

THERMAL AND ELECTRICAL BEHAVIOURS OF THE ARBOFILL „LIQUID WOOD”

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Abstract: Thermal and electrical properties of the Arbofill „liquid wood” considered as a partially biodegradable composite (a novel bio-polymer class of material consisting in various amounts of lignin, natural fibers and bio-bonds aditives) are analyzed. The results are discussed in terms of differential scanning calorimetry (DSC), of X-Ray diffraction (XRD), of infrared spectrometry (FTIR) and of dielectrical spectroscopy analyzes (DS).

DSC thermal analysis specifies that the Arbofill material presents a glass transition between 64,7oC and 88oC (second order transition with 24 mW/mg absorbed energy). XRD analysis reveals that, during this transformation, the Arbofill material presents a crystalline structure, whose complex nature is characterized through FTIR analysis. The dependence of dielectric constant and AC conductivity on frequency are shown by DS electrical analyzes, while the AC conductivity dependence on temperature reconfirms the existence of above mentioned transition.

Key words: Arbofill, FTIR, XRD, DSC.

1. INTRODUCTION

Lately, the demand on green materials for different engineering and product applications have increased considerable due to the change of worldwide legislations which force the reduction of carbon footprints. The gradually ending out of natural resources (petroleum, natural gas) had conducted at many researches in order to analyze the feasibility and the viability of using green composites materials.

In support of these research Institutului Fraunhofer Institute together with Helmut Nägele and Jürgen Pfitzer have developed Arboform and Arbofill materials after 13 years of work. These products are commonly known as "liquid wood" because they are amorphous at normal temperatures. They presents plastics properties, but unlike these they are obtained from renewable resources and are biodegradable.

In contrast to other types of “liquid wood”, Arbofill is composed of 60-65% lignin and petrochemical polymers such as polyethylene or polypropylene, mixed with natural fibers such as hemp, cotton or wood. By modulation of the polymer component, different types of Arbofill can be obtained depending on the needs of the individual customer and the purpose use of the material. Even this product is completely recyclable and has the appearance of a light wood, [1].

Several typical applications of Arbofill material are: household items, office supplies, packaging, clothes hangers, technical profiles, chairs.

2. TECHNOLOGY AND EXPERIMENTAL PLAN

The experiments on the behavior of the thermodynamic were performed on a thermal analyzer F1 Jupiter, Netzsch STA 449, with simultaneous recording of data TG (Thermal Gravimetric Analysis in the mass of the sample is measured by the temperature variation) and DTA (differential thermal analysis in which measured the temperature difference between the sample and reference temperature dependent). The software used for evaluation of the data was Proteus 6.0. [2]

Samples analyzed consisted of grains Arbofill with mass about 40 mg. The experimental conditions were: rate of heating 10K / min, alumina crucibles agent isolation from the external environment was a flow of nitrogen with the volumetric flow rate $Q_v = 40 \text{ ml / min}$.

Non-isothermal experiments were performed on a Netzsch STA 449 F1 Jupiter thermal analyzer, with simultaneous recording of TG and DTA data. Proteus 6.0 software was used for data evaluation.

The samples submitted to analysis consisted of

granulated Arbofill, respectively, with a sample mass of about 40mg. Experimental conditions were: heating rate of 10 K/min, alumina crucibles, under constant nitrogen flow of 40 ml/min.

Processes for heating, cooling had the initial reference temperature $t_0 = 20^{\circ}\text{C}$.

Regarding change electrical properties of "liquid wood" after a period of one year and their variation with temperature we measured the electrical conductivity and relative permittivity and the variation in two sizes depending on the temperature, [3].

The dielectric measurements were performed at room temperature with a Novoncontrol setup (Broadband dielectric spectrometer Concept 40, GmbH Germany), in the frequency range of $1 \div 10^6$ Hz, placing the samples with uniform thickness between two copper plated round electrodes biased at 1V.

Following the results obtained to verify the assumptions we have made analysis and determinations XRD crystal structure was carried out by X-ray samples in powder form, the technique used is getting radiation X length $\lambda = 1.54182 \text{ \AA}$ obtained a anticatod of Cu Ka.

By performing these analyzes we sought to observe if there is any correlation between the structure and the thermal experiments and to determine substances in those materials that are very important in the thermodynamic behavior of the material.

3. RESULTS AND DISCUSSIONS

For interpretation, the results were entered into the software OriginPro 8 allowed plotting graphs.

Arbofill is seen in the graph a second order phase transformation which most likely is crystallization.

This phase transformation starts at $t = 64.7^{\circ}\text{C}$ and continues until at 88°C where we can say that crystallization of the whole substance of the material in question, after which it again becomes amorphous. The melting process begins at 165.8°C and the whole mass of material melts completely at 176.4°C .

