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UTILIZATION OF WASTE PAN FIBERS AS ADSORBENTS BY CHEMICAL AND THERMAL MODIFICATION

JOHANNIS SIMITZIS,[1]* EKATERINA TERLEMESIAN[2] and IVAN MLADENOV[2]

[1]Department of Chemical Engineering, Laboratory of Special Chemical Technology, National Technical University of Athens, 9 Heroon Polytechniou Str., Zografou Campus, GR-157 80 Athens, Greece and [2]Department of Technology of Polymers, Textile and Fur, Higher Institute of Chemical Technology, 1156 Sofia, Kl. Ohridiski Str., Bulgaria

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Abstract—Polyacrylonitrile (PAN) polymers obtained from industrial waste fibers (i.e. "Bulana") were modified with ethylene diamine (EDA) at low and high concentration. The structural changes after the chemical treatment were determined by IR-spectroscopy following dissolution in concentrated sulfuric acid. The cross-linking formation as well as the formation of various groups (such as amine, imine, amide, carbonyl) were observed. The unmodified and EDA-modified polymers were pyrolyzed in a nitrogen stream at temperatures up to 600°C. The weight losses measured by weighing the sample before and after pyrolysis and thermogravimetric analysis revealed three regions (up to 300 and 500°C having very high weight losses and above 500°C having lower weight losses), while associated changes of the various groups of the polymers were determined by IR-spectroscopy. The adsorption (discoloring) ability of the polymers was examined by using aqueous solution of methylene blue or alizarin yellow. The experimental results were correlated with those of model polymers based on polyacrylonitrile, having known structure, and interpreted on the basis of electron donor–acceptor (EDA) interaction concept between the main groups of the polymers and the dyes. The adsorption ability of the pyrolyzed polymers up to 300°C (especially for the unmodified and low amine modified forms) for both dyes were improved in comparison with the corresponding unmodified polymer. The pyrolyzed polymers treated above 400°C showed no discoloring ability because of the absence of nitrile groups (completely lost through cyclization reactions) and other groups.

INTRODUCTION

Acrylic fibers comprise at least 85 wt% of acrylonitrile units (–CH_2–CH(CN)–) and they are used in a variety of knits, carpets, blankets, man-made furs as well as the main precursor material [i.e. polyacrylonitrile (PAN) fibers] in production of carbon and graphite fibers [1–3]. Acrylic fibers are the third important type of synthetic fibers after polyester and polyamide fibers [4].

Some ways for utilizing PAN wastes (from the production of polymers) for technical applications are known. Ion exchange fibers are obtained by means of polymer analogous conversion of polyacrylonitrile (PAN) nitrile groups, e.g. by alkaline or acid saponification, and by cross-linking of the polymer with certain bifunctional compounds (e.g. hydrazine hydrate) [5, 6]. Modified PAN fibers reacted with ethylene diamine (EDA) reveal polyfunctional properties, while fibers treated with hydrazine hydrate (HH) or diethylene triamine (DETA) exhibit anion exchange properties [7, 8]. Acrylic polymers or copolymers are used as fibers, sorbents and stationary phases of gas chromatography [9].

Recently [10], PAN (non-fiber) has been modified with H_2SO_4 or NaOH, and in addition copolymers of acrylonitrile with acrylic acid, acrylamide and methylene bisacrylamide have been prepared and investigated, to examine their ability to adsorb dyes from aqueous solutions. The results were interpreted in terms of electron–donor (EDA) interactions between the main groups of the polymers and the dyes.

The aim of this work is to investigate the possibility of making adsorbents by thermal treatment of chemically modified wastes of PAN fibers which contain various functional groups. The ability of the untreated and thermally treated polymers (i.e. pyropolymers which are organic polymers pyrolyzed at low temperatures) to adsorb various dyes from aqueous solutions was also to be investigated.

EXPERIMENTAL

Production method

PAN fibers "Bulana" (manufacturer: BG Bulgaria) taken as waste from the industrial production were used. These fibers are made from a copolymer of acrylonitrile with 5% methyl methacrylate and 1% sodium vinyl sulfonate. After cutting, the fibers were treated with ϵ-caprolactam at 120°C and soluble material extracted in hot water, to constant weight. The product was obtained as a porous powder. This was modified by reaction with ethylene diamine at both low or high concentrations, at pH = 10 [11]. The unmodified and EDA modified materials were pyrolyzed in a horizontal oven under a nitrogen stream at various temperatures up to 600°C with an average heating rate of 3.3°C/min and with a hold-on time of 1 min at the final temperature.

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*To whom all correspondence should be addressed.

