

Pyrolysis of Polyacrylonitrile/Technical Hydrolytic Lignin Composites

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Abstract

One important problem is utilization of technical hydrolytic lignin (the waste formed in paper-and-pulp and hydrolysis industry). For a practical implementation, the essential task of transforming insoluble hydrolytic lignin into low molecular weight products with high degree of functionalization should be performed. In prospect, these products can serve as raw materials for synthesis of various organic compounds demanded in chemical industry. Among other things, activation and fragmentation of hydrolytic lignin yields low molecular weight compounds which may be used for modifying synthetic polymers (polymer-analogous transformations). In the present work, the search for the optimal solvents (activators) for technical hydrolytic lignin (THL) has been conducted; the dimethyl sulfoxide/water binary mixture proved to be the best solvent. Methods of thermal analysis (thermogravimetric analysis, TGA; differential thermal analysis, DTA; differential scanning calorimetry, DSC; thermal volumetric analysis, TVA) combined with pyrolysis-gas chromatography/mass spectrometry (GC-MS) were used to determine the grades of technical hydrolytic lignin most suitable for activation and fragmentation. The necessary conditions for thermal treatment of lignin samples and concentrations of initial compounds (lignin and polyacrylonitrile, PAN) in the binary solvent mixture (dimethyl sulfoxide/water) facilitating maximum THL fragmentation and its successful interaction with PAN were found. When using the dimethylsulfoxide-water binary mixture (70:30 mass ratio) as a solvent, homogeneous forming solution of initial components (THL-PAN) was prepared. With the use of syringe method, form-stable fibers with a maximum lignin content of 80% and strength of about 50 MPa were obtained. Analytical pyrolysis of composites (products of THL-PAN interaction in the binary solvent) allowed us to suggest a mechanism for THL fragmentation involving the binary solvent.

1. Introduction

One important problem of realizing the “Green Chemistry” principles [1] is utilization of wood-working industry waste and reducing its amount. In this context, the matter of application of technical hydrolytic lignin (THL) is the most urgent, since the amount of the used THL is incomparably lower than that of THL discarded as waste. Meanwhile, THL is a promising material for developing composites with synthetic polymers. Several successful attempts in this direction are described in [2–6], and the number of similar publications is constantly growing. These papers include the results

of scientific and engineering research concerning combination of various lignins with a wide range of synthetic polymers obtained by polymerization and polycondensation. However, the common well-studied polymer possessing a number of unique characteristics (polyacrylonitrile, PAN) has attracted little attention.

In our previous publications [7–12], the interaction between THL and PAN was studied, and some possible applications of the resulting compounds were described. The goal of the present work is a thermoanalytical study of the formation of composite precursors which are promising for use as carbon materials.

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2. Experimental

2.1. Materials

It is well-known [1, 6] that THL samples obtained in hydrolysis industry differ in a number of technological parameters, even though delignification of wood pulp is carried out under similar conditions. In our work, the most suitable material was selected from a set of four samples manufactured at Kirov Biochemical Plant: (1) non-treated lignin (NTL), (2) lignin subjected to extraction by ethanol/toluene mixture (EL), (3) micronized lignin with a particle size of 5–10 μm (ML), and (4) the Klason lignin (KL). The THL samples were treated according to the following technique. Non-treated lignin (product of softwood conversion) was manufactured at Kirov Biochemical Plant, LLC according to the Russian State Standard GOST 18300. The product possessing an initial humidity of 65–70% was spread in thin layers (2 cm) onto closed platforms and dried at ambient temperature for 7 days until the humidity lowered down to 4–5%. After sieve fractionation, the product (in the form of grains with dimensions of 1–0.25 mm) was dispergated using an Omicron fine grinding instrument. In the following experiments, the fractions with grain dimensions of less than 5 μm (the ML sample) were used.

The EL sample was obtained by extraction of the NTL product according to the following technique. Extraction of technical lignins was carried out in the Soxhlet apparatus using ethanol/toluene solvent mixture, the ratio between components being 1:2. A weighed amount of lignin dried in air (with a mass of about 75 g) was placed in the extraction chamber. 500 mL of the mixed solvent was placed in the boiling flask. Extraction was performed at vigorous boiling until solvent coloration disappeared (50 cycles). Then the solvent was removed by rotary evaporation. The flask with precipitate was dried at 50 ± 2 °C until constant weight was reached and then weighed.

