

THERMAL STABILITY AND KINETIC STUDY OF THERMAL DEGRADATION OF A WOOD FLOUR-REINFORCED PHENOLIC FOAM

J.C. Domínguez^a, B. Del Saz-Orozco^{a*}, M. Oliet^a, V. Alonso^a, F. Rodríguez^a

^a*Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain*

Keywords: Thermal stability, FTIR, phenolic foam, kinetics

Abstract

In the present work, thermal stability and kinetics of thermal degradation of a phenolic and wood flour-reinforced phenolic foams, and the wood flour employed as reinforcement were studied. The activation energies of their degradation processes were obtained by model-free kinetic methods. The reinforcement increased the initial thermal stability of the foam enhancing its original properties. The values of the activation energies obtained for the phenolic foam are in a range between 110 and 170 kJ.mol⁻¹ and for the reinforcement the value is constant for almost all the conversion range, 162 kJ.mol⁻¹. Wood-flour reinforced foam showed a structure similar to phenolic foam according to the FTIR results.

1. Introduction

Phenolic foams show high thermal stability in a broad range of temperature, excellent fire properties (low flammability, no dripping combustion and low smoke density) and low thermal conductivity [1]. These materials are usually employed in insulating and structural applications where fire resistance is critical, such as in buildings and aircrafts. In addition, phenolic foams have low cost and density compared to other polymeric foams, which makes them quite interesting for these industries. Therefore, the thermal degradation of phenolic foams is an important field to study for its final application. In the present work, thermal stability and kinetics of thermal degradation of a wood flour-reinforced phenolic foam, a phenolic foam and the wood flour employed as reinforcement were studied in order to evaluate their thermal stabilities, compare the structural changes occurred during their degradation and to obtain the activation energies of their degradation processes. These activation energies were calculated by applying Kissinger-Akahira-Sunose (KAS) [2], and Flynn-Wall-Ozawa (FWO) [3] model-free kinetic methods.

2. Theory

Chemical reactions, such as the degradation process of a composite material, are commonly described by a single step kinetic equation:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

where α represents the conversion (defined as the ratio between the instant mass loss and the total mass loss); t is the time; $k(T)$ is the rate constant, which depends on temperature; and $f(\alpha)$ is the process mechanism function. $k(T)$ is usually assumed to follow the Arrhenius.

Nowadays, the kinetics of thermal degradations processes is commonly studied using model-free kinetics (MFK); therefore, the dependence of the activation energy on the conversion can be obtained. MFK methods are a useful tool that allows obtaining the activation energy of degradations process independently of the mechanism function that describes the kinetics of the reacting system, and therefore also allow studying possible changes in the reaction mechanism during the global degradation process.

Several MFK methods have been developed in the literature. Integral methods, such as the methods of Kissinger-Akahira-Sunose (KAS) [2], and Flynn-Wall-Ozawa (FWO) [3], are some of the most used methods in the determination of the activation energies of degradations processes. The methods of KAS and FWO, which provide approximated solutions to the temperature integral obtained from Eq. (1) in order to determine the activation energy of the process, are described by Eqs. (2) and (3), respectively:

$$\ln\left(\frac{\beta}{T_{\alpha}^2}\right) = \frac{E_a}{R \cdot T_{\alpha}} - A' \quad (2)$$

$$\log(\beta) = A - 0.4567 \cdot \frac{E_a}{R \cdot T_{\alpha}} \quad (3)$$

where E_a is the activation energy of the process, T_{α} is the temperature at a fixed conversion, R is the universal gas constant, and β is the heating rate.