Table 1. Modification, solubility and cross-linking of PAN porous polymers

Symbol no.	Modification with ethylene–diamine	Solubility in conc. H_2SO_4 at 96°C, 90 min (%)	Cross-linking
1	not (without)	99.6	practically not
2	low concentration	82.0	low
3	high concentration	1.3	high

Characterization of the pyro-polymer products

The *weight losses during the pyrolysis* were determined by weighing the sample before and after treatment (discontinuous method). Weight loss was also determined by thermogravimetric analysis under a nitrogen stream with linear heating rate of 10°C/min using a Perkin–Elmer TGS-2 thermogravimetric analyzer (continuous method). In the latter case, the first derivate of the weight losses was simultaneously recorded.

The *infrared* (*IR*)*-spectra* of the polymers were carried out using pellets of the polymer dispersed in KBr powder.

The *specific surface area* of the polymers was measured according to the standard method of DIN 66132 with nitrogen as gas.

The *solubility* of the unmodified and modified with EDA polymers was determined in concentrated H_2SO_4 [12] at 96°C for 90 min by weighing the sample before and after treatment and the degree of cross-linking of the polymers was determined.

The *discoloring* (*adsorption*) *ability* of the polymers was examined by using aqueous solutions of methylene blue or alizarin yellow R, with an initial concentration of 0.0320 g/l in both cases. In this determination a known amount of the polymer was mixed with a definite amount of an aqueous solution of the dye at 25°C without stirring. The ratio of polymer to initial solution of the dye (wt:vol) was 20 g/l. The color of the solution for various time intervals was determined using a colorimetrical calibration scale according to standard solution concentrations, or with the aid of the Colorimeter Lovibond Tintometer Model E.

RESULTS

Table 1 presents three examples of PAN (unmodified and modified with ethylene diamine) as a porous powder.

Figure 1 shows the weight losses of unmodified and modified with EDA PAN powders, during their pyrolysis up to 600°C. The weight losses of the samples determined by weighing them before and after the pyrolysis at the final temperature (discontinuous method), are higher than those obtained by *in situ* continuous measurements of the thermogravimetric analysis (compare No. 1 with 1T and No. 2 with 2T).

Figures 2–5 show the IR-spectra of the polymers. The presence of various groups of the polymers can be concluded from the corresponding absorption peaks [13–15]. The unmodified polyacrylonitrile powder without cross-linking has the same groups as the industrial PAN fibers "Bulana" [Fig. 2(a)]. The absorption bands that find particular interest are: C≡N (at 2.243 cm^{-1}) from acrylonitrile and C=O (at 1.727 cm^{-1}) from methyl methacrylate comonomer units. Other absorption bands due to various groups are: OH (at 3.600 cm^{-1}), CH_2 (at 2.940 cm^{-1}), CH_2 (at 1.455 cm^{-1}), CH, =CH–X or possibly O–H (at 1.362 cm^{-1}), CH, C–N, C–O (at 1.222 cm^{-1}), C–OH (at 1.127 cm^{-1}).

In the spectrum of the low cross-linked polymer [Fig. 3(a)] two intense bands are visible at 1.630 and 1.569 cm^{-1}. The first one could be assigned to C=O of amide group and C=N of imine group, and the

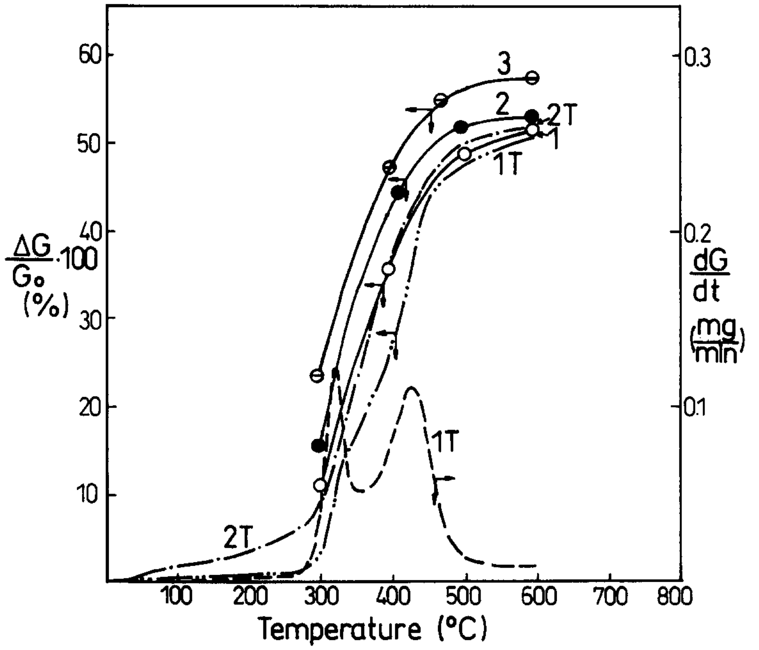


Fig. 1. Weight losses of PAN fibers during their pyrolysis (for Nos 1, 2 and 3 see Table 1. The symbol "T" indicates the continuous curves receiving by thermogravimetric analysis. ΔG: weight losses, G_o: initial weight).

