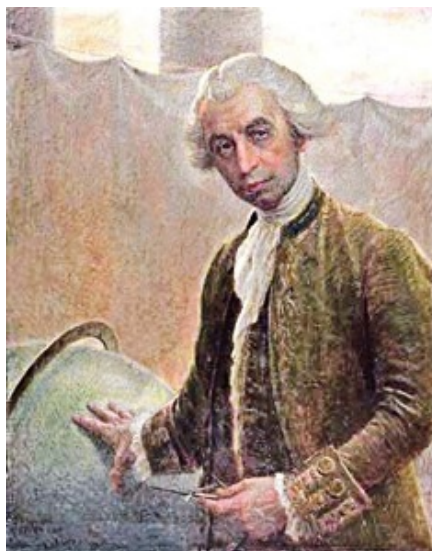




# ОТЕН 2022 ОЛЕН 5055



RUDJER BOSKOVIC  
(1711 - 1787)

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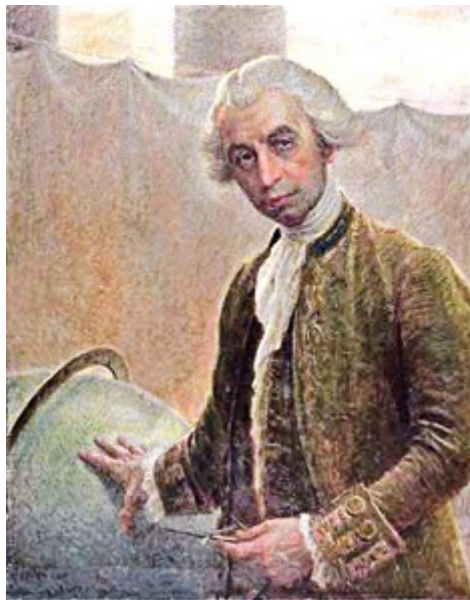
Belgrade, 13-14 October 2022  
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10<sup>th</sup> INTERNATIONAL SCIENTIFIC CONFERENCE  
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**OTEH 2022**

**Belgrade, 13-14, October 2022**



**Rudjer Boskovic**

(1711 – 1787)

He has left an indelible imprint in mathematics, astronomy, physics, optics, geodesy, architecture, archeology, pedagogy, philosophy, literature and diplomacy.

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## FIRE-RESISTANT COMPOSITES BASED ON ACRYLIC-FUNCTIONALIZED LIGNIN AND POLYESTER RESIN OBTAINED FROM WASTE POLY(ETHYLENE TEREPHTHALATE)

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**Abstract:** This paper investigates the using potential of acryl-functionalized kraft lignin (AKL) in reducing the flammability of polymer composites based on recycled unsaturated polyester resins (UPR). Acryl functionalization of kraft lignin was performed by direct esterification of free polyphenolic groups with acryloyl chloride, after what, the AKL was blended in UPR resin synthesized from the polyols obtained by catalytic depolymerization of waste poly(ethylene terephthalate). The AKL was homogenized in UPR resin in different weight ratios: 2.5, 5.0, 7.5, and 12.5 wt.%. Structural and dynamic-mechanical characteristics of acryl-functionalized kraft lignin and composites were determined using FTIR spectroscopy, dynamic-mechanical analysis (DMA), and tensile tests. The influence of functionalization and mass fraction of AKL on tensile and thermal properties of UPR resin was studied. The thermal properties of the composite were tested according to the standard UL-94 method, based on which the highest category of heat-resistant materials is a composite with 12.5 wt.% acyl-functionalized lignin.

**Keywords:** Lignin modification, UPR-lignin composites, dynamic-mechanical testing, tensile testing, flame retardancy

### 1. INTRODUCTION

Polymers are widely used in various economy and defense sectors including housing, construction, transportation, rocket technology and aerospace due to their good mechanical and chemical properties and easy-processing. However, most industrial polymers (polyesters, epoxides, poly(ethylene), poly(propylene), etc.) are highly flammable and thermally unstable, which is especially expressed in hyperthermal conditions [1]. Due to the increasingly widespread use of such polymeric materials, fire resistance must be improved by the incorporation of different additives. Using-potential of some commonly applied flame retardants such as antimony trioxide and halogenated flame retardants is become limited due to environmentally issues. Nowadays, using non-toxic, biobased and environmentally friendly