The residual lignin content in the treated material was defined using the Klason-Komarov method.

30 mL of 72% solution of H_2SO_4 was poured in several steps into a vessel containing a weighed amount of extracted lignin dried in air (2 g); the solution was stirred every 15 min for 3 h, then kept at ambient temperature for a day. The mixture was diluted with 400 mL of distilled water and refluxed for 1 h. When the diluted mixture cooled, it was left for a day to let lignin particles precipitate. Then lignin was filtered off under vacuum. The filter with precipitate was dried at 100 °C until constant weight was reached.

Polyacrylonitrile used in our experiments is a technical copolymer of acrylonitrile with methacrylic (6%) and itaconic acids (1%) manufactured by Scientific-production association “Nitron”. Its molecular weight is 20–40·10³ Da, MWD is 4–6. The commercial solvent (reagent grade dimethyl sulfoxide (DMSO) (specifications 600-3818-89)) was obtained from “Vekton” JSC.

2.1.1. Preparation of samples for analysis

Primary thermal analyses (TGA and DTA) of the NTL, EL, ML and KL lignins were performed using the products in the form of a powder. A series of experiments aimed at revealing the role of binary solutions in the formation of composites was conducted using the samples in the form of solutions, films and fibers.

2.1.2. Preparation of solutions

Polyacrylonitrile was dissolved in DMSO (mass ratio of components was 1:9).

After exposure for 1 day at ambient temperature, THL was added to the formed solution at mixing; the mixture was homogenized for 2 days. The THL: PAN mass ratio was 80:20, the total amount of polymeric components in DMSO solution was 3%.

2.1.3. Preparation of films and fibers

The obtained forming solutions were used for preparing films and fibers. Films were obtained by spill casting onto glass surface, and fibers were molded using a SV-1000 syringe pump at a rate of 150 mL·h⁻¹. Fiber molding was carried out in precipitating bath at 80 °C for 15 min. The molded fibers were preoxidized at temperatures from 20 to 230 °C at a heating rate of 7 grad·min⁻¹; the product was exposed at 230 °C for 30 min. Then the fibers were carbonized in argon atmosphere; the temperature was increased up to 800 °C at a similar rate.

2.2. Thermal analysis (TGA, DTA, DSC, TVA)

Thermal analysis in oxidizing atmosphere (air flow rate was 50 mL·min⁻¹) was performed using a MOM Derivatograph-C (Hungary) at a constant heating rate (10 grad·min⁻¹); sample weight was 50 mg, Al_2O_3 was used as a standard. The TGA scale was 1/5, DTA scale was 1/3. The analysis in inert atmosphere (argon) was performed using a Netzsch TG-209 F1 instrument (TG, DTG curves) and a Netzsch DSC-204-F1 differential scanning

calorimeter, Germany (DSC curves) at a heating rate of $10 \text{ grad} \times \text{min}^{-1}$; sample weight was 1–3 mg, DSC scale (q) unit is $\text{mW} \times \text{g}^{-1}$. Thermal characteristics of forming mixtures based on THL and PAN solutions in binary solvents were obtained using a Netzsch STA 449 F3 and a Netzsch STA 449 F3A thermal analyzers in argon atmosphere. The heating rate was $20 \text{ grad} \times \text{min}^{-1}$.

The setup for thermal volumetric analysis (described in [13]) is a sealed glass system equipped with quartz reactor for pyrolysis, programmed heater and LTM-2 filled-system transducers.

2.3. Pyrolysis-gas chromatography/mass spectrometry

The selective pyrolysis of THL samples treated with the DMSO/H₂O solvent mixture (at various DMSO/H₂O ratios) was performed. An EGA/PY-3030 pyrolysis reactor (Frontier Lab) equipped with a cryotrap (cooled to $-197 \text{ }^\circ\text{C}$) was used; helium was used as a carrier gas. The heating rate was $30 \text{ grad} \times \text{min}^{-1}$; the final temperature was $800 \text{ }^\circ\text{C}$. Samples were taken in the following four temperature ranges (corresponding to the boundaries of peaks of releasing volatile thermodestruction products): 40–100, 100–250, 250–450, and 450–800 $^\circ\text{C}$. Chromatographic studies of pyrolysis products were performed using an Ultra-Alloy 5MC capillary column (0.25 mm in diameter, 30 m in length, with helium as a carrier gas and gas flow rate of $1 \text{ mL} \times \text{min}^{-1}$). The heating rate was $10 \text{ grad} \times \text{min}^{-1}$; the final temperature was $280 \text{ }^\circ\text{C}$. The mass (m/e) scanning range was 15–600.