3. Experimental procedure

Thermogravimetric analyses (TGA) of a 8.5 wt.% wood flour-reinforced phenolic foam (WRPF), a phenolic foam (PF) and the wood flour used as reinforcement were performed in a Mettler-Toledo TGA/DSC 1^o. The foams were both manufactured according to a previous work [4]. The size of samples was 5 ± 0.3 mg in the case of the foams (WRPF and PF), and 10 ± 0.3 mg in the case of wood samples. Foams were cut in small cubic samples and wood was milled in a MM301 Retsch ball mill during 2.5 min at 30 Hz. All of them were heated from 30 to 900 °C at heating rates of 6, 8, 10, 12 and 14 °C.min⁻¹. These tests were used to study the kinetics of thermal degradation. Thermograms obtained at 10 °C.min⁻¹ were employed to study the thermal stability of the materials and the reinforcement. Nitrogen was used as the carrier gas with a flow rate of 20 mL/min. At least three replicates were analyzed.

The changes in chemical structure of the materials during thermal degradation were determined using Fourier transform infrared spectroscopy (FTIR). Previously, the samples were degraded using temperature programs from 30 to 225, 375, 500 and 800 °C and a heating rate of 10 °C/min in a TGA apparatus. FTIR spectra were recorded with a Mattson Satellite 5000 spectrophotometer using the potassium bromide pellet method. The pellet was prepared from a mixture of potassium bromide and sample (150:1 ratio). The acquisition conditions were: spectral width of 4000–400 cm⁻¹, 32 accumulations, 1 gain, 4 cm⁻¹ resolution and signal processing by triangular apodization.

4. Results and Discussion

4.1 Thermal stability

The study of thermal stability and the analysis of the stages of degradation of foams and reinforcement (wood flour) was performed from the thermograms (TG) obtained at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and the corresponding curves (DTG). This heating rate is normally used in the study of thermal stability of the polymeric materials [5,6]. In Figures 1a and 1b, thermograms and DTG curves, respectively, are shown for each of the studied materials.

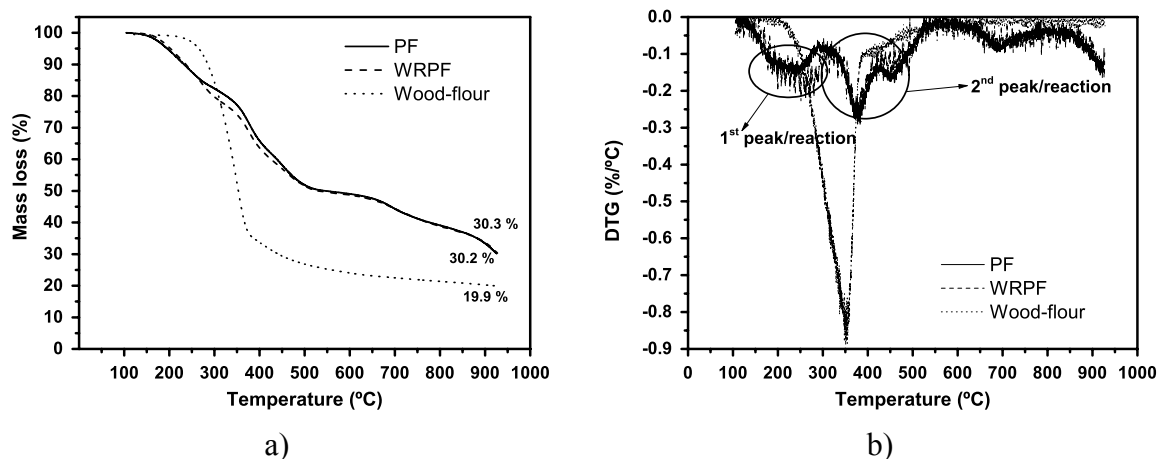


Figure 1. TGA measurements: a) themograms; b) DTG curves.