fillers/additives and flame retardants in polymers increases the researcher's attention. Further, the increased daily consumption of polymers such as poly(ethylene terephthalate), PET, and increased amount of PET waste generated, imposes the development of new PET recycling methods, which give an applicable products. This achieves exceptional ecological and economic benefits, which are summarized in saving natural resources and reducing the consumption of water and energy [2,3]. The most significant recycling technique for waste PET is the chemical one, which involves depolymerization of the polymer chain to its basic structural/monomer units [4]. PET monomers, obtained by the glycolytic depolymerization process, can be used for the re-synthesis of PET, or the synthesis of alkyd, epoxy, and polyester resins as it is presented in this research.



Considering previous statements, the development of fire-resistant composites based on the unsaturated polyester resin, originated from recycled waste PET, and modified lignin as sustainable and renewable fire-resistant additive is shown. Lignin is widely used as filler/additive in composite production due to its chemical structure (natural aromatic polymer), which consists of three branched polyphenols/monolignols. Moreover, it is possible to perform chemical modification of the lignin surface to adjust its reactivity, surface and thermal properties [5,6,7]. Amount and type of the lignin functional groups depend on the source/feed and the process used for its extraction. Acrylic modification of kraft lignin to improve its functional properties is achieved by direct esterification of free polyphenolic groups with acrylic acid or acryloyl chloride.

This paper presents novel modification method for acrylic surface functionalization of the kraft lignin and investigates the using-potential of acrylic-functionalized lignin (AKL) as flame retardant in unsaturated polyester resin (UPR) based on waste PET.

