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Carbonization of polymeric nonwoven materials

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ABSTRACT

Carbonization process of resol phenol formaldehyde resin–polyvinyl butiral copolymer is discussed. Gaseous products of pyrolysis were analyzed by means of GC/MS. These data along with data from periodic sources were used to offer probable scheme of pyrolysis process of this copolymer. Kinetic parameters of the process were obtained from dynamic thermogravimetric measurements. The parameters were used to calculate constant mass loss rate temperature program. BET areas and pore size distributions of samples prepared using constant heating rate and constant mass loss rate temperature programs were calculated from nitrogen adsorption isotherms.

1. Introduction

Phenol formaldehyde resins (PFRs) are widely used as precursors of miscellaneous carbon materials from glassy carbon to highly porous activated carbon materials. The distinctive feature of PFR-originated porous carbon materials is their dominantly microporous structure making them promising materials for gas adsorbents. Fibrous morphology of adsorbents is preferable to monolith activated composites due to large transport pores reducing diffusion limitations.

Pristine PFR is brittle and plasticizer is required to get fine and flexible fibers. Common plasticizers for PFRs are polyvinyl butyral (PVB) [1,2] and polyvinyl alcohol [3]. Carbon porous materials were prepared earlier from nonwoven PFR–PVB copolymer [2] however carbonization process was not optimized as pore size distribution of sample carbonized using temperature program listed in [2] was wide. Special thermal treatment like “a constant mass loss carbonization” may narrow down pore size distribution in the material and allow more precise and simple control of an average pore size. Such carbonization procedure changes mass transfer conditions so that rate at which gaseous products of pirolysis evolve from material stays constant. Understanding of carbonization mechanism and knowledge of its kinetic parameters are essential for such treatment. Although carbonization of PFRs was extensively studied by different authors [4–7], data on pyrolysis of both PVB and PFR–PVB copolymer are scarce. A pyrolysis mechanism of PVB in N_2 atmosphere was studied by Grachev et al. [8]. Ozaki et al. [9] suggested probable mechanism of decomposition of novolac PFR–PVB blend cured by HCl-formaldehyde solution, but the paper focuses on decomposition of PFRs in blend. Kinetic of pyrolysis processes is studied only for PFRs [4,5].

This paper is concerned with carbonization of resol PFR–PVB copolymer nonwoven material.

2. Experimental

2.1. Reagents

Industrial BF-2 phenolic glue (complied with GOST R 12172-74) was used as a polymeric precursor. This glue is 14–17% ethanol solution of resol PFR–PVB blend with 1:1 PFR–PVB mass ratio. Chemically pure toluene sulphonic acid hydrate in amount of 10 mass% of PFR was added to the solution as a curing agent.

2.2. Spinning of nonwoven materials

Polymeric nonwoven materials were prepared by conventional electrospinning process with a single capillary and vertically aligned electrode (Fig. 1). Voltage, distance between electrodes and spinning rate were adjusted to obtain polymeric nonwoven material with diameter of fibers around 2–3 μm.

The polymer felt was cured by a slow heating in air up to 150 °C with a rate of 10 °C per hour. According to [10] an oxidative treatment is important to obtain a highly porous carbon material from phenol formaldehyde precursor; therefore the cured material was further heated in air up to 250 °C with a rate of 5 °C per minute with an isothermal stage of 30 min at 250 °C.