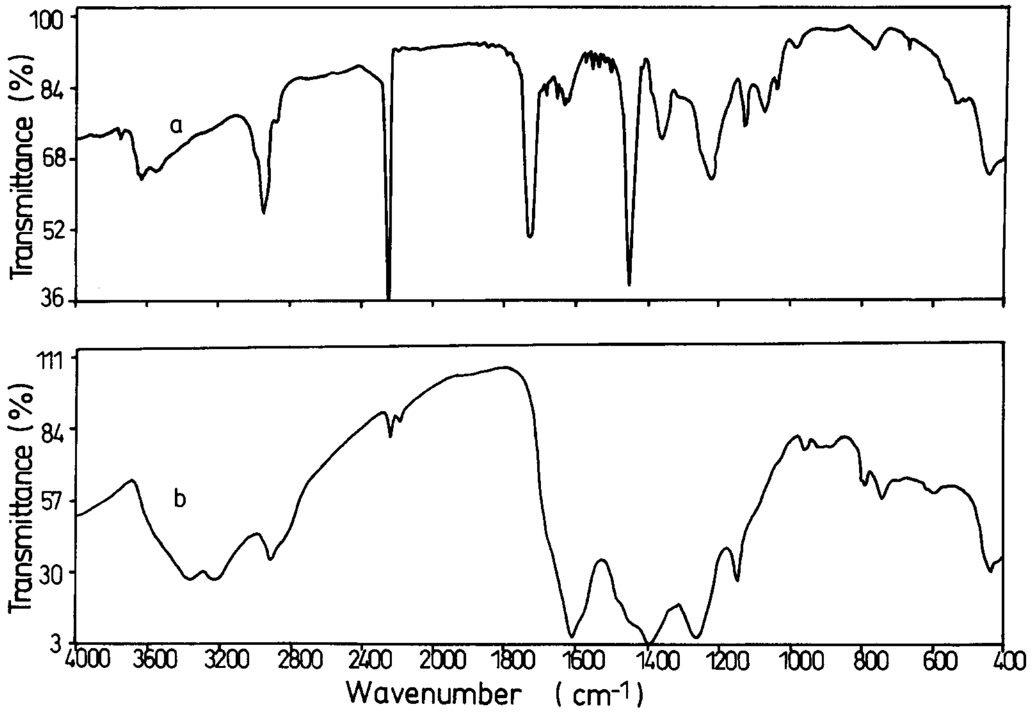


Fig. 2. IR-spectra. (a) No. 1 (see Table 1): unmodified PAN fibers; and (b) No. 1/300°C: unmodified PAN fibers pyrolyzed up to 300°C.