## 2. EXPERIMENTAL PART

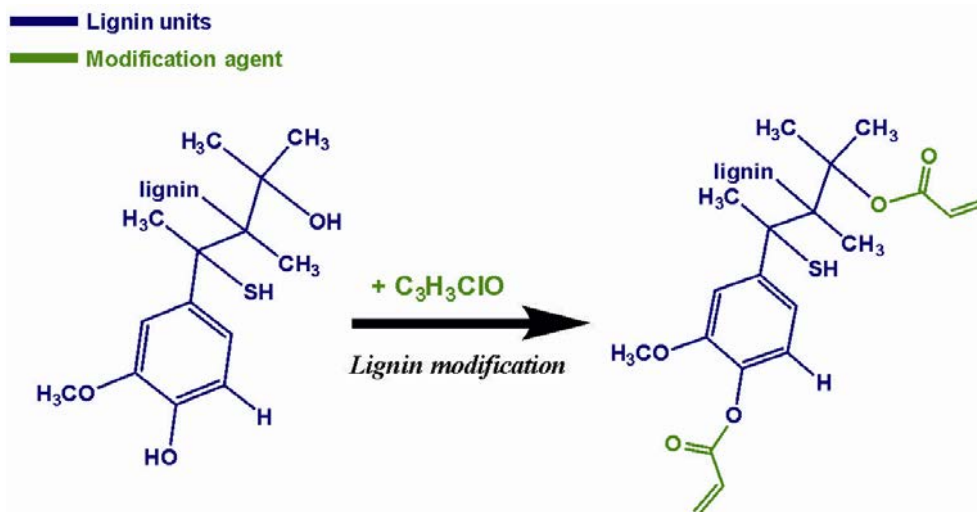
### 2.1. Materials

The UPR was synthesized from maleic anhydride and

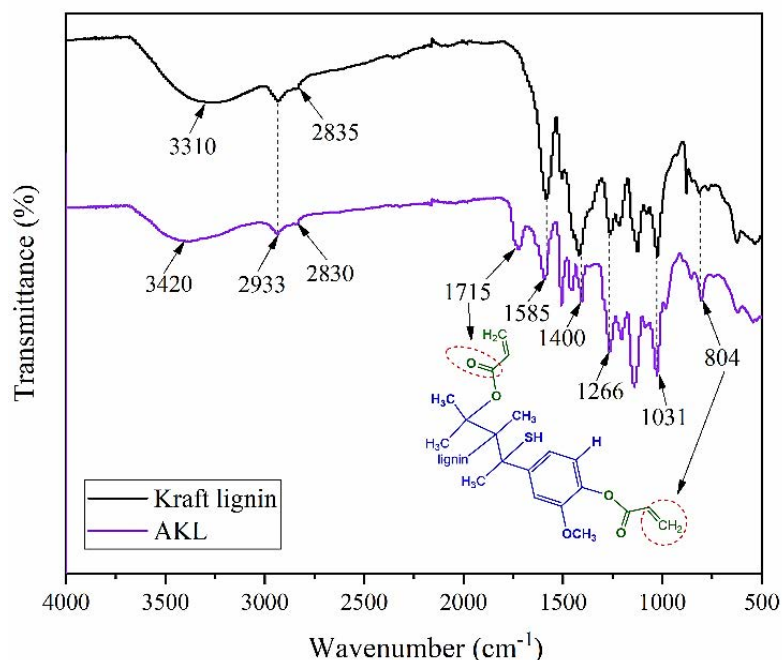
products obtained by depolymerization of PET with propylene glycol (PG) in the presence of a tetrabutoxytitanate (TBT) catalyst. The molar ratio of PET and PG, used for glycolysis, was 1:2. The procedure of glycolysis was described earlier in the literature [8]. Kraft lignin with a low sulfonate content, tetrahydrofuran (THF), sodium hydroxide (97%, reagent grade), acryloyl chloride, isopropyl alcohol, methyl ethyl ketone peroxide (MEKP), cobalt octoate (Co-oct) were obtained from Sigma-Aldrich Company and are used as received.

### 2.2. Chemical modification of kraft lignin – AKL

Chemical modification of lignin was carried out by dissolving 5 g of kraft lignin in 21 cm<sup>3</sup> of H<sub>2</sub>O/NaOH/THF (3:1:3) mixture at room temperature in a 250 cm<sup>3</sup> three-neck flask. After dissolving the lignin (30 min), acryloyl chloride (120 cm<sup>3</sup>) was added dropwise to the mixture over 1 h at -3 °C. After that, the contents of the flask were mixed for 2 hours at a temperature of 0 °C. After the reaction, the mixture was left overnight in cold deionized water and ice to precipitate the final product. The formed technical layer was decanted, and the precipitate was washed three times in isopropyl alcohol and three times in deionized water. The final product was separated by centrifugation and dried for 10 hours at 50 °C in a vacuum oven.



**Figure 1.** Schematic illustration of chemical modification of kraft lignin



**Figure 2.** FTIR analysis of the kraft lignin (black line) and AKL (violet line)

The structural characterization of non-acrylate and acrylate kraft lignin was investigated by recording the FTIR spectrum (Figure 2). The analyzed spectra clearly show the success of the modification.

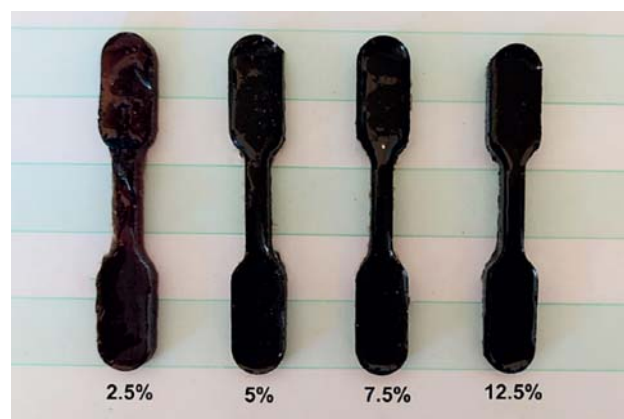
The bands at  $3310\text{ cm}^{-1}$  and  $3420\text{ cm}^{-1}$  belong to the O-H stretching vibration of a hydroxyl and phenolic groups in the kraft lignin and AKL. The region at  $2933\text{--}2835\text{ cm}^{-1}$  is related to the C-H bending vibration of symmetric and asymmetric methyl and methylene groups in the unmodified and modified lignin. The new peak at  $1715\text{ cm}^{-1}$  noticed after arylation process was assigned to the C=O stretching vibrations of acrylate group [9]. In the range of the stand spectrum between  $1585\text{--}1400\text{ cm}^{-1}$  are assigned of aromatic skeletal vibrations of lignin [9]. The asymmetric and symmetric vibration of the C-O-C and C-O groups of in the structure of lignin appear in the region  $1266\text{--}1031\text{ cm}^{-1}$ . As a result of the successful acrylation, intensity of C-H deformation vinyl groups was noticed at  $804\text{ cm}^{-1}$ .