3. Results and Discussion

3.1. Thermal analysis

Thermal analysis of the selected samples demonstrated the pronounced differences between their TGA and DSC curves obtained both in inert (Fig. 1) and oxidizing (Fig. 2) atmospheres. It can be seen that destruction of each sample is specific and depends on sample history. The comparison between the NTL kinetic curve of weight loss and those of treated samples (curves 1) shows considerable difference in weight loss rates in the first stage (up to approximately $100 \text{ }^\circ\text{C}$) and, particularly, during destruction within the $200\text{--}450 \text{ }^\circ\text{C}$ temperature range. Within this temperature range, dramatic transformations in chemical structure of lignin occur, as was observed in previous studies [11, 12]. The DTG curve of the NTL sample obtained during

thermodestruction in inert atmosphere demonstrates the general weight loss effect; the maximum decomposition rate is observed at $336 \text{ }^\circ\text{C}$. In the $255\text{--}460 \text{ }^\circ\text{C}$ range, decomposition of both low and high molecular weight products of wood hydrolysis takes place [14].

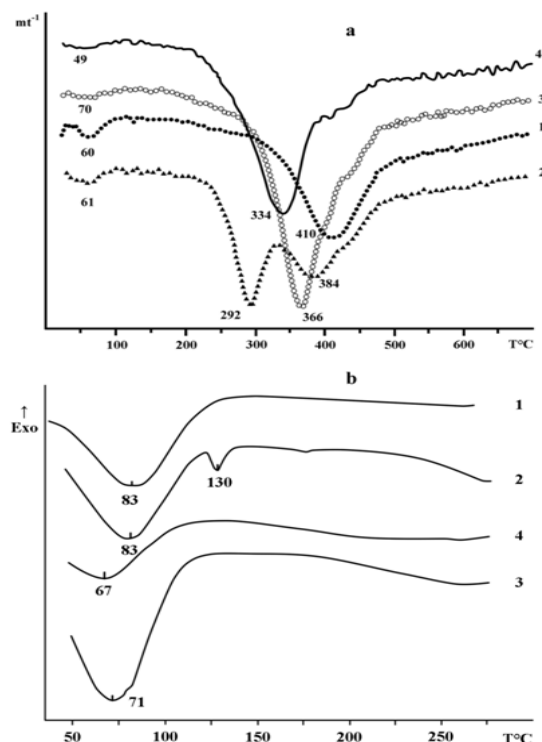


Fig. 1. The DTG (a) and DSC (b) curves of technical hydrolytic lignin obtained in inert atmosphere; T is the temperature: 1 – the KL sample; 2 – the EL sample; 3 – the NTL sample; 4 – the ML sample.

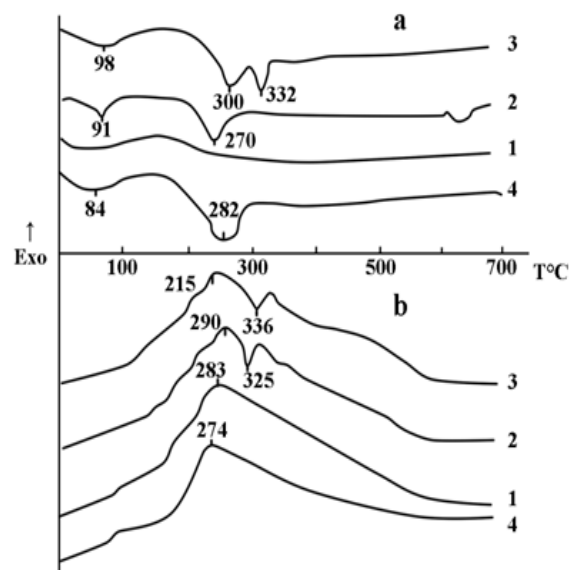


Fig. 2. The DTG (a) and DTA (b) curves of technical hydrolytic lignin obtained in oxidizing atmosphere. T is the temperature: 1 – the KL sample; 2 – the EL sample; 3 – the NTL sample; 4 – the ML sample.