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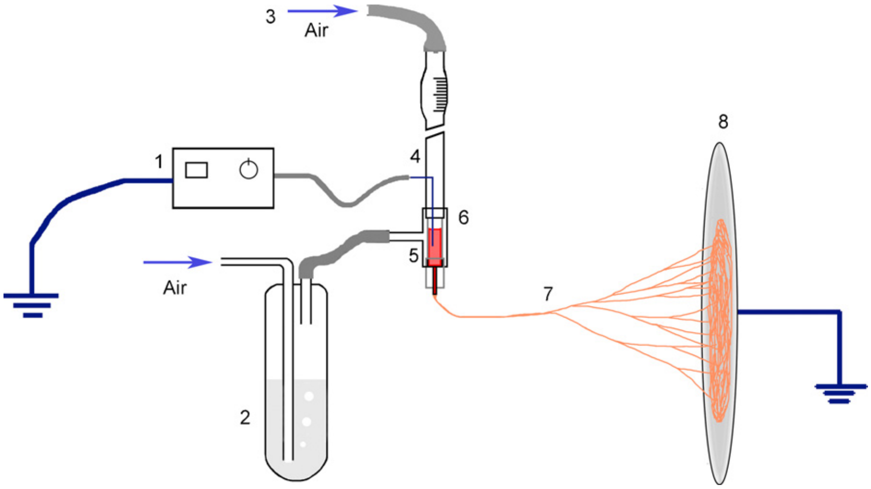

Fig. 1. Single capillary electrospinning apparatus. 1: High voltage source, 2: thermostatted bulb with ethanol, 3: dosaging pressure supply, 4: platinum electrode, 5: stainless steel tip with ethanol vapor supply, 6: polymer solution, 7: polymer jet, 8: collecting electrode (either flat or rotating drum).

2.3. GC/MS measurements of pyrolysis

Pyrolysis of oxidized polymer was performed in Trace DSQ II (Thermo Electron Corp.) GC/MS apparatus with a pyrolytical cell Pyroprobe 5000 (CDS Analytical Inc.). A sample was placed into a pyrolysis tray and heated up by platinum wire at rate of 50 °C/min. Argon (99.998% purity) with a constant flow of 1.2 ml/min was used as a carrier gas. A temperature of both the tray and the sample was determined by measuring an electric resistance of the wire. Gaseous products of pyrolysis were sampled for 10 s at temperatures of 300, 400, 500, 600 and 700 °C; during the sampling a tray temperature was stabilized.

2.4. Thermogravimetry of pyrolysis process

Thermogravimetric analysis was carried out using TG 209 F3 thermobalance (Netzsch Geratebau GmbH). Oxidized samples were heated in Al_2O_3 crucibles from 40 to 950 °C with 2.5, 5, 10 and 20 K/min heating rates in a dynamic argon atmosphere with a constant flow of 60 ml/min; masses of samples were in a range of 10–12 mg.

2.5. Specific surface area and pore size distribution measurements of carbonized samples

Specific area and pore size distribution measurements were obtained from nitrogen adsorption measurements using Sorptomatic 2000 apparatus (Thermo Electron Corp.). Samples were heated up to 200 °C in vacuum for 3 h prior to measurements to remove adsorbates like water and carbon dioxide. The specific surface area was calculated according to Brunauer–Emmeth–Teller (B.E.T.) theory. A mesopore size distribution and a pore volume were calculated according to Dollimore-Heal model [11], whereas a micropore size distribution and a micropore volume were calculated according to Horvath-Kawazoe model [12].

3. Results and discussion

3.1. GC/MS analysis

Main pyrolysis products of PFR–PVB polymer at 300 °C are phenol and butanal. Increasing temperature to 400 °C results in alkyl carbonyl compounds with different chain lengths such as 3-buten-2-one and 3,5-hexadien-2-one being evolved. These products can be associated with destruction of PVB chain. Aromatic compounds such as toluene, xylene, benzofuran, naphthalene and phenol derivatives are also detected at this temperature but in smaller amounts. Their presence can be attributed to destruction of PFR and products of its curing with PVB. Between 500 and 600 °C amount of alkyl carbonyl compounds in the pyrolysis products is drastically decreased, whereas amount of aromatic compounds especially condensed ones such as methylnaphthalenes, anthracene and phenanthrene is increased. This is an indication of internal curing and condensation processes occurring in the material in this temperature range. At 700 °C only phenol and methyl phenols as well as the condensed aromatic compounds are detected. Phenols are evolved due to continued scission of terminal and internal groups, while the condensed aromatic compounds with two or more aromatic cycles are emitted from polyaromatic fragments formed in the sample. Thus, pyrolysis of PFR–PVB polymer consists of three consecutive overlapping processes: destruction of PVB chain, internal curing and condensation and formation of large polyaromatic fragments.