### 2.3. UPR/AKL composites preparation

Waste PET-based UPR (2 g) was used as a polymer matrix for composites preparation. AKL was mixed in polymer matrix and the mass ratio varied from 2.5 wt.% to 12.5 wt.%. Homogenization of AKL with UPR was achieved using a modified laboratory homogenizer. MEKP (1.5 wt.%) and Co-oct (0.5 wt.%) were used as curing initiator and activator, respectively. After adding the initiator, the resulting dispersion was poured into molds for uniaxial tensile measurements (ASTM D882 test standard dimension  $60\times 10\times 4\text{ mm}$  with narrowed neck area –  $15\times 4\times 4\text{ mm}$ ) and for dynamic-mechanical analysis (standard dimension  $60\times 10\times 4\text{ mm}$ ). The obtained cured neat UPR resin as well as UPR/AKL composites were presented in Figure 3.

**Table 1.** Compositions for preparation of neat UPR and UPR/AKL composites

Sample	UPR, g	AKL, g	MEKP, $\text{cm}^3$	Co-oct, $\text{cm}^3$
UPR		0 (0%)		
UPR/AKL	2	0.05 (2.5%)	0.350	0.150
		0.10 (5%)		
		0.15 (7.5%)		
		0.25 (12.5%)		



**Figure 3.** Standard test molds for uniaxial tensile measurements

### 2.4. Characterization methods

Recognition of existing functional groups in synthesized materials was obtained by Fourier transform infrared spectroscopy (FTIR). For this purpose, Nicolet™iSTM10 FTIR Spectrometer (Thermo Fisher SCIENTIFIC) with Smart iTR™ Attenuated Total Reflectance (ATR) was used. All spectrums are recorded between  $4000$  and  $500\text{ cm}^{-1}$ .

Uniaxial tensile measurements of standard cured samples (ASTM D882) [11] were performed using an Instron tester 1122. All tests were performed at 20 °C and adjusted at a crosshead speed of 10 mm/min.

Optical micrographs of the cured composites after tensile tests were made using a BTC STM-8T Trinocular Stereo Microscope ZOOM with 50x magnification.

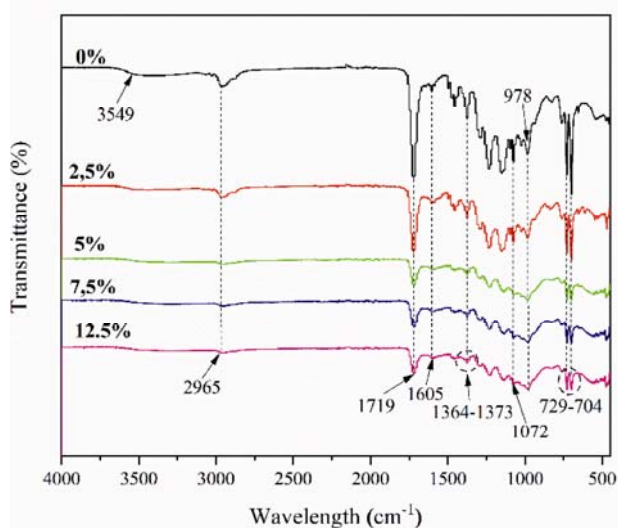
Dynamic mechanical analysis (DMA) study of the cured composite samples was performed in torsion deformation mode using the Modular Compact Rheometer MCR-302 (Anton Paar GmbH, Austria) equipped with standard fixtures (SRF12) for rectangular bars, temperature chamber (CTD-620) having high temperature stability ( $\pm 0.1$ ). The standard sample of a rectangular bar shape (44×10×4 mm) was tested by using "temperature ramp test" at temperature range from 40 °C to 130 °C, the heating rate was 5 °C min<sup>-1</sup>, the single angular frequency of 1 Hz and strain amplitude was 0.1%.

Flame-resistant properties were analyzed by the UL-94 flammability test [10].

### 3. RESULTS AND DISCUSSION

#### 3.1. FTIR analysis

The FTIR spectra of the UPR/AKL composite and the pure resin are shown in Figure 4.