The noticeable change in thermodestruction mechanism can be observed when the DTG curves of NTL and EL samples are compared. The well-defined peak at 292 °C and clear but wider and diffuse peak at 384 °C with a shoulder at 410 °C are visible in curve 2. This shape of the DTG curve indicates that after extraction of the NTL sample by ethanol/toluene mixture, low molecular weight fraction of hydrolytic lignin is removed (including some phenolic compounds). These compounds start to liberate at 150 °C; the maximum is reached at 300 °C. This conclusion is supported by the TGA data; it can be seen that until the temperature of 290–330 °C is reached, weight loss differences between the NTL and EL samples do not exceed 15%. In the low temperature region (from ambient temperature to 200 °C) difference in weight loss values is also noticeable (less than 2% for the NTL sample and about 4% for the EL sample). The DSC curves presented in Fig. 1b reflect considerable differences in heat absorption of the studied samples. While the NTL samples demonstrate endothermic effect at 71 °C ($q = 115.1 \text{ J} \times \text{g}^{-1}$, curve 3), the EL sample gives two peaks at 83.0 and 130 °C with the q values equal to 65.7 and $2.17 \text{ J} \times \text{g}^{-1}$, respectively (curve 2).

It can be concluded that extraction of the initial technical lignin leads to removal of a portion of low molecular weight impurities (which are soluble in ethanol/toluene mixture) and certain separation of the remaining portion into fractions with different thermal stability; one of these fractions comprises oriented formations with a melting point of about 130 °C (Fig. 1b, curve 2).

When thermal analysis is conducted in oxidizing atmosphere (Fig. 2a), the reverse occurs. Weight loss parameters shift to low temperature region, and for the NTL sample, as opposed to the EL sample, two stages of weight loss are observed (with maximums at 300 and 332 °C), while the destruction of the EL sample includes only one stage (the maximum at 270 °C) and proceeds at lower rate. Therefore, thermal oxidation of extracted lignin starts at lower temperatures and involves both fractions formed after extraction. The DTA data (Fig. 2b) demonstrate the presence of both fractions more clearly; Fig. 2b shows a certain interval between thermal oxidation peaks of the NTL and EL samples. The DTG, DSC and DTA curves of micronized lignin (the ML sample) and the Klason lignin (the KL sample) given in the same figure also demonstrate certain features differing from those of thermal and thermo-oxidative destruction of the NTL and EL

samples. According to the obtained results, we selected the micronized technical hydrolytic lignin as an object for further studies.

Since the process of formation of THL/PAN composite, in addition to initial macromolecular compounds, involves dimethyl sulfoxide (this compound was selected in previous studies [10, 12]), the role of this solvent was also investigated using combined thermal analysis (TGA, DSC, TVA).

Table 1 gives characteristics of the studied forming solutions, powders, films and fibers. Thermal analysis of these samples led us to certain conclusions and suggestions concerning the influence of concentration of initial components and temperature of destruction on the interactions between THL, PAN and DMSO.

Analysis of series of samples using TGA, DTG and DSC in inert atmosphere (Ar) was performed at a heating rate of $20 \text{ grad} \times \text{min}^{-1}$; sample weight varied from 3.2 to 32.8 mg.

The curves obtained for Samples 7–9 (Fig. 3a-b) are quite informative, since they demonstrate real changes in physico-chemical parameters of materials and serve as references in the analysis of composites. Any change in the shape of thermoanalytical curve (in integral or differential form) allows to obtain qualitative (conventionally) and quantitative characteristics of the analyzed sample. Thus, symmetrical shape of the DSC peak allows us to consider the studied DMSO sample as a sufficiently pure product. Slight deviation of the TG curve near 100 °C and corresponding deviation of the DSC curve in this region may be attributed to the presence of a small amount of water which is inevitably present in DMSO.