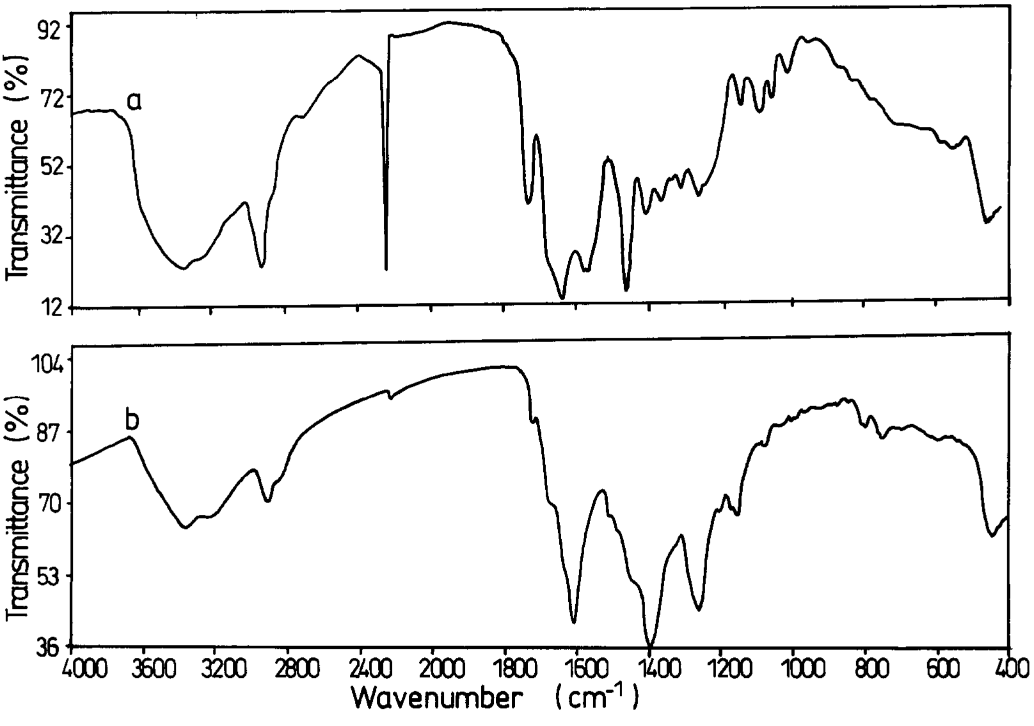


Fig. 3. IR-spectra. (a) No. 2 (see Table 1): PAN fibers modified with ethylene diamine of low concentration; and (b) No. 2/300°C: PAN fibers modified and pyrolyzed up to 300°C.

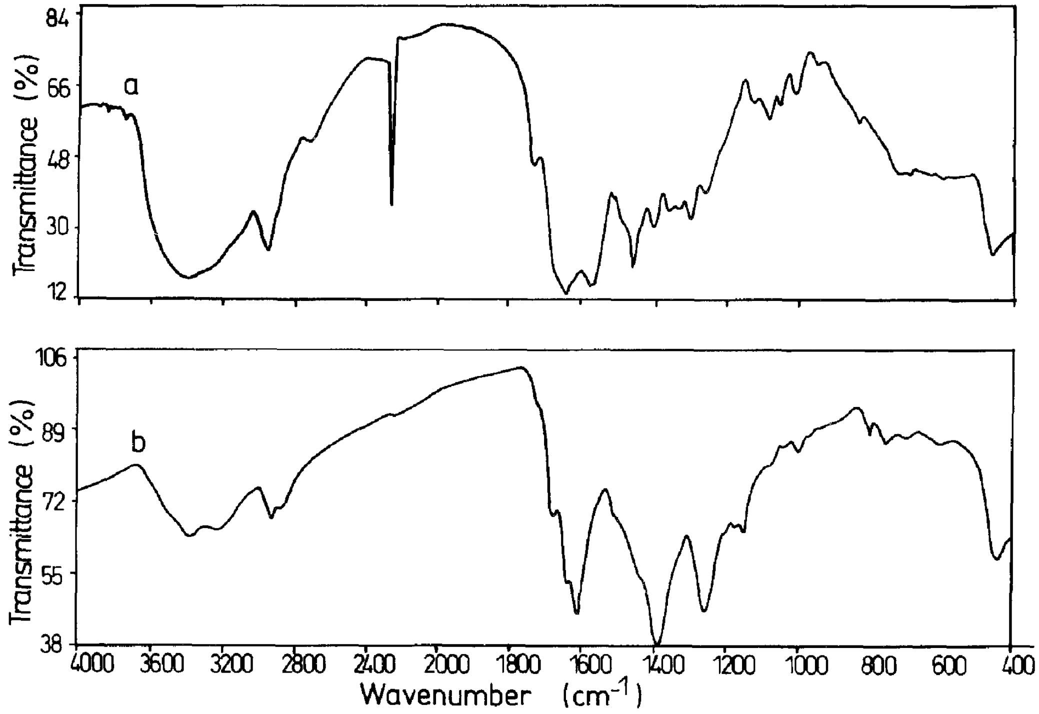


Fig. 4. IR-spectra. (a) No. 3 (see Table 1): PAN fibers modified with ethylene diamine of high concentration; and (b) No. 3/300°C: PAN fibers modified and pyrolyzed up to 300°C.