From Figure 1b, three different degradation stages were determined for WRPF and PF foams. Moisture release data have been removed from all the thermograms. The first degradation stage occurred between 150 and 250 °C, which is attributed to the volatilization of molecules of low molecular weight occluded in the structure of the foam during the curing process, such as water, monomeric phenol and formaldehyde [7]. The second stage took place between 250 and 500 °C. The most important mass loss occurred during this stage mainly due to the release of formaldehyde and water, as a result of bond breaking (mostly methylene ether) of the material and its conversion into more stable structures [7]. The last stage of thermal degradation of foams was comprised between 500 and 900 °C. For this stage, the mass loss was associated with the decomposition of the carbonaceous material structures to decomposition products such as water, carbon monoxide, carbon dioxide, methane and phenol [7]. Wood flour showed two different stages. During the main degradation stage cellulose, hemicellulose and lignins are decomposed into degradation products.

The thermal stability of the materials and reinforcement was assessed by measuring $T_{5\%}$, $T_{25\%}$ (temperatures at 5 % and 25 % mas loss) and ash content at 900 °C. Furthermore, estimations for these values were calculated applying the rule of mixtures (using the weight fractions of PF and wood flour reinforcement). These values are exhibited in Table 1.

β (°C/min)	PF	WRPF (measured)	Wood Flour	WRPF (estimated)
			T_{5%} (°C)	
6	188.0 ± 1.5	191.6 ± 0.4	260.9 ± 0.2	193.2 ± 1.3
8	193.2 ± 0.3	195.0 ± 1.4	263.9 ± 0.1	199.2 ± 0.3
10	194.7 ± 0.8	202.3 ± 0.5	265.7 ± 0.9	200.8 ± 0.8
12	198.8 ± 1.9	202.9 ± 3.4	269.1 ± 0.6	204.7 ± 1.7
14	202.5 ± 1.4	202.5 ± 2.1	271.4 ± 0.4	208.4 ± 1.2
			T_{25%} (°C)	
6	350.5 ± 0.0	336.8 ± 4.5	311.1 ± 0.6	347.2 ± 0.1
8	356.7 ± 2.1	338.6 ± 0.7	314.8 ± 0.5	353.1 ± 2.0
10	361.3 ± 1.3	343.4 ± 0.9	318.3 ± 0.7	357.7 ± 1.2
12	368.4 ± 1.0	345.3 ± 1.2	321.8 ± 0.5	364.5 ± 0.9
14	369.9 ± 2.0	344.5 ± 1.7	325.0 ± 0.4	366.0 ± 1.9
			Ash content at 900 °C (%)	
6	27.50 ± 0.4	32.2 ± 0.6	19.9 ± 0.3	26.9 ± 0.4
8	33.5 ± 1.0	33.6 ± 1.2	19.1 ± 0.9	32.2 ± 0.9
10	33.4 ± 1.2	34.3 ± 2.4	19.9 ± 0.7	32.2 ± 1.1
12	34.2 ± 0.9	36.2 ± 0.2	19.7 ± 0.4	33.0 ± 0.8
14	34.5 ± 1.2	35.6 ± 1.8	20.3 ± 0.8	33.3 ± 1.1

Table 1. Measured and estimated T_{5%}, T_{25%} and ash content at 900 °C for WRPF and PF foams.

The incorporation of wood flour in the phenolic foam slightly increased thermal stability of the material in the first stage of degradation, decreased it in the second stage and had not influence in the third stage. T_{5%} of WRPF (191.6-202.5 °C) was higher than for PF (188.0-202.5 °C) due to the addition of the reinforcement, which is noticeably more stable than PF. The increase of this temperature was in agreement with the temperature predicted by the rules of mixtures taking into account the weight fractions of PF and reinforcement. In the case of T_{25%}, for WRPF a significant reduction of this value with respect to PF was found. This reduction was higher than the reduction predicted by the rule of mixtures. A possible explanation for this behavior is the incompatibility between the fibers and the polymer matrix, the formation of aggregates during processing of the material and its lower fire resistance. These difficulties are due to the interaction between the reinforcement and the matrix, weakening the interface between them and therefore the thermal stability of the material [8]. The ash content measured at 900 °C was the same for both foams for all the employed heating rates, besides 6 °C.min⁻¹, ranging from 33.5 to 36.2 %. Thus, the addition of reinforcement did not cause any change in the ashes content at 900 °C.