The TG and DSC curves obtained for PAN (curves 7 in Fig. 3a-b) at temperatures up to 300 °C are not complicated by side effects caused by the presence of impurities. The DSC maximum is typical for exothermic PAN cyclization and, essentially, is a signature of this polymer. Almost complete absence of weight loss indicated by the TG curve of Sample 8 (lignin) is typical of cross-linked hydrolytic lignins.

The studies of the second series of Samples (13, 14, 27, 28) (Fig. 4) demonstrated the influence of temperature on the process of formation of THL and PAN films accompanied by interactions with DMSO. The comparison between the TG and DSC curves of THL samples prepared at 20 and 120 °C shows considerable differences in temperature and weight parameters of the analyzed films. These differences allowed us to conclude that interaction

between DMSO and THL becomes stronger during isothermal heating at 120 °C. This effect is also visible in comparison between TG curves of Samples 13 and 14 (considering temperature boundaries and two-stage weight losses) in the 120–220 °C range.

The series of analyses of fiber samples (22, 23

and 24, Fig. 5a-b) formed from solutions containing THL and PAN (with THL: PAN ratio being equal to 80 : 20) at 20 and 70 °C gives us ground to assume that thermal properties of fiber composite samples change only slightly with increasing the temperature of heating of forming solution.

Table 1
Characteristics of samples studied by methods of thermal analysis^a

Sample № (in thermogram)	Components of sample	Temperature of preparation, °C	Form of sample	Sample mass, mg
9	DMSO	Ambient	Liquid	23.1
8	THL (ML)	Ambient	Powder	3.2
7	PAN	Ambient	Powder	3.4
13	THL+DMSO	20	Film	7.6
14	THL+DMSO	120	Film	10.7
27	PAN+DMSO	20	Film	7.0
28	PAN+DMSO	120	Film	4.2
23	THL+PAN+DMSO	20	Fiber	4.0
24	THL+PAN+DMSO	70	Fiber	4.9
22	THL(EL)+PAN+DMSO	20	Fiber	4.7

^aThe content of components in Samples 7–9 is 100%; the polymer content in forming solutions in DMSO used for film casting (Samples 13, 14, 27, 28) is 10%; fiber samples (22, 23, 24) were formed at 20 and 70 °C from 3% solution containing THL and PAN (THL: PAN ratio was 80 : 20). All lignin samples (except #22) are of the ML type..

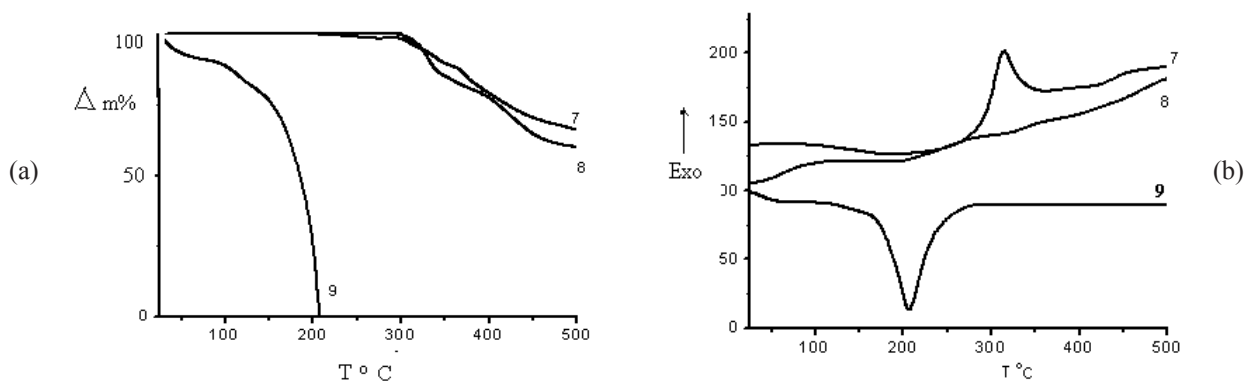


Fig. 3a. The TG curves of Samples 7–9. Fig. 3b. The DSC curves of Samples 7–9.