**Figure 4.** FTIR spectra of UPR and UPR/AKL composite (2.5 wt.%, 5 wt.%, 7.5 wt.%, 12.5 wt.%)

The peak around 3549 cm<sup>-1</sup> originates from the aliphatic and aromatic O-H vibration [12]. The intensity of this spectrum after the alkylation of lignin and incorporation into UPR is reduced. The wide peak at 2965 cm<sup>-1</sup> originates from the stretching vibration of the methyl or methylene group. In the region 1364-1373 cm<sup>-1</sup>, asymmetric and symmetric C-H deformation vibrations of methyl and methylene groups can be observed. These vibrations overlap with the C-H stretching vibrations from the isopropyl moiety's methyl (CH<sub>3</sub>) groups. The intense peak at 1719 cm<sup>-1</sup> is attributed to stretching vibrations of the ester C=O groups of UPR matrix. The narrow peaks identified at 729 cm<sup>-1</sup> and 704 cm<sup>-1</sup> are skeletal  $\gamma$ (CH) vibrations of the phenyl moiety. A lower intensity band

with an absorption maximum of 1072 cm<sup>-1</sup> originates from C-O valence vibrations. The consumption of the C=C bond in unsaturated polyesters was followed by the change in the peak area at 978 cm<sup>-1</sup>. The spectrum at 1605 cm<sup>-1</sup> is due to the vibration of C=C group.

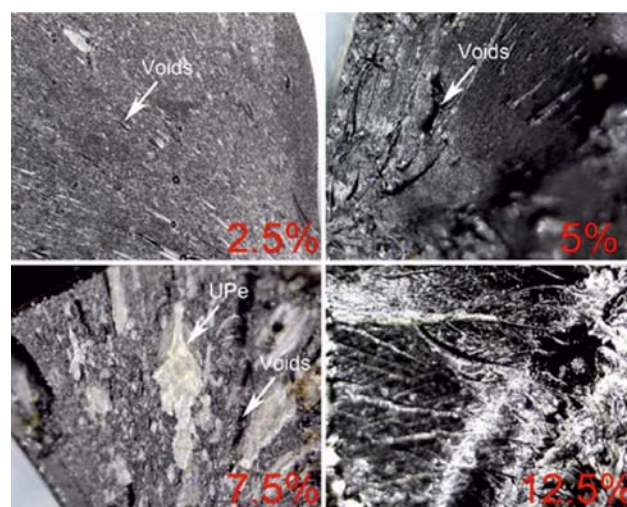
#### 3.2. Tensile properties and microscopic fracture section of the investigated composites

In order to examine the contribution of AKL additives to the tensile properties of the UPR matrix, uniaxial tensile tests of cross-linked composites based on unsaturated polyester resins and acrylate lignin were performed. The obtained values are shown in the Table 2. The results show that  $\sigma$  and  $E$  increase with an increase in the proportion of acrylated lignin up to 7.5 wt.%, while an increase in AKL load leads to a decrease in the elongation value but a higher value of the elastic modulus, which can be associated with defects in the structure of AKL particles.

**Table 2.** The values of stress at break ( $\sigma$ ), elongation at break ( $\epsilon$ ), tensile modulus ( $E$ ) and energy adsorption

Sample	$\sigma$ , MPa	$\epsilon$ , %	$E$ , GPa
UPR	21.60	2.85	0.98
UPR/AKL 2.5%	9.16	4.72	0.140
UPR/AKL 5%	17.47	12.86	0.169
UPR/AKL 7.5%	19.19	7.16	0.289
UPR/AKL 12.5%	1.31	30.38	0.0084

The best results are given by the sample with 7.5 wt.% AKL as a result of good filler distribution and interfacial interactions between the UPR matrix and lignin particles. The deviation from the continuous growth of the value (12.5 wt.%) can be attributed to heterogeneity in the composite structure due to steric hindrance of the methylene group from the loose segment of the isopropyl alcohol, which requires additional optimization of the crosslinking conditions of polymer matrices with this modified lignin.