4.2 FTIR analysis

FTIR spectra of the WRPF and PF foams and the wood flour at room temperature are shown in Figure 2.

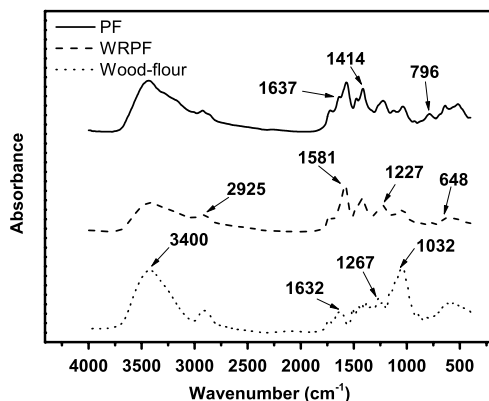


Figure 2. FTIR spectra for the three materials obtained at room temperature.

WRPF and PF foams showed a band around 2925 cm^{-1} at room temperature, which is associated with the stretching vibration of C-H bond and corresponds to hydrocarbon structures [9], more specifically to the groups -CH and -CH₂ [10]. The signal obtained at 648 cm^{-1} is associated with the vibration of the CH bond [9]. The bands around 1000 and 1200 cm^{-1} are attributed, as well as the 800 and 1000 cm^{-1} band, to -OH functional groups, in particular to the stretching vibration of CO [10]. The absorption band at 1414 cm^{-1} is associated with the deformation vibration of the CH bond [9]. Finally, the signal found at 1581 cm^{-1} is attributed to the double bond C=C [9], indicating the presence of aromatic rings. The bands described refuted the fact the foams are mainly composed of structural units containing phenolic rings. The WRPF foam presented an additional band at 1637 cm^{-1} , which is due to aromatic compounds in the wood flour (1632 cm^{-1}) [11]. FTIR spectra obtained for the three materials at different final degradation temperatures are shown in Figure 2.