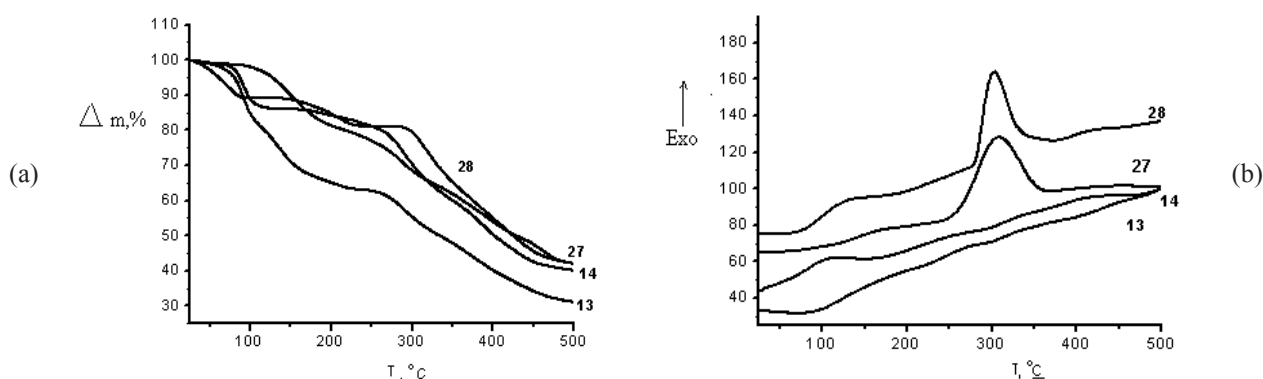


Fig. 4a. The TG curves of Samples 13, 14, 27 and 28. Fig. 4b. The DSC curves of Samples 13, 14, 27 and 28.

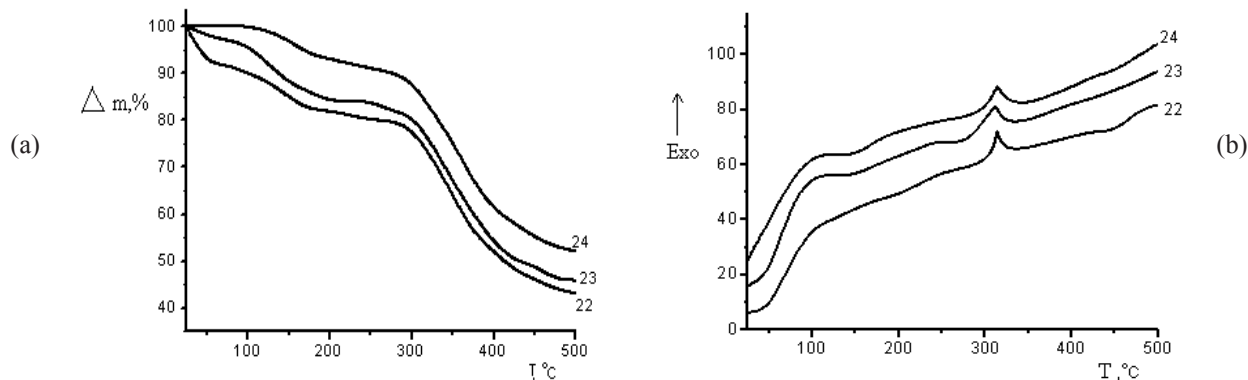


Fig. 5a. The TG curves of Samples 22–24. Fig. 5b. The DSC curves of Samples 22–24.

The more pronounced influence on the shape of TG curves is exerted by the properties of the initial THL; the curves obtained for the extracted sample (EL) demonstrate visibly different shape.

Thus, thermoanalytical measurements aimed at studying interactions between components of our composites (hydrolytic lignin, polyacrylonitrile and dimethyl sulfoxide) revealed certain effect of components ratio and heating temperature on the efficiency of interactions. This phenomenon is caused by loosening of the THL structure occurring under the action of DMSO and at increasing heat treatment temperature; in these conditions, reactive complexes are formed which participate in interpolymer interactions with PAN.

The effect described above was used for functional activation of THL necessary for conducting polymer-analogous transformations involving polyacrylonitrile.