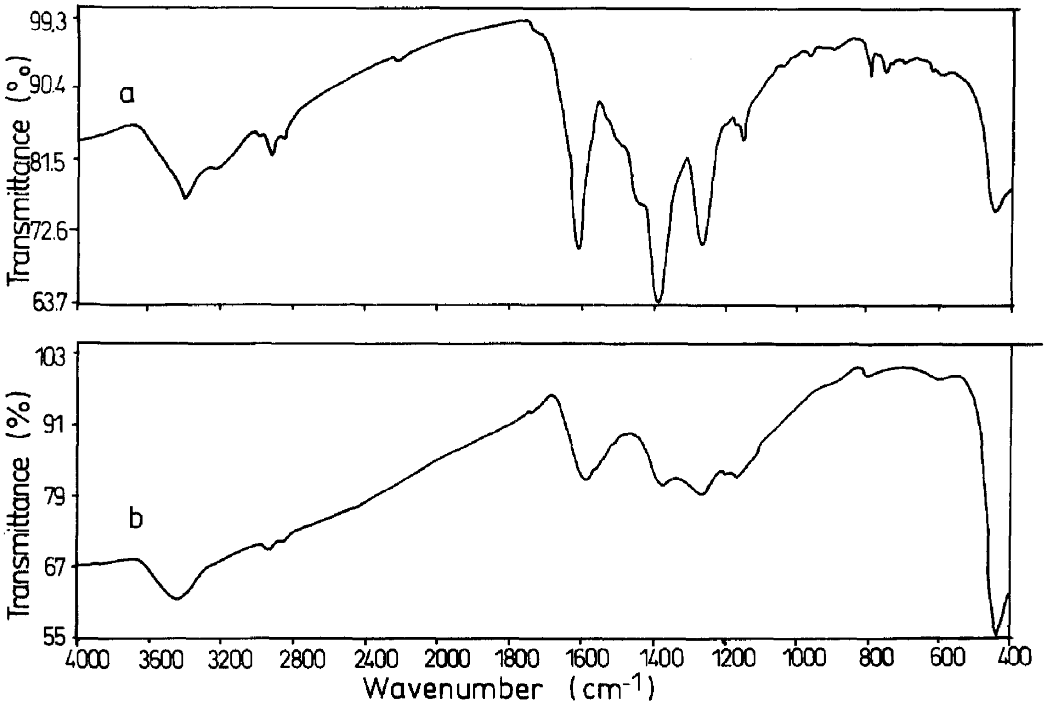


Fig. 5. IR-spectra. (a) No. 2/400°C: PAN fibers of No. 2 (see Table 1) pyrolyzed up to 400°C; and (b) No. 1/600°C: PAN fibers of No. 1 (see Table 1) pyrolyzed up to 600°C.

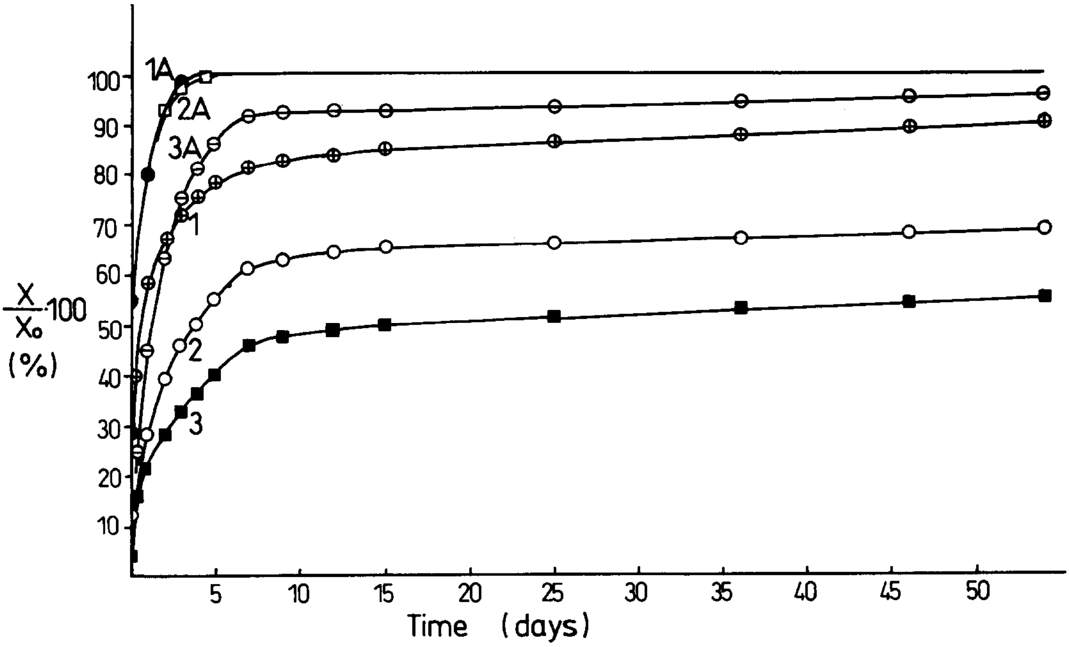
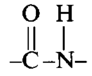