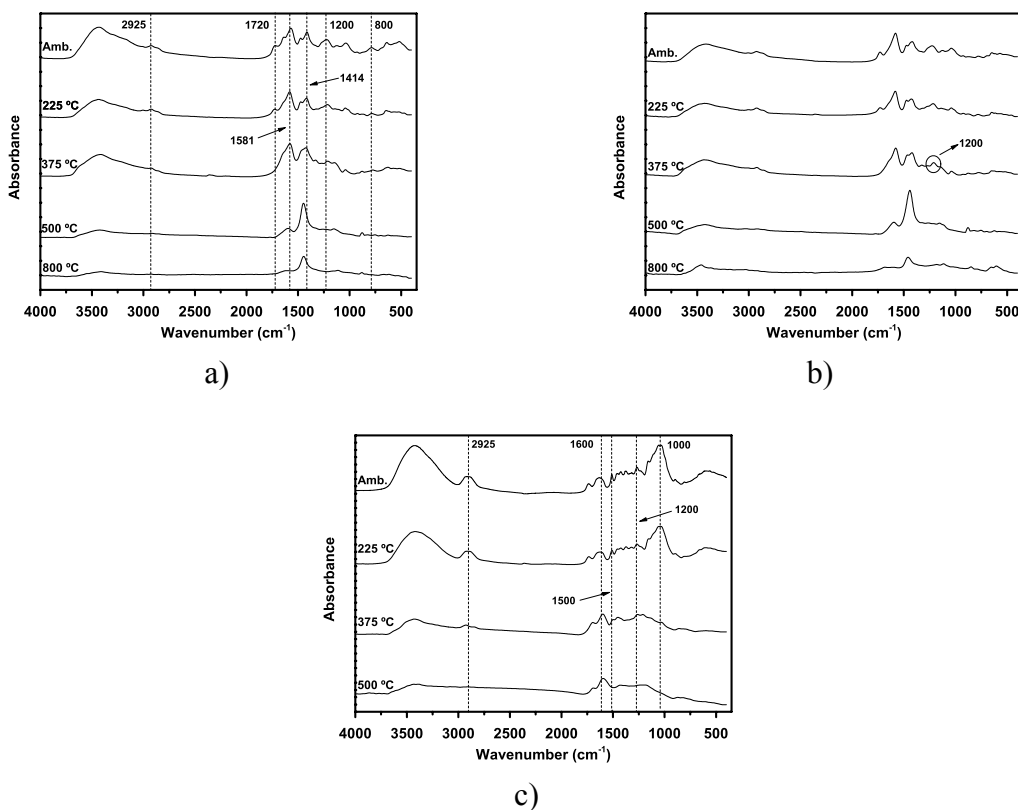


Figure 3. FTIR spectra: a) PF foam, b) WRPF foam, c) wood flour reinforcement.

Spectrum obtained at room temperature for the PF foam was similar to 225 °C, indicating that the foam did not undergo changes in its chemical structure below 225 °C. In the spectrum obtained at 375 °C, significant differences from the previous two were appreciated. The 1720 cm⁻¹ band, which is associated to the C = O and hence the presence of formaldehyde [9,10], was not longer present, indicating that this compound was degraded. The intensity of the signal located at 1200 cm⁻¹ was highly reduced, suggesting that the phenolic structural units were almost fully degraded at 375 °C. Moreover, the 800 cm⁻¹ band was vanished, indicating that the phenolic monomers and low molecular weight structures were consumed. At 500 °C, phenolic structures were fully degraded since 1200 cm⁻¹ band was not present and 1581 cm⁻¹ band presented a marked reduced intensity. The spectrum obtained at 800 °C did not show important differences from the previous, proving that in the last stage of degradation (500-900 °C) the material was degraded to a residue formed by carbonaceous structures.

The FTIR spectra of the reinforced foam had almost no changes with respect to the PF foam, which showed that the amount of reinforcement was not high enough to cause marked structural changes during its degradation.

Finally, the main degradation process of wood flour takes place between 250 and 450 °C; therefore, spectra obtained at 375 and 500 °C showed the changes in its functional groups. The 1000 and 1200 cm⁻¹ bands at 225 °C were not observed in the spectrum at 375 °C, which is due to the degradation of phenol groups in cellulose ether groups in the lignin [9]. The decrease in the intensity observed for the 1500 and 2925 cm⁻¹ bands, is related to tension and deformation vibrations of C-H bonds of hydrocarbon structures. Furthermore, the bands between 1200 and 1500 cm⁻¹, also related to C-H bonds, were vanished because of the degradation of wood components.

4.3 Kinetic study of thermal degradation

The activation energies as function of the reached conversion for the first degradation stage (Figure 1b) of the reference and reinforced foam and wood flour obtained by applying Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods to the measured thermograms are shown in Figure 4.

The activation energy for the PF foam increased for the conversion range between 0.1 and 0.5, reaching maximum values of 125 kJ.mol⁻¹ and 135 kJ.mol⁻¹ KAS and FWO methods, respectively. These values of the activation energy suggested that degradation of the material weaker bonds took place for this conversion range [12]. For the conversion range between 0.5 and 0.9, the activation energy reached remained constant. The final increase of the activation energy for conversions higher than 0.9 suggests an overlapping between the first and the second degradation stages where the degradation of more thermally stable compounds starts [12].