3.2. Thermogravimetric analysis

A differential thermogravimetric (DTG) analysis (Fig. 2) indicates a carbonization process as a multi-stage one. At least three features can be distinguished on the DTG curve. One feature appeared as a DTG peak at around 100 °C is most likely related to water desorption. Other features appeared as at least two or much

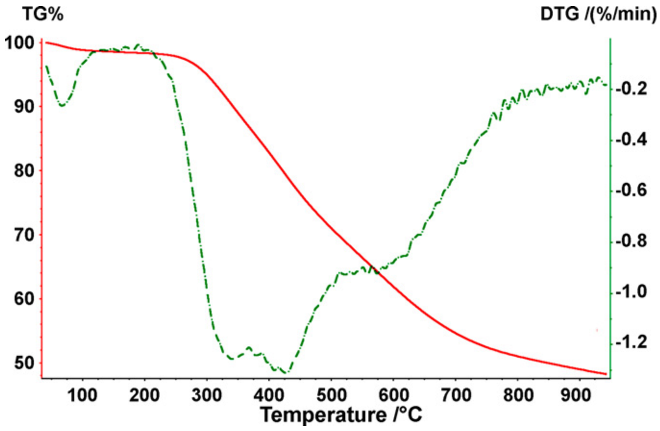

Fig. 2. TG and DTG curves of oxidized resol PFR–PVB blend fibers.

more likely three overlapping peaks in 300–800 °C temperature range.

Three-stage model of copolymer pyrolysis may be suggested from the pyrolysis data for PVB [8] and PFR polymers [4,5]. Decomposition of polyvinyl butyral chain occurs in a temperature range of 300–450 °C and decomposition products react with PFR macromolecules. In a range of 400–550 °C condensed aromatic compounds with furan and pyran cycles are formed. Finally, in a temperature range of 550–850 °C polyaromatic fragments containing three or more condensed aromatic cycles nucleate and grow. The carbonization process is characterized by removal of heteroatoms such as O and H as CO_2 and water as well as parts of polymer chains.

GC/MS data do not contradict with suggested 3-stage pyrolysis scheme.

3.3. *Kinetic analysis*

Rate of heterogenic decomposition reactions $A_{soloid} \rightarrow B_{solid} + C_{gaseous}$ is described by following equation:

$$\frac{dp}{dt} = Y(p, r, t, T) \qquad (1)$$

where *p* is concentration of products, *r* is concentration of reagents, *t* is time and *T* is temperature. Function Y can be described using two different separable functions:

$$\frac{dp}{dt} = k(T(t))f(r, p) \qquad (2)$$

Function $k(T)$ can be expressed through Arrhenius equation and with additional definition of heating rate $\beta = dT/dt$ equation (2) becomes:

$$\frac{dp}{dT} = \frac{k_0}{\beta} \cdot e^{\frac{-E_a}{RT}} f(r, p) \qquad (3)$$

where k_0 is pre-exponential factor and E_a is apparent activation energy.

For single step processes $f(r, p)$ is reduced to $f(r)$, where $r = 1 - \alpha$, and $p = \alpha$, where α is the degree of conversion which is defined as $\alpha = (m_0 - m)/(m_0 - m_\infty)$ with m_0 being the initial mass of sample, m the actual mass and m_∞ the final mass. Thus Eq. (2) is transformed into

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \cdot e^{\frac{-E_a}{RT}} f(\alpha) \qquad (4)$$

Type of conversion function $f(\alpha)$ depends on nature of process and is usually determined *a priori*. For multi-step processes Eq. (2) can be transformed in system of differential equations with inseparable variables which can be solved only in most simple cases. Several techniques were developed [13] to calculate kinetic parameters from experimental data for complicated cases. They can be divided into isoconversional (model-free) methods and model-fitting methods. Each type has its own advantages and disadvantages, but best results are achieved using combination of isoconversional and model-fitting method.