-Not observed mass loss during the heating process until reaching the melting.

Losing weight begins to occur at 300°C getting to be the maximum temperature of 380°C occurs when the second phase transformation, most likely evaporation.

The latent heat of melting is about 0.299 mW/mg and the calorific capacity of the Arbofill is 32.69 J/g . Based on these observations and find possible explanations for the behavior of thermodynamic for the material have conducted a series of experiments analyzing the diffraction X-ray diffraction (XRD - X-ray diffraction) and spectral infrared (FTIR - Fourier transform infrared spectroscopy).

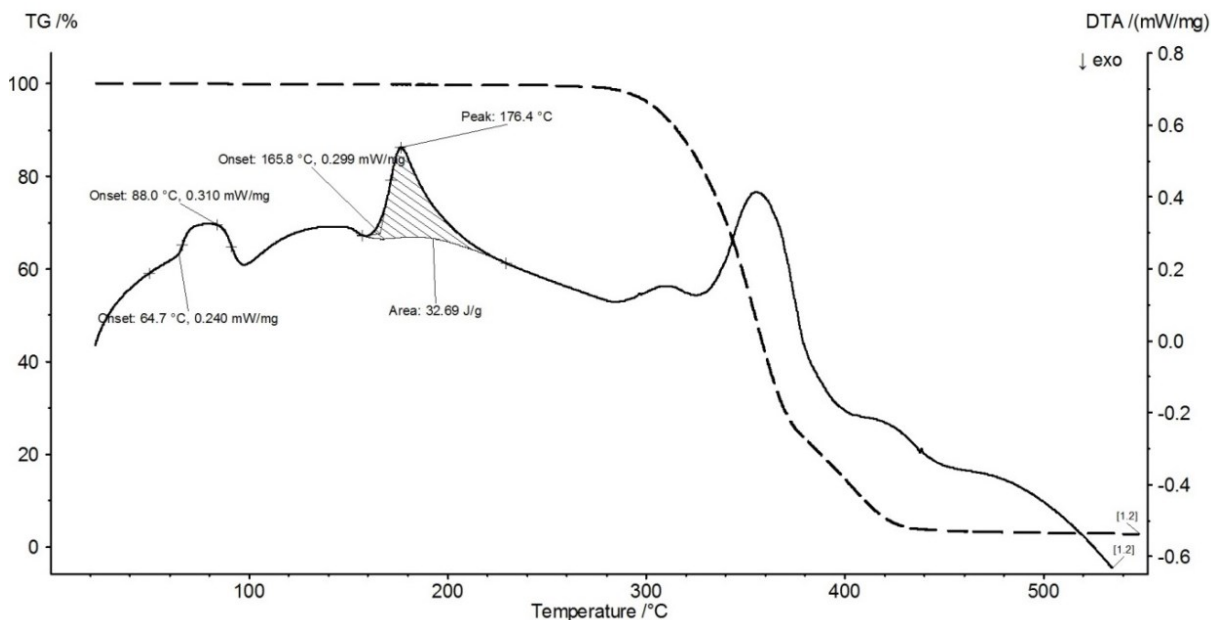


Fig.1. Heating curve graph for sample Arbofill

Regarding the determination of thermal properties for the three materials we obtained the following graphs, (figure 1).

From the study of the three graphs notice several important aspects:

XRD analyzes where we obtained a series of charts that confirm the existence of a second kind transitions corresponding to a vitreous transition from crystalline to amorphous state in the state of the material that we observed phase transitions of second kind, (figure 2).

