

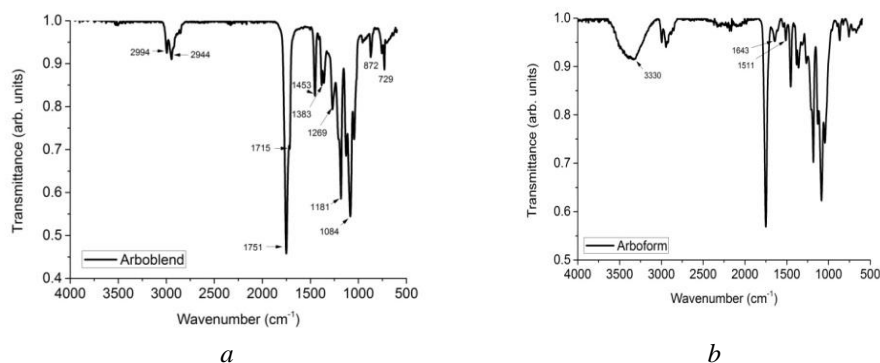


Fig. 4 – a) Grafic FTIR arboblend; b) Grafic FTIR arboform.

The samples don't seem to contain polymers with aminic and/or amidic functions. Arboblend it looks like it doesn't contain OH functions and only very small or no aromatic functions; it is possible however that the OH functions were crosslinked during manufacturing (the estheric and etheric signal is stronger than in Arboform, plus the probable supplementary estheric signal is

from 1269 cm^{-1}). Arboform has spectral characteristics relatively close to Arboblend (possibly a high percentage of polihydroxycanoates and other added polyesters/polyethers), the notable exceptions being given by the presence of OH functions and a signal possibly given off by aromatic rings from lignin derivatives (Puiu Costescu *et al.*, 2017).

The dielectric characteristics of materials - illustrated by the dielectric constant, ϵ' , the dielectric loss, ϵ'' AC conductivity, σ etc. - hinge on their chemical architecture. The dielectric feedback has been recorded in the 1 Hz – 1 MHz frequency spectrum and in the 20 – 100°C temperature interval.

Fig. 5 displays the development of the dielectric constant with regard to frequency, for analyzed samples. ϵ' diminishes steadily along with the frequencies, because of the capability of dipolar units to adjust themselves in the path of the exterior field. As such, at small frequencies, the dipoles have sufficient time to trail the alternate electric field but, as frequency escalates, the dipoles require more time than the applied field, thus the magnitude of ϵ' is reduced.

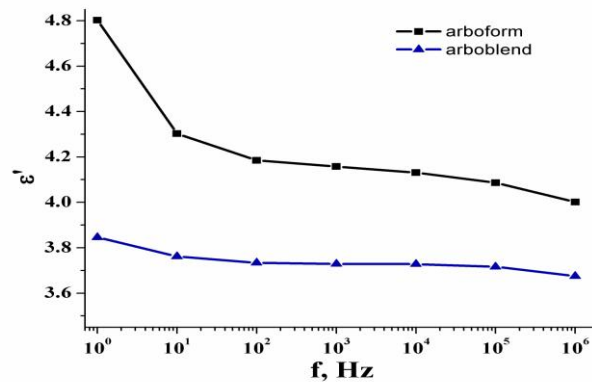


Fig. 5 – Comparative evolution of the dielectric constant function of frequency ($T = 30^\circ\text{C}$).

AC conductivity was obtained from the dielectric loss with the help of the following formula:

$$\sigma_{AC} = \epsilon_0 \omega \epsilon'' \quad (1)$$

where ϵ_0 is the permittivity of free space, ω is the angular velocity and ϵ'' is the dielectric loss.

AC conductivity grows together with frequency in an obverse way than the dielectric constant (Fig. 6). At a frequency of 1 Hz, the values of conductivity are: 4.2×10^{-13} S/cm for Arboform, 5.1×10^{-13} S/cm for Arboblend and 1.2×10^{-13} S/cm for Arboblend sample. The values are specific to insulator materials.

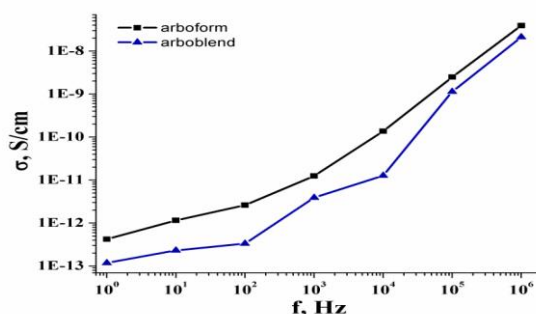


Fig. 6 – AC conductivity change in concert with frequency at 30°C.

Fig. 7 shows the temperature dependencies of conductivity for all analyzed samples. Accordingly, one can observe the possible thermal transitions at 25°C, 70°C and around 90°C.

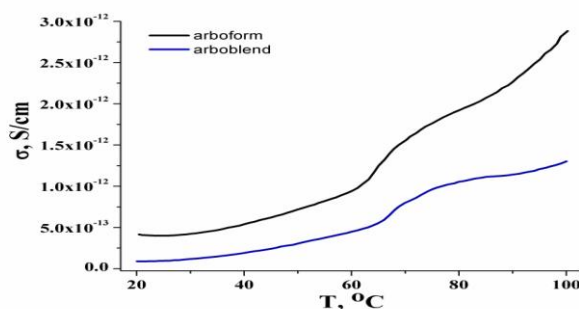


Fig. 7 – Temperature dependences of AC conductivity.

3. Conclusions

The studied materials behave during the heating process as amorphous solids. Arboform have in their composition a substance which can be found in a crystallized form in the temperature interval [65°C – 90°C]. Arboblend exhibits a loss of mass until it reaches its liquid state. A possible cause may be the evaporation of one of its constituents. It might be a substance which acts as a binder for the material.

During the melting process, Arboform loses mass, the explanation being similar to the one for Arboblend. The melting temperature of Arboform is bigger than in the case of Arboblend; this means that this material is more stable, from a temperature point of view. Arboform evaporates at a smaller temperature than Arboblend. This aspect might induce the idea that this material has a higher degradability than Arboblend.

The lignin that can be found in the composition of the three materials has undergone transformations and is not to be found anymore in the molecular shape present in wooden fibers.

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COMPORTAMENTUL TERMODINAMIC AL „LEMNULUI LICHID”

(Rezumat)

Fiind un material asemănător unui „termoplastic” este foarte important de determinat comportamentul termodinamic al „lemnului lichid” cât și proprietățile termice și electrice ale acestuia. Ne-am propus să studiem comportamentul lemnului lichid în cadrul procesului de încălzire-răcire. Studiul comportamentului termodinamic s-a efectuat pentru diverse intervale de temperatură a ciclurilor de încălzire și răcire. Aceste intervale de temperatură au cuprins și temperaturi negative de până la -40°C și temperaturi ridicate de până la 800°C . S-au efectuat determinări și în ce privește degradarea termică a „lemnului lichid” sub două forme de prezentare: arboform și arboblend. Ținând cont că anterior am efectuat studii asupra proprietăților electrice ale „lemnului lichid” am căutat să vedem cum se modifică aceste proprietăți la variația temperaturii. Rezultatele obținute sunt de natură să încurajeze continuarea cercetărilor, proprietățile termodinamice ale „lemnului lichid” îl recomandă spre a fi utilizat în multe domenii de activitate, înlocuind cu succes alte materiale clasice, dar care sunt poluante, având o biodegradabilitate foarte scăzută, care se produce într-un interval de timp de câteva sute de ani.