Both types of methods are implemented in Netzsch Thermokinetics 3 software used to calculate kinetic parameters of pyrolysis process from obtained results of TG measurements. This software was described by Opfermann [14] and was successfully used earlier [15]. Model-fitting operates through multivariate non-linear regression with Marqardt–Levenberg hybrid algorithm. The algorithm assumes that mechanism of process and type of conversion function $f(\alpha)$ does not change with changing the heating rate. This assumption is not always valid and needs to be verified. To do it affine transformation of TG curves into normalized time ($t_i/t_{0.5}$)—fractional reaction coordinates was performed (Fig. 3). Variances between curves of parallel measurements with same heating rate and between curves of measurements with different heating rates were determined and *F*-test value was calculated as ratio of variances (degrees of freedom for each set of curves were equal). It was found to be $F_{exp} = 1.42$, while $F_{critical} = 2.20$ for degree of confidence 0.95, which means F_{exp} is below critical value and all curves coincide within error margin and assumption required to apply non-linear regression is valid.

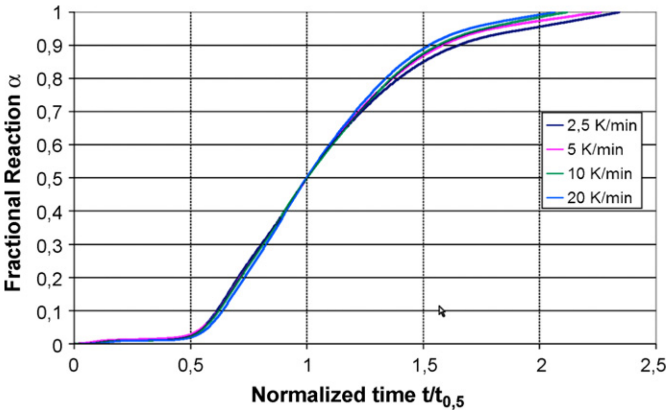

Fig. 3. TG curves with different heating rates in normalized time–fractional reaction coordinates.

Standard operating procedure suggested by Opfermann is to estimate activation energy of process using Ozawa–Flynn–Wall [16] isoconversional method and use obtained value as initial value for non-regression procedure. For multi-stage processes calculated apparent activation energy is function of actual activation energies for each of processes undergoing at set fractional reaction. This causes significant errors in estimation of activation energies for each process and may lead to major errors in calculation of kinetic parameters using non-linear regression due to nature of procedure. In case of process with mixed consecutive and parallel stages possible errors in estimation of initial values are certainly big. Carbonization is one of such processes. To overcome this limitation whole curve was represented as superposition of single-stage processes. DTG curves for each stage were obtained by means of the peak deconvolution software (Netzsch Peak Separation) (Fig. 4).

Partial areas of each separated peak were constant within error margin for every heating rate, which confirms description of

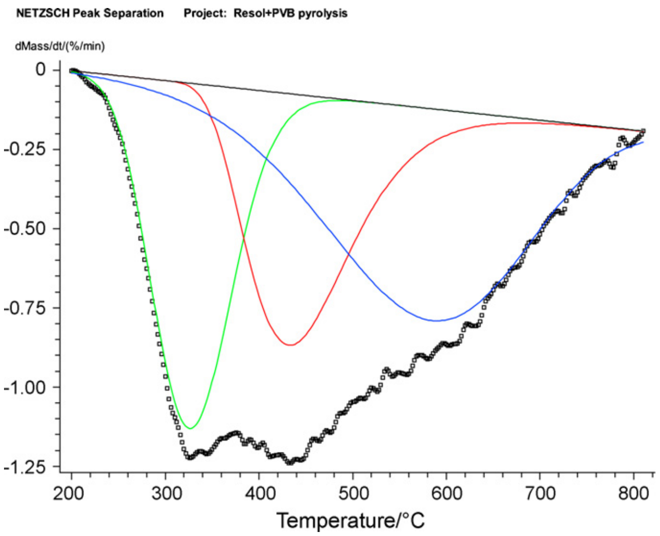

Fig. 4. DTG peaks deconvolution.