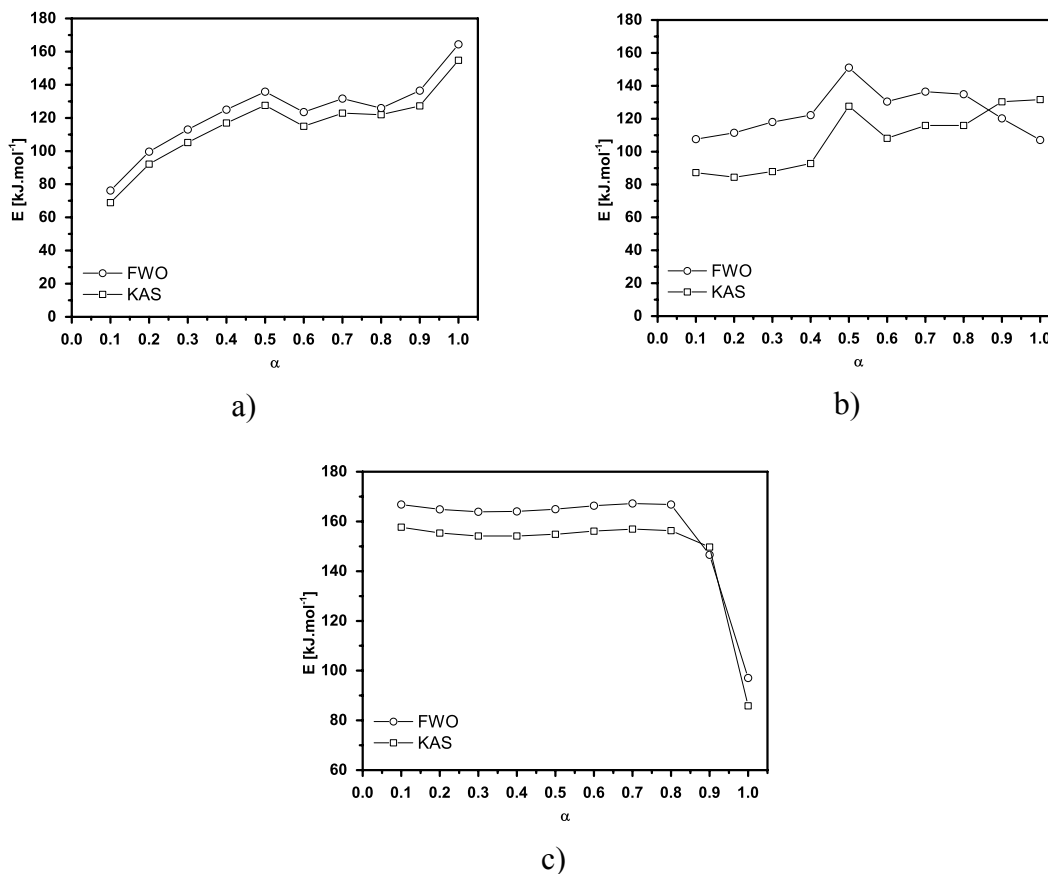


Figure 4. Activation energy vs. conversion: a) PF foam, b) WRPF foam, c) wood flour reinforcement..

The reinforced foam showed a different behavior than the reference foam, for conversions between 0.1 and 0.4, the activation energy was fairly constant: 90 and ca. 120 kJ.mol⁻¹ for KAS and FWO methods, respectively. A maximum value of the activation energy was reached at 0.5 (120 and 150 kJ.mol⁻¹ for KAS and FWO methods, respectively). As happened for the reinforced foam, the plateau for the activation energy was found within the conversion range from 0.6 to 0.8 with similar values than those obtained for the reference foam. The different behavior found for conversions higher than 0.9 compared to the reference foam was assumed to be due the overlapping of the degradation reaction of the foam with the onset of the degradation reaction of the wood reinforcement since the beginning of the degradation of wood-flour started at ca. 300 ° C, which coincides with conversions above 0.9. The values of the activation energy obtained for both foams were similar to those found in the literature for other polymer foams such as polystyrene foam (113.3 kJ.mol⁻¹) [13].