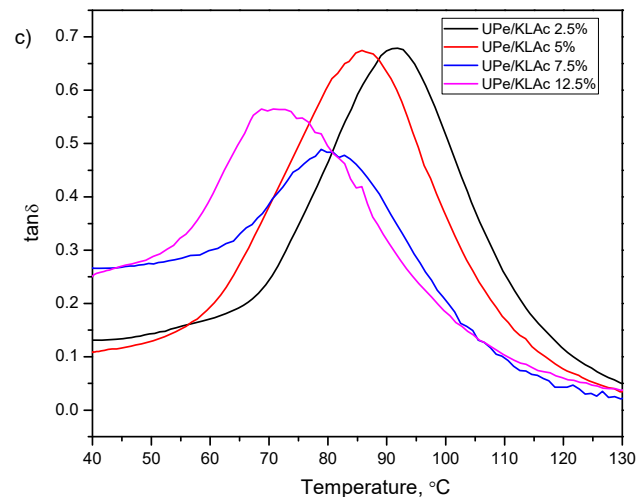
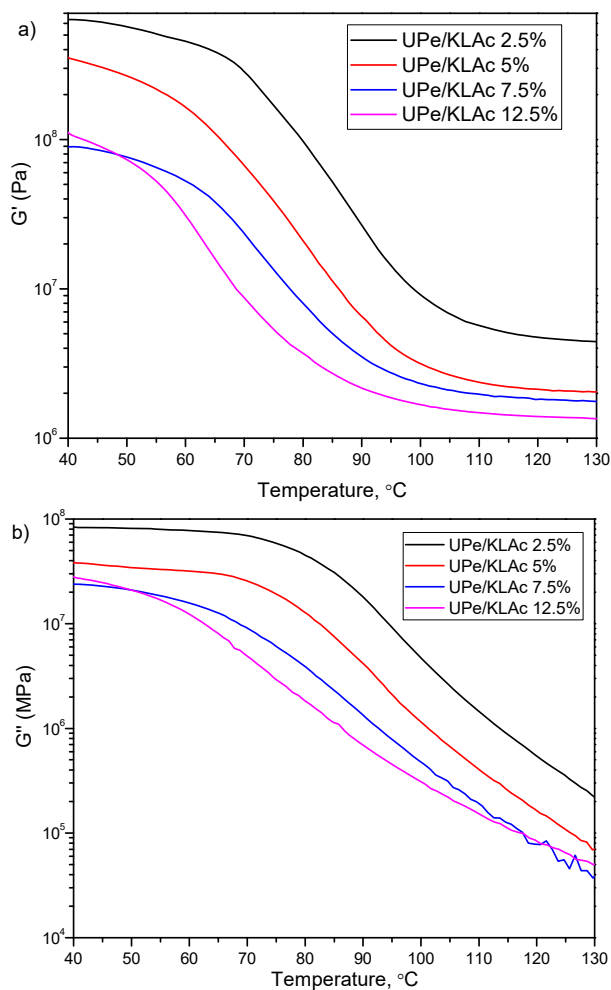
**Figure 5.** Microscopic view of broken test tubes with different parts AKL

The surface of the fracture, which was created by stretching the test tube, was recorded with an optical microscope with a magnification of up to 50x. Images of

the resulting fractures are shown in Figure 5. On the cross-sections of the samples with 2.5 wt.% and 5 wt.% AKL, the uniform distribution of the acrylate lignin into the UPR polymer matrix is clearly remarked. Compared to the higher loading of AKL (7.5 wt.% and 12.5 wt.%), segments of only cross-linked resin without AKL can be observed, which represent a weak segment in the structure and lead to poor mechanical properties, as confirmed by the values of  $\sigma$  and  $E$  in Table 2. Cracks on the sections of the 2.5 wt.% and 5 wt.% samples are caused by a mechanism that is characteristic of brittle polymers and polymer composites. Fractures on samples with 7.5 wt.% and 12.5 wt.% AKL in the matrix are more tough.

### 3.3. Dynamic-mechanical testing results

The rheological properties of cured polymeric composites are influenced by the polymer chain structure and its interactions with fillers. The results of the DMA properties of the UPR/AKL composites are presented as a temperature dependences of storage modulus ( $G'$ ), loss modulus ( $G''$ ), and their ratio (damping factor -  $\tan\delta$ ) about temperature. The temperature increases from 40 °C to 130 °C during the DMA tests. Based on the obtained DMA diagrams, the glass transition temperature  $T_g$  ( $\tan\delta$ ) was determined. Figure 6. shows the DMA diagrams of cross-linked UPR and UPR/AKL.