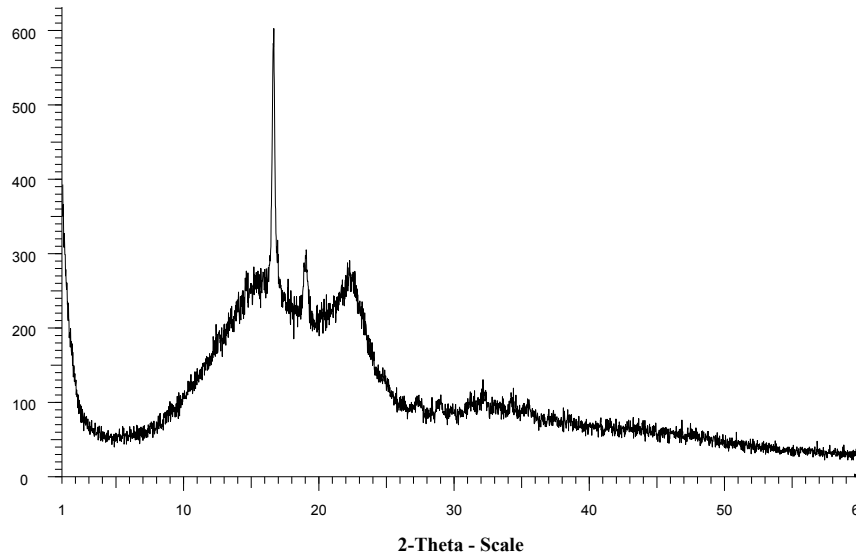


Fig.2. XRD Arbofill

The lignin has an effect on the crystallization and melting behavior of the composites that can be studied in non-isothermal DSC experiments. The degree of crystallinity can be calculated using the following equation, [4, 5]:

$$\chi(\%) = \frac{\Delta H_m}{f \cdot \Delta H_m^0} \times 100 \quad (1)$$

Lignin acts as a forming agent of biodegradable composite and facilitates crystallization. The value of the lignin content (amorphous in nature) plays a role in the polymer crystallization activity.

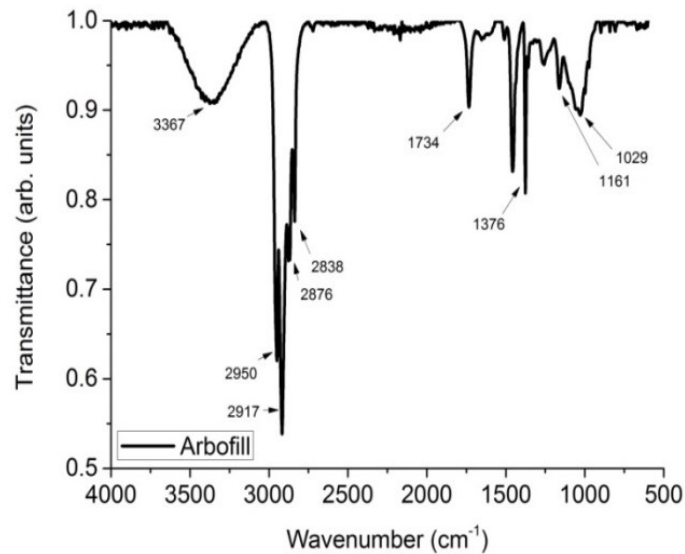


Fig.3. FTIR chart of Arbofill

The seen vibrations from the graph provide information about the chemical compounds that constituting the material:

3330-3367: O-H (lignin derivatives, polyesters, alcohols, traces of water);
 2838-2950: C-H (lignin derivatives, polyolefins, polyethylene, polypropylene, polyhydroxyalkanoates, polyesters, etc.);
 1715-1751: C=O (lignin derivatives, polyhydroxyalkanoates, polyesters, etc.);
 1643: C=O (bonded by hydrogen bonds);

1511: possibly lignin aromatic ring;
 1453: CH₂ (bending);
 1376-1383: CH₂ (wagging);
 1269: C(O)-O (asymmetrical stretching) polyesters;
 1161-1181: C(O)-O (symmetrical stretching) polyesters;
 1029-1084: C-C-O; C-O-C polyethers, lignin derivatives;
 729-872: C-H; CH₂ (rocking); there may be other variants; seem to be correlated with the ester part.
 The main observations that can be extracted are listed

below, but they also show a degree of material composition.

Arbofill, the particularly strong signal given by hydrocarbon chains at the expense of C-O linkages.

Sample does not appear to contain polymers with amine and / or amide functionalities, from polyesters and polyethers seems to indicate a complete replacement of these with fully or at least prepolymerized hydrocarbon chains (For example polyolefins such as polypropylene or polyethylene). The weak carbonyl signal from 1734 cm^{-1} certify the presence of lignin and / or other carbonyl additives.

Electrical determinations have confirmed that these materials are degradable and that at a certain temperature they have a vitreous transition.

The dielectric properties of materials, expressed by dielectric constant, ϵ' , dielectric loss, ϵ'' , AC conductivity, σ etc. depend on their chemical structure. The dielectric response has been registered in the 1 Hz – 1 MHz frequency range and in the (20 – 100) $^{\circ}\text{C}$ temperature domain.

Figure 4 presents the evolution of dielectric constant with frequency, for Arbofill sample. The dielectric constant decreases gradually with frequencies due to ability of dipolar units to orient themselves in the direction of the external field. Thus, at low frequencies, the dipoles have enough time to follow the alternative electric field but, as frequency increasing, the dipoles need longer time than the applied field and the magnitude of ϵ' decreases.