Table 1
Calculated kinetic parameters for separate stages.

Stage No., i	$(E_a)_i/R$, K^{-1}	Pre-exponential factor, $\log A_i$	Reaction order, n_i
1	12,800 ± 200	7.0 ± 0.2	2 ± 0.02
2	17,400 ± 400	8.4 ± 0.3	3 ± 0.06
3	39,700 ± 2600	17.3 ± 1.3	0.19 ± 0.01

Table 2
Kinetic parameters for each stage calculated from whole DTG curves.

Stage No., i	$(E_a)_i/R$, K^{-1}	Pre-exponential factor, $\log A_i$	Reaction order, n_i
1	12,600 ± 100	7.1 ± 0.1	1.33 ± 0.01
2	10,800 ± 100	4.3 ± 0.1	3 ± 0.01
3	28,700 ± 100	12.2 ± 0.1	0.15 ± 0.01

complicated carbonization process through superposition of three limiting stages.

Kinetic parameters of each stage were estimated using model-free isoconversional Osawa–Flynn–Wall [16] method and refined using non-linear regression procedure. Since type of conversion function $f(\alpha)$ was unknown, non-linear regression procedure was used for each type of conversion function available in Thermokinetics software and statistical comparison of fit qualities was performed. Fit quality was estimated as a sum of least squares of deviations between calculated DTG curves and experimental ones. Best curve fit for first and second stages was obtained using n-th order reaction equation $f(\alpha) = (1 - \alpha)^n$, while third stage was best fit using Avrami–Erofeev equation $f(\alpha) = (1 - \alpha) \cdot (-\ln(1 - \alpha))^{(n-1)/n}$. Calculated kinetic parameters for each stage are listed in Table 1.

Kinetic parameters calculated for each stage were used as initial parameters for non-linear regression optimization of whole DTG curve. Several combinations of parallel, competitive and consecutive processes were used and fit qualities were determined for each model. Best fit quality was obtained for three consecutive reactions model. Kinetic parameters for each stage of whole curve are listed in Table 2.

While kinetic parameters of each stage for the whole curve are different from those obtained for the separate curves, there are no changes in types of conversion functions. This fact supports the suggested pyrolysis model.

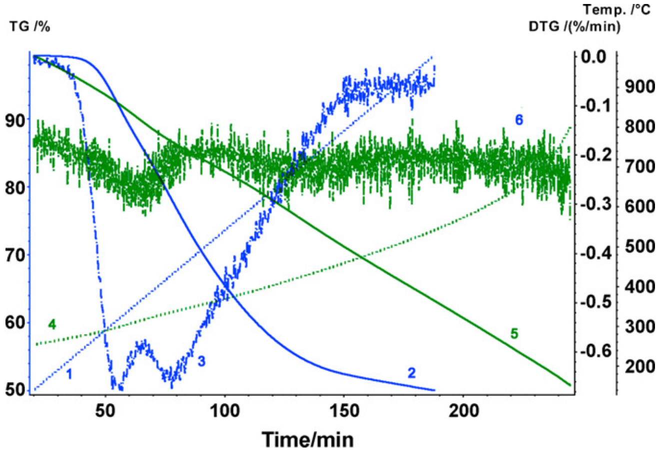

Fig. 5. TG experiments with heating rate 5K/min and according to calculated program. 1: Curve of temperature program for constant heating rate, 2: mass loss curve for constant heating rate temperature program, 3: mass loss rate for constant heating rate temperature program, 4: calculated temperature program, 5: actual mass loss curve for sample heated according to calculated temperature program, 6: actual mass loss rate curve for sample heated according to calculated temperature program.

Table 3
BET specific area and pore characteristics of carbonized samples.