Fig. 6. Adsorption of methylene blue from aqueous solution on PAN-based polymers. X: adsorbed amount of methylene blue; X_0: initial amount of methylene blue in the solution before the adsorption. Symbols: 1,2,3: Nos 1, 2 and 3 (see Table 1). A: pyrolyzed up to 300°C.

second one to N–H of amide group. Thus, it appears that modification with EDA and cross-linking, results in the formation of NH_2,


$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$$

and C=N–H groups from the nitrile groups. These structural changes are further indicated by the reduction in intensity of the nitrile band and the appearance of a broad band in the range of 3.200–3.600 cm^{-1}, attributed to NH_2 and N–H structure with significant intermolecular association [16]. Other absorption bands due to various groups are CH_2 (at 2.243 cm^{-1}), C=O (at 1.727 cm^{-1}), CH_2 (at 1.455 cm^{-1}), CH, =CH–X or possibly O–H (at 1.395, 1.354, 1.294 cm^{-1}), CH, C–N, C–O (at 1.247 cm^{-1}), and C–OH (at 1.127 cm^{-1}). The same but more pronounced changes could be recognized in the spectrum of the high cross-linked PAN [Fig. 4(a)]

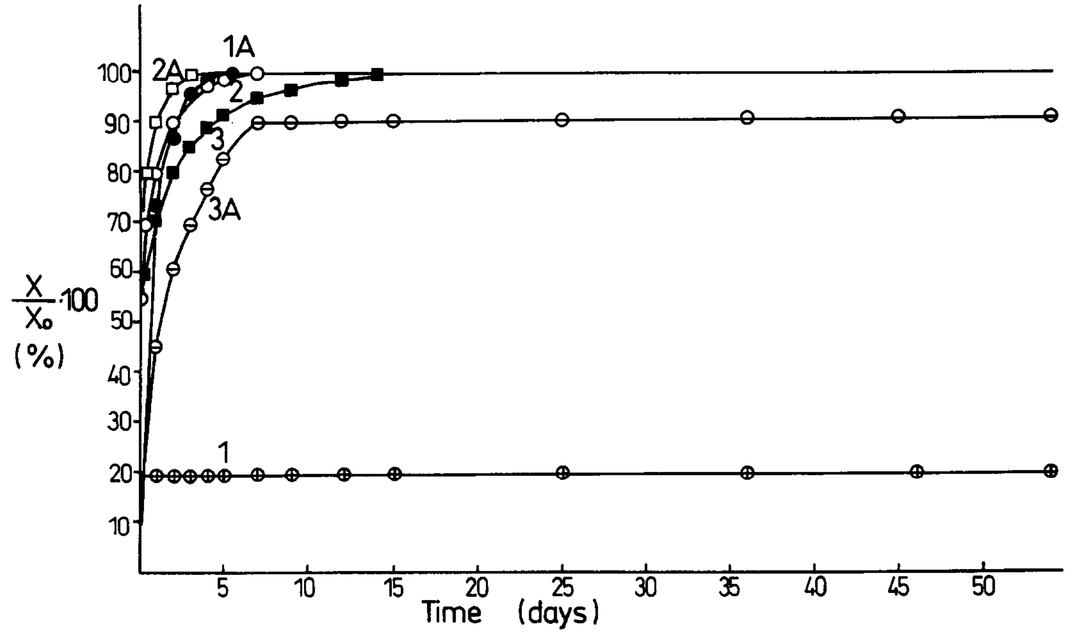


Fig. 7. Adsorption of alizarin yellow from aqueous solution on PAN-based polymers. X: adsorbed amount of alizarin yellow, X_0: initial amount of alizarin yellow in the solution before the adsorption. Symbols: 1,2,3: Nos 1, 2 and 3 (see Table 1). A: pyrolyzed up to 300°C.

compared to low cross-linked material [Fig. 3(a)], i.e. the corresponding peaks are at the same wavenumbers but the intensities can differ (i.e. there is a different amount of the corresponding groups).