The data obtained in the studies of DMSO influence on the formation and properties of THL/PAN composite confirmed the capability of this solvent for active influence on transformations of THL structure. However, as shown above, the process of dissolution of hydrolytic lignin is controlled not only by high activity of DMSO, but also by the nature of bonds existing between fragments of cross-linked THL system. It is known that hydrophilic-hydrophobic interactions with a solvent can be facilitated by using binary mixtures containing solvents of different nature. The DMSO/H₂O mixture is a unique combination and possesses an ability to penetrate deeply into lignin structure [15]. The studies of these penetration processes were performed using fiber THL samples impregnated with DMSO/H₂O mixture at ambient temperature and at 70 °C; the DMSO : H₂O ratios were the following: 100:0; 70:30; 50:50; 30:70 and 0:100. Kinetics of releasing volatile products of thermolysis under vacuum ($5\text{--}7 \times 10^{-2}$ mm Hg) was studied by TVA using the setup described in [13].

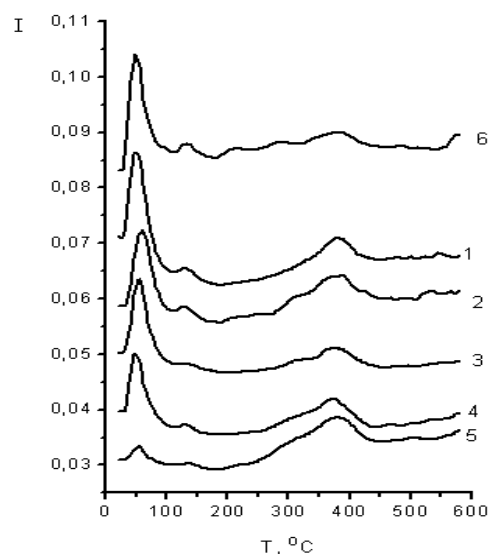


Fig. 6. The TVA curves of the THL samples impregnated with the DMSO/water binary mixture: 1 – DMSO + THL, sample weight is 0.0454 g; 2 – 70% of DMSO + 30% of water + THL; 3 – 50% of DMSO + 50% of water + THL; 4 – 30% of DMSO + 70% of water + THL; 5 – Water + THL; 6 – 70% of DMSO + 30% of water at 70 °C. The weight loss of the studied sample is 90–95% from the initial sample weight.

Figure 6 gives the combined thermogram of six THL samples impregnated with the binary solvent mixture (curves 2–6), the samples treated with DMSO (curve 1) and water (curve 5).

Analysis of TVA curve shape demonstrates that release of binary mixture components in vacuum takes place at heating up to 100 °C (the one peak is present in the thermogram). The maximum lies within the 50–59 °C temperature range and corresponds to the boiling temperatures of azeotropic mixtures of solvent components. Similar pattern is observed when peak areas are compared. It can be noted that at increased temperature of impregnation (curve 6), small shoulder at 76 °C appears. The appearance of this shoulder may be explained by stronger

interaction of one component of binary mixture with hydrolytic lignin molecules. Besides, all TVA curves include a maximum at 130 °C indicating the release of products of low temperature THL destruction. Mass spectrometry data obtained earlier [14] show that these products are aromatic aldehydes (sinapic, coniferyl, lilac and vanillic aldehydes). When temperature is increased up to 200 °C and higher, thermodestruction pattern changes significantly. In the temperature region below 500 °C, a number of peaks and TVA curve inflections within the 250–470 °C range are clearly visible. As is known, this area is attributed to massive release of THL thermodestruction products enriched with compounds containing active functional groups (carboxylic, ketonic, hydroxylic and other oxygen-containing compounds). The possibility of application of these compounds in polymer-analogous transformations of polyacrylonitrile was demonstrated earlier [7, 8].

To get further confirmation of the efficiency of DMSO/H₂O binary mixture in the process of THL fragmentation, pyrolysis of the above-mentioned THL samples impregnated with the binary mixture was performed. Temperature intervals of pyrolysis

approximately corresponded to the boundaries of TVA peaks (i.e., 40–100, 100–250, 250–400 and 450–800 °C).