Characteristic	CHR sample	CMLR sample
BET area (m^2/g)	477	675
Mesopore volume (cm^3/g)	0.09	0.10
Median mesopore radius (nm)	3.15	3.0
Micropore volume (cm^3/g)	0.22	0.29
Median micropore radius (nm)	0.4	0.3

3.4. Constant mass loss rate carbonization

Obtained kinetic parameters were used to calculate temperature program for carbonization with constant mass loss rate 0.2%/min. Calculation was performed using standard Netzsch Kinetics 3 function Actual TG experiment displayed what this temperature program allows carbonization of PFR–PVB copolymer with significantly smoother mass loss rate (Fig. 5) compared to constant heating rate temperature programs. Mass loss rate during carbonization according to temperature program was within 0.22 ± 0.04%/min range. Such deviation from desired 0.2%/min value is acceptable for practical use.

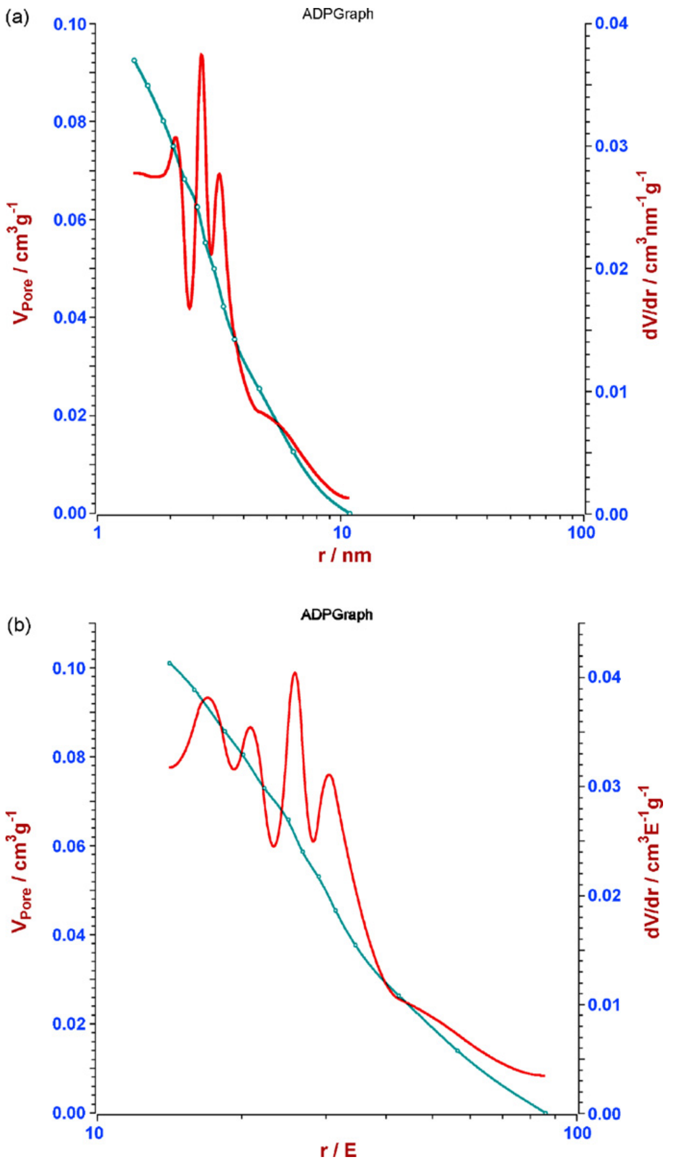

Fig. 6. Mesopore size distribution of CHR (a) and CMLR (b) samples.