The spectra of the unmodified PAN without cross-linking (No. 1), low cross-linked (No. 2) and high cross-linked (No. 3) polymers after pyrolysis at 300°C are shown in Figs 2(b), 3(b) and 4(b), respectively. The pyrolysis residue up to 300°C of the unmodified PAN is thought to contain the following groups [Fig. 2(b)]: OH and/or NH (at 3.371 and 3.228 cm^{-1}), CH_2 (at 2.922 cm^{-1}), C≡N (at 2.239 cm^{-1}), C=C or C=N conjugated with aromatic ring (at 1.612 cm^{-1}), CH, =CH–X or possibly O–H (at 1.398 cm^{-1}), CH, C–N, C–O (at 1.260 cm^{-1}), C–OH (at 1.150 cm^{-1}), CH-wagging (at 800 and 750 cm^{-1}). The pyrolysis residue up to 300°C of the PAN modified with low EDA concentration [Fig. 3(b)] has the same groups with the corresponding unmodified PAN [Fig. 2(b)] at the same wavenumbers but with different intensities. The same changes could be recognized in the spectrum of the pyrolysis residue up to 300°C of the high modified PAN [Fig. 4(b)] having practically the same groups with the Fig. 3(b) and Fig. 2(b) (the same position of the peaks but with different intensities). The move to higher wavenumber (3.452 cm^{-1} at 600°C instead of 3.371 cm^{-1} at 300°C) for OH, NH groups is observed, with increasing the pyrolysis temperature [Fig. 5(a) and (b)]. The C≡N (at 2.239 cm^{-1}), CH_2 (2.922 cm^{-1}) and CH-wagging (at 800 and 750 cm^{-1}) have practically disappeared after treatment at above 400 and 600°C, respectively, but are still present at 300°C [Figs 2(b), 3(b) and 4(b)].

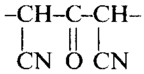
The thermally treated acrylic fibers have not sufficient porous structure. Their specific surface area is lower than 50 m^2/g, measured with N_2. Figures 6 and 7 show the discoloring ability of the polymers with aqueous solutions of methylene blue and alizarin yellow, respectively. The order of the discoloring ability of methylene blue (Fig. 6) is: No. $1 > 2 > 3$, where the maximum adsorption for No. 1 is 90%. The pyrolyzed polymers up to 300°C reveal higher adsorption than the non-pyrolyzed polymers, giving rise to 100% adsorption (No. 1/300°C, 2/300°C) or near 100% adsorption (No. 3/300°C). The pyro-polymers prepared at higher temperatures (400, 500 and 600°C) reveal no discoloring ability (No. 1/400°C exhibits some discoloring ability which is less than that of the corresponding non-pyrolyzed polymer). The adsorption ability of alizarin yellow (Fig. 7) follows the order: No. $2 > 3 > 1$, where Nos 2 and 3 exhibit 100% adsorption but No. 1 is very low. The pyrolyzed polymers up to 300°C reveal higher discoloring ability than the corresponding non-pyrolyzed (see Table 1, comparing No. 2 pyrolyzed at 300°C with No. 2 and No. 1 pyrolyzed at 300°C with No. 1), while in the case of the high modified polymer, the opposite (comparing No. 3 with No. 3 pyrolyzed at 300°C) is observed. The pyro-polymers prepared at higher temperatures (400, 500 and 600°C) reveal no discoloring ability.

DISCUSSION

The solubility of the polymers in concentrated H_2SO_4 depends on the degree of cross-linking of the polymer. According to the solubility the polymers obtained are of three types (see Table 1): without cross-linking (No. 1), low cross-linked (No. 2) and high cross-linked (No. 3).

The weight loss of the samples determined by weighing them before and after the pyrolysis at the final temperature (discontinuous method), are higher than those obtained by *in situ* continuous measurements of the thermogravimetric analysis (see Fig. 1, comparing No. 1 with 1T and No. 2 with 2T). The explanation is connected with the lower heating rate (3.3°C/min instead of 10°C/min) and the additional residence time during the cooling of the pyrolysis oven leading to additional degradation reactions in the first case compared to the second one. The weight losses at the whole range of pyrolysis temperature follows the order: No. $3 > 2 > 1$ (for both methods, i.e. discontinuous or continuous). This order is also followed with the degree of modification or degree of cross-linking (see Table 1). According to the first derivate of weight losses, two peaks at 310 and 430°C are observed indicating the maximum rate of weight losses. Three main ranges of pyrolysis temperatures can be distinguished namely up to 300°C having low weight losses, between 300 and 500°C having very high weight losses and above 500°C having lower weight losses.

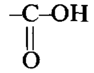
During the thermal degradation of polyacrylonitrile at low temperatures (e.g. to 250°C), the dehydrogenation and cyclization reactions (i.e. –C≡N to >C=N– conjugated in aromatic ring) occurred. The cyclization of PAN can be self-initiated (mainly by defects in the polymer) or initiated by additives such as bases, acids or oxygen. The β-ketonitrile group