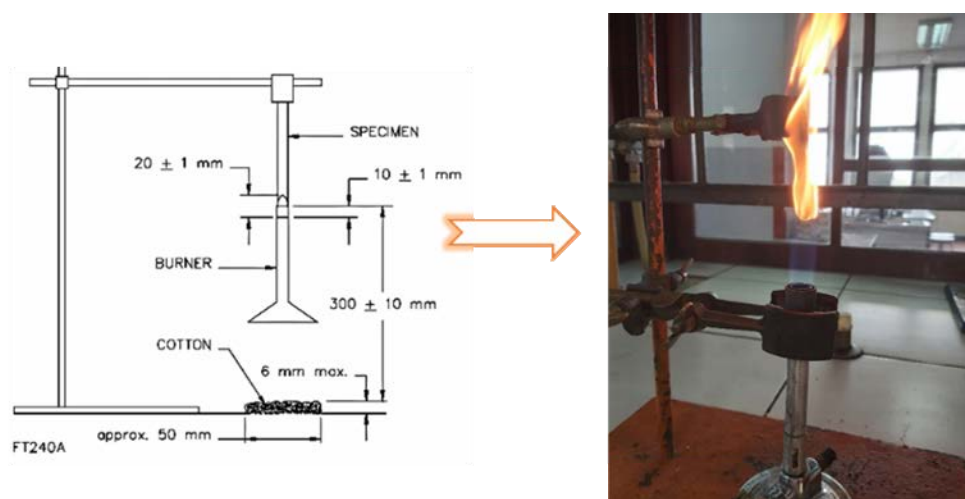


**Figure 6.** Temperature dependence of a) storage modulus ( $G'$ ), b) loss modulus ( $G''$ ) and c)  $\tan\delta$  of cured UPR and corresponding composites

According to the DMA results presented in Figure 6. it can be concluded that  $T_g$  ( $\tan\delta$ ) decreased with higher AKL content within the UPR matrix. Higher amount of filler particles creates agglomerates, which weakens interaction between polymer chains and reinforcements making macromolecule segments more movable. Moreover, the  $\tan\delta$  peak height also decreased indicating more elastic response of materials with high amount of AKL.

### 3.4. Thermal stability testing results

The thermal stability of the formed composites was tested according to the standard flammability test method, known as UL-94V (flammability test of plastic materials for parts in devices and appliances). Test describes the material's tendency to extinguish or spread the flame after igniting the test tube. Samples can be classified as non-flammable (V-0), less flammable (V-1), explosive (V-2), and highly flammable (unclassified). The setup of the apparatus for the practical test is shown in Figure 7.



**Figure 7.** Standard and laboratory setup of apparatus (right) for vertical testing of thermal stability of samples[10]

Formed test tubes with dimensions of 60x10x4 mm were used to test the thermal properties. A blue flame of 20 mm height is placed on the lower edge of the vertically placed test tube for 10 s, after which the flame is removed, and the time is measured. The flame is applied again for another 10 s, and the time to extinction is recorded. It is expected that by increasing the mass fraction of modified lignin, the fire resistance of the material will also increase. After testing the flammability of all test tubes, the sample with 12.5 wt.% ALK was completely charred. Since there was no dripping/cracking of the sample and the flame extinguished itself after 25 s, according to the UL-94V test, this sample can be classified as the V-1 category. Samples with a smaller proportion of lignin started to crack after being exposed to the flame and extinguished faster, even in 100-120 s.

#### 4. CONCLUSION

In this work, acrylic functionalization of kraft lignin was performed and its valorization as a flame retardant additive in recycled UPR was investigated. The structure of the formed UPR/AKL composites, as well as the pure resin, was analyzed using FTIR method. The effect of lignin in UPR matrix was studied by examining the thermal stability, flame resistance and mechanical properties of the prepared composites. Flame resistance is increased by cross-linking a larger amount of AKL, which is confirmed by the charring of the sample after exposure to fire. According to the standard flammability test, the sample with 12.5 wt.% lignin achieves the V-1 category, which makes it an extremely fire-resistant material. Contrary to this are the results of the mechanical properties (tensile strength and modulus of elasticity). The tensile properties of all composites based on UPR resin and modified lignin are improved compared to the tensile properties of pure resin, and the values of  $\sigma$ ,  $\epsilon$  and  $E$  increase with the increase of the lignin content up to 7.5 wt.%, after which they decrease due to the heterogeneous distribution of filler particles. These results confirm the application potential of the developed material as a fire-resistance material.

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