The wood flour used as reinforcement showed a constant activation energy for almost the entire range of conversion studied: 155 and 165 kJ.mol⁻¹ for KAS and FWO methods, respectively. For conversions higher than 0.8, the activation energy of the wood-flour went down sharply to ca. 85-95 kJ.mol⁻¹.

5. Conclusions

The incorporation of wood as reinforcement improves the thermal stability of the material in the first stage of degradation, whereas decreases the thermal stability of the foam in the second stage and has no influence on the final stage. The reinforcement enhanced the

properties of the phenolic foam in applications where the exposure temperature is below 250 °C. The structural changes of the reinforced phenolic foam occurred during its degradation process reveal that this foam has a similar structure than the reference structure.

The values of the activation energies obtained for the phenolic foam are in a range between 110 and 170 kJ.mol⁻¹. In turn, the activation energies obtained for the reinforcement are constant for almost all the conversion range, 162 kJ.mol⁻¹. For wood-flour, constant activation energy of 162 kJ.mol⁻¹ was determined for almost all the conversion range. Both model-free kinetic methods showed high correlation coefficients when applied to the experimental data. Both results are consistent with those found in literature.

References

- [1] P. T. Kelly. Phenolic foams. *Handbook of Polymeric Foams and Foam Technology*:447-456, 2004.
- [2] T. Akahira and T. Sunose. *Joint convention of four electrical institutes*. 1971.
- [3] T. Ozawa. A new method of analysing thermogravimetric data. *Bull Chem Soc Jpn*, 38(1):1881-1886, 1965.
- [4] B. Del Saz-Orozco, M. Oliet, M. V. Alonso, E. Rojo and F. Rodríguez. Formulation optimization of unreinforced and lignin nanoparticle-reinforced phenolic foams using an analysis of variance approach. *Composites Science and Technology*, 72(6):667-674, 2012.
- [5] L. Jiao, G. Xu, Q. Wang, Q. Xu and J. Sun. Kinetics and volatile products of thermal degradation of building insulation materials. *Thermochimica Acta*, 547(0):120-125, 2012.
- [6] K.-K. Yang, X.-L. Wang, Y.-Z. Wang, B. Wu, Y.-D. Jin and B. Yang. Kinetics of thermal degradation and thermal oxidative degradation of poly(p-dioxanone). *European Polymer Journal*, 39(8):1567-1574, 2003.
- [7] L. Hu, Y. Zhou, M. Zhang and R. Liu. Characterization and properties of a lignosulfonate-based phenolic foam. *BioResources*, 7(1):554-564, 2012.
- [8] Z. N. Azwa, B. F. Yousif, A. C. Manalo and W. Karunasena. A review on the degradability of polymeric composites based on natural fibres. *Materials & Design*, 47(0):424-442, 2013.
- [9] M. A. Llorente and A. H. Horta. *Técnicas de caracterización de polímeros*. Universidad Nacional de Educación a Distancia, UNED, Madrid, 1991.
- [10] N. Sarier and E. Onder. Thermal characteristics of polyurethane foams incorporated with phase change materials. *Thermochim Acta*, 454(2):90-98, 2007.
- [11] R. Soto, J. Freer and J. Baeza. Evidence of chemical reactions between di- and polyglycidyl ether resins and tannins isolated from *Pinus radiata* D. Don bark. *Bioresource Technology*, 96(1):95-101, 2005.
- [12] M. Alonso, M. Oliet, J. Domínguez, E. Rojo and F. Rodríguez. Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resol resins. *Journal of Thermal Analysis and Calorimetry*, 105(1):349-356, 2011.
- [13] P. Kannan, J. J. Biernacki and D. P. Visco Jr. A review of physical and kinetic models of thermal degradation of expanded polystyrene foam and their application to the lost foam casting process. *Journal of Analytical and Applied Pyrolysis*, 78(1):162-171, 2007.