$$\begin{array}{ccc} -CH- & C- & CH- \\ | & \| & | \\ CN & O & CN \end{array}$$

is formed during polymerization and it acts as initiator for the cyclization during heat treatment [17]. At a temperature of approx. 300°C, ammonia is liberated because imine groups break up. Such imine groups may be formed where the cyclization is interrupted, e.g. at the end of the chain or when a change of tacticity occurs. At higher temperatures, hydrogecyanide is liberated (having a first maximum at 400°C) which originates from no-cyclizated nitrile groups. Methane is liberated between 400 and 600°C from aliphatic groups. Above 400°C, hydrogen is formed as dehydrogenation product. Between 400 and 500°C, the appearance of carbon monoxide indicates the decomposition of methyl acrylate [14]. The three ranges of the weight losses (up to 300°C, between 300 and 500°C and above 500°C, see Fig. 1) consequently arise from the release of the above mentioned gases. The higher weight losses at 300°C especially for No. 3 (and No. 2) in comparison with that of No. 1 can be attributed to the decomposition of the additional imine groups contained in polymer No. 3.

The thermally treated acrylic fibers have not sufficient porous structure and therefore it is thought that their discoloring ability is mainly due to their functional groups. The molecule of the methylene blue [18] includes an organic cation, which is the functional part of the dye. This organic cation contains: S^+ (electron donor) and two groups of $N^+(CH_3)_2$ (electron donor). The molecule of alizarin yellow [18] contains: $-NO_2$ (electron acceptor), $-N{=}N-$ (electron acceptor),



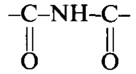
$$-\underset{\displaystyle O}{\underset{\|}{C}}-OH$$

(electron acceptor), –OH (electron donor).

With regard to the groups contained in the unmodified or modified PAN, the electron-donating groups are, e.g. $-NH_2$, NR_2, $-OH$, $-CH_3$ and the electron-accepting groups are, e.g. $-COCH_3$, $-COOH$, $-CN$, while the amide groups ($CONH_2$) exhibit polarity and therefore they can interact with both electron-donors or electron-acceptors [19].

Several remarks about the structure of the polymers based on PAN fibers can be made by comparing the discoloring ability of the latter with the discoloring ability of some model polymers, such as the modified polyacrylonitriles [10].

- The discoloring ability of No. 1 (Table 1) is: methylene blue (up to 90%)≫alizarin yellow (low). The same behavior reveals copolymer of acrylonitrile with acrylic acid which contains $-C{\equiv}N$ and COOH.
- The discoloring ability of Nos 2 or 3 (Table 1) is: alizarin yellow (100%) > methylene blue (intermediate percentage). The same behavior reveals the copolymer of acrylonitrile with acrylamide which contains $-C{\equiv}N$ and $CONH_2$ or the copolymer of acrylonitrile with methylene-bisacrylamide which contains $-C{\equiv}N$, $CONH_2$, CONH, and also cross-links. The group



$$-\underset{\displaystyle O}{\underset{\|}{C}}-NH-\underset{\displaystyle O}{\underset{\|}{C}}-$$

is formed by imidation of two $CONH_2$ of two neighboring molecules leading to cross-linking.
- The discoloring ability of the pyrolyzed polymers up to 300°C, i.e. No. 1/300°C, and No. 2/300°C is: alizarin yellow (100%) ≥ methylene blue (100%). The same behavior is followed by modified polyacrylonitrile with a 50% aqueous solution of H_2SO_4. The modified polymer contains $-C{\equiv}N$, $CONH_2$ and a few COOH. The dehydrogenation and cyclization reactions have progressed but the $-C{\equiv}N$ has not disappeared.
- The discoloring ability of No. 3/300°C is: methylene blue (95%) ≥ alizarin yellow (90%) while the non-pyrolyzed corresponding case No. 3 reveals higher discoloring ability for alizarin yellow (100%) and lower for methylene blue. This could be attributed to additional reactions during the pyrolysis of No. 3 up to 300°C (see also higher weight losses than Nos 1 and 2 in Fig. 1) leading to a decrease of electron donor groups (e.g. removal of NH_2 or NR_2 under formation of NH_3).
- The absence of discoloring ability of the pyrolyzed PAN above 400°C correlates with the absence of $C{\equiv}N$ [Fig. 5(a)] which indicates that the cyclization is complete and that other groups originally present during the initiation of the cyclization have been reduced or disappeared.

CONCLUSIONS

In conclusion, the selectivity of the discoloring ability of the non-pyrolyzed polymers for methylene blue and alizarin yellow dyes, disappears for the pyrolyzed polymers up to 300°C (Nos 1 and 2) indicating their ability to adsorb completely (100%) both dyes. For the best discoloring ability, the dehydrogenation and cyclization reactions in pyrolysis must have been progressed no further, that the $-C{\equiv}N$ group is still present. In addition, the pyrolyzed polymers should be similar to the PAN-model having $-C{\equiv}N$, $CONH_2$ and a few COOH.

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