Pyrolysis/gas chromatography/mass spectrometry was carried out in order to register the presence of DMSO in pyrolysis products. In the analysis of spectral characteristics obtained by this method, special attention was given to quantitative characteristics (peak areas) of sulphur-containing products. These are the following fragments (molecular masses are given in parentheses): C₂H₆S (62), C₂H₆OS (78), C₂H₆O₂S and C₂H₆S₂ (94), C₄H₈OS (104) and C₃H₈S₂ (108). The bulk of sulfur-containing compounds comprises dimethyl sulfoxide (C₂H₆OS); it is present in the products of pyrolysis conducted at 40–100 and 100–250 °C; small amount of this compound (about 0.5–1.2%) was registered at higher temperatures. The portions of other detected fragments (except C₂H₆S) in samples did not exceed 0.02–1% of total amount of sulfur-containing compounds. Table 2 gives the content of these compounds in pyrolysis products depending on pyrolysis temperature and ratio between components of the binary solvent (DMSO:H₂O).

Table 2

Composition and content of sulfur-containing compounds in the products of pyrolysis of THL/binary solvent mixtures^a (percentage of the total amount)

Sample № and temperature range of pyrolysis (°C)	Formulae and molecular masses of compounds					
	C ₂ H ₆ S-62	C ₂ H ₆ OS-78	C ₂ H ₆ O ₂ S-94	C ₂ H ₆ S ₂ -94	C ₄ H ₈ OS-104	C ₃ H ₈ S ₂ -108
1						
40–100	-	84.05	0.12	0.05	-	0.07
100–250	22.64	94.58	0.07	-	-	-
250–400	-	1.20	-	1.07	-	4.20
2						
40–100	-	82.62	0.03	-	-	-
100–250	30.42	62.95	0.06	0.68	-	0.03
250–400	-	0.76	-	0.15	-	0.06
3						
40–100	-	92.27	0.02	0.01	-	0.01
100–250	-	85.74	0.03	-	-	-
250–400	-	0.48	0.23	-	-	-
4						
40–100	-	89.18	-	-	-	-
100–250	-	82.61	-	-	-	-
250–400	-	-	-	-	-	-
5						
40–100	-	98.20	0.40	-	-	-
100–250	-	72.97	2.00	-	0.24	-
250–400	-	-	-	-	-	-

^a The composition of binary solvent mixture: 1 – 100% DMSO; 2, 5 – DMSO:H₂O = 70:30; 3 – DMSO:H₂O = 50:50; 4 – DMSO:H₂O = 30:70. No sulfur-containing compounds were found within the 450–800 °C range. Sample №5 was prepared at 70 °C; other samples were prepared at 20 °C.

The analysis of the obtained data shows that in the process of pyrolysis of HL treated with the binary solvent, dimethyl sulfoxide is released not only at its boiling temperature. Judging from the considerable amount of this compound liberated in the 100–250 °C interval, its interaction with THL is not restricted to adsorption. Apparently, a fraction of DMSO molecules forms hydrogen bonds with lignin functional groups, the strength of these bonds depending on the nature of a given lignin functional group. The formation of hydrogen bonds facilitates deeper permeation of DMSO into THL structure and, therefore, leads to THL loosening and increasing the rate of its fragmentation during pyrolysis. The water participating in this process probably shifts balance of donor-acceptor interactions and thus weakens intramolecular bonds in THL.

This assumption is supported by the following observations: decrease in the amount of DMSO in pyrolysis products at temperatures higher than 100 °C and the presence of its fragments in high-temperature area of the thermogram. Thus, dynamics of release of sulfur-containing compounds of THL pyrolysis in the presence of binary solvent mixture is in agreement with the thermal analysis data (this conclusion deals both with destruction temperatures and mass characteristics of fragments).

The obtained data give us reason to conclude that using the DMSO/H₂O mixture facilitates activation (fragmentation) of THL and, therefore, enables successful polymer-analogous transformations involving synthetic polymers to be performed.

4. Conclusions

1. The combined thermal and gas chromatography/mass spectrometry analysis of technical hydrolytic lignin samples was performed; the sample capable of polymer-analogous transformations was detected.

2. It was found that the dimethyl sulfoxide/water 70:30 mass ration solvent mixture serves as an active medium for hydrolytic lignin fragmentation and providing the formation of homogeneous forming solution of the composite polymer (hydrolysis lignin-polyacrylonitrile) with a maximum lignin content of 80%.

3. The possibility of obtaining hydrolytic lignin/polyacrylonitrile composites in the binary solvent (in the form of films and fibers) was demonstrated.

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