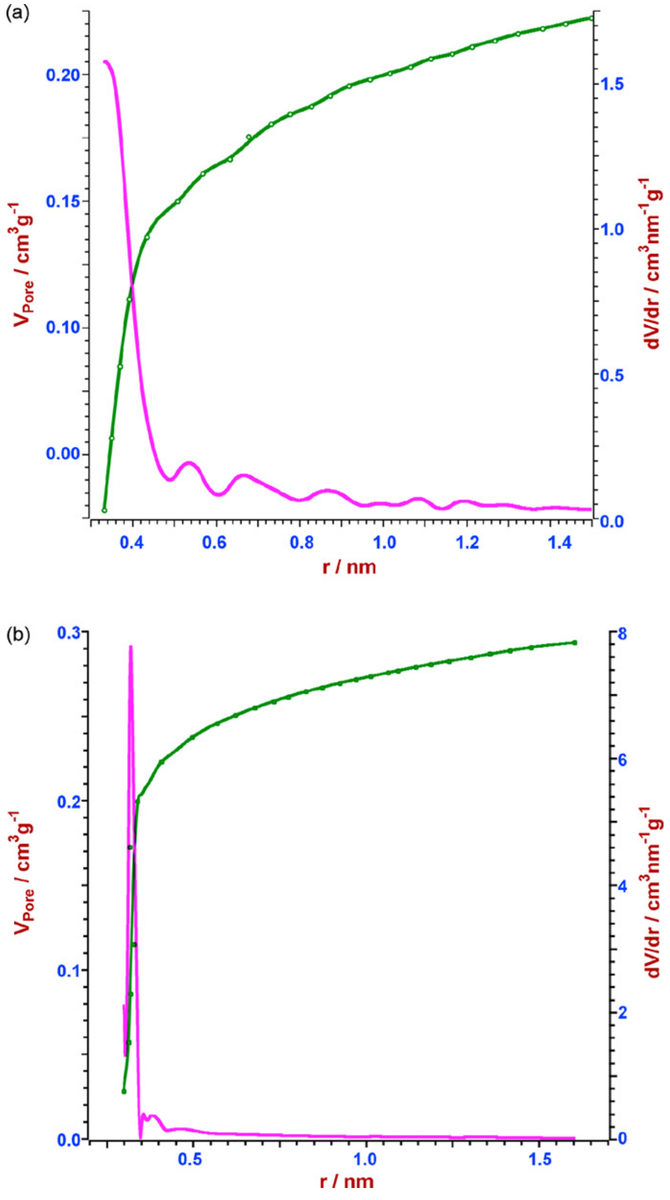

Fig. 7. Micropore size distribution of CHR (a) and CMLR (b) samples.

3.5. *Specific surface and pore characterization of carbonized materials*

Specific surface and pore characterization measurements were performed on 100 mg samples, which were prepared by carbonization of 500 mg samples of oxidized PFR–PVB nonwoven material in tube furnace under dynamic nitrogen atmosphere according to constant heating rate of 5 K/min (sample CHR) and constant mass loss rate of 0.2%/min (sample CMLR) temperature programs.

B.E.T. specific areas of samples, mesopore and micropore volumes and peaks' width are given in Table 3. Mesopore and micropore size distributions in samples are given in Figs. 6 and 7. B.E.T. area and pore volumes of CMLR sample are higher than those in CHR sample, extra surface area is due to increased amount of micropores. Pore size distribution of sample CMLR is narrower in both mesopore and micropore region, and pore sizes are smaller than those in CHR sample.

4. Conclusions

Oxidized resol PFR–PVB copolymer carbonizes in three-stage process. Major pyrolysis products detected by GC/MS are butanal and phenol at 300 °C, alkyl carbonyl compounds at 400–500 °C and methyl phenols and condensed aromatic compounds at 600–700 °C. Kinetic parameters E_a, k_0 and conversion function $f(\alpha)$ of each stage were determined on the base of dynamic TG measurements in assumption of three consecutive reactions model.

Constant mass loss rate program was calculated on the basis of determined kinetic parameters. Actual mass loss rate in TG experiment according to calculated program was in fair agreement with rate assumed in calculation.

Samples prepared according to constant mass loss rate program show narrower pore size distribution compared to samples prepared using constant heating rate. It shows advantage of constant mass loss rate carbonization procedure compared with standard constant heating rate carbonization.

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