AC conductivity has been determined from dielectric loss with the formula:

$$\sigma_{AC} = \epsilon_0 \omega \epsilon'' \quad (2)$$

where ϵ_0 is the permittivity of free space, ω is the angular velocity and ϵ'' is the dielectric loss. AC conductivity increases with frequency in an opposite way than dielectric constant (figure 5). At a frequency of 1 Hz, the value of conductivity is $5.1 \times 10^{-13}\text{ S/cm}$, revealing that the Arbofill sample belongs to insulator class of materials.

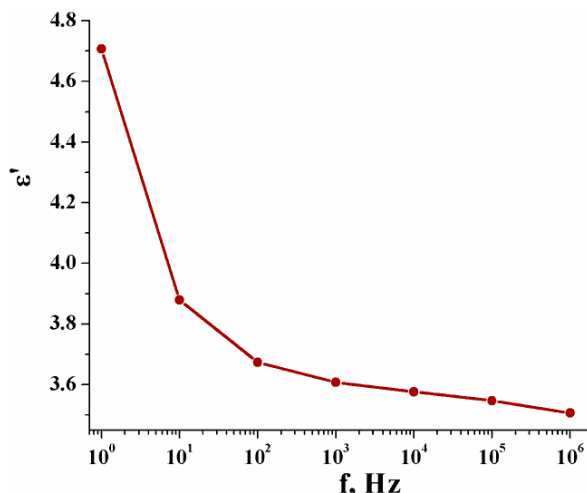


Fig.4. The evolution of dielectric constant function of frequency (T=30 $^{\circ}\text{C}$)

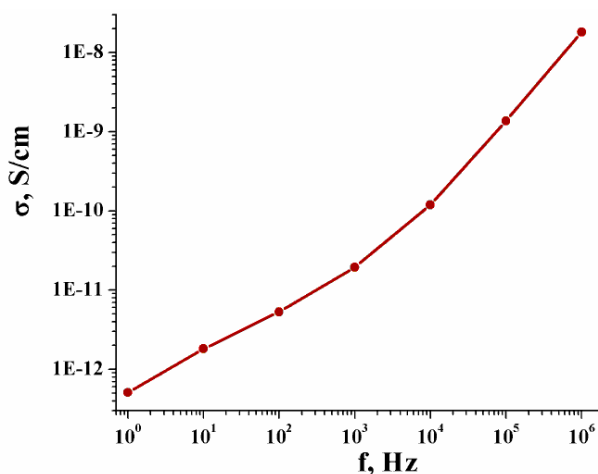


Fig.5. AC conductivity evolution with frequency at 30 $^{\circ}\text{C}$

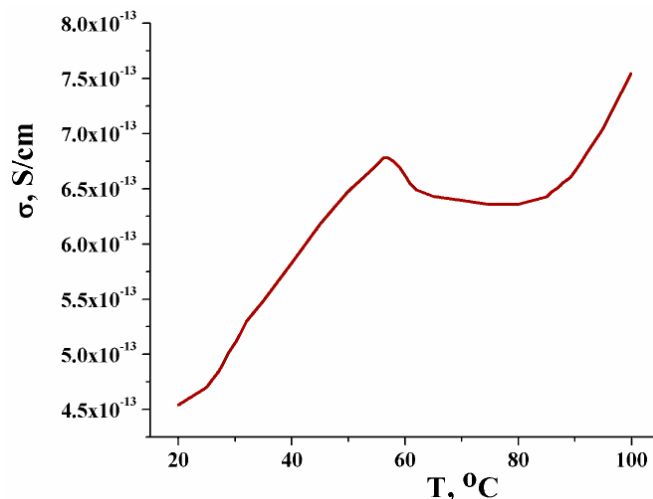


Fig.6. Temperature dependency of AC conductivity for Arbofill sample

Figure 6 shows the temperature dependency of conductivity for Arbofill-type sample. Generally, the AC conductivity increases with temperature, excepting the (57–85)°C temperature range, where a critical point is observed around 57°C. Accordingly to that, one can observe a possible thermal transition around 60°C.

4. CONCLUSIONS

The studied material behaves during the heating process as an amorphous solid.

It has in its composition a substance that presents itself in crystalline form in the temperature range of (65 – 90)°C.

The melting temperature is higher compared to other materials of the same class (Arboform, Arboblend).

It evaporates at a relatively low temperature relative to similar materials of the same class, this fact leads to the conclusion that this material has a more rapid and accentuated degradability.

The lignin which enters in the composition of the material it has gone through transformations and is no longer found in the molecular form encountered in wood fibers.

The material can not be included in the group of classical biocomposite materials because it does not present a well-determined matrix.

The material can be included in the group of natural degradable polymers obtained from renewable resources.

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