



## Characterization of Modification Acrylic Fibers Waste for Dyes Removal material



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### Abstract

Acrylic fibre wastes as well as waste water cause environmental problems. The main goal of processing acrylic fibre waste is to obtain absorbent materials for dye residues from wastewater, the treatments on acrylic fibre waste under various circumstances. Sodium hydroxide and its mixtures with ethanol, DMF, and sodium ethoxide have been applied for modifying acrylic fibre waste under different operating conditions, including duration, temperature, and concentration. The previously mentioned treatments improved dye removal, and the most promising hydrolysis efficiency is that of Na-Ethoxide. The investigation of this treatment and determining the optimum condition has been studied and characterized using SEM, FTIR, zetapotential, DSC, XRD and TGA measurement. TGA studies revealed its moderate thermal resistance. Scanning Electron Microscopy (SEM) clarifies minor surfaces during the modification process as soon as related to the increase in fibre diameter and reduction in the fibre surface area. FTIR indicates monitoring the carboxyl groups and amid a group produced during hydrolysis, zeta optional. That reflects a significant drop in nitrogen concentration and the creation of negatively charged surfaces

Keywords: alkaline Hydrolysis, modification acrylic fibre waste and characterization

### 1. Introduction

The acrylic fibers are generally characterized by chemical resistance thermal stability, and very good mechanical properties, [1, 2]. Various modifications of the acrylic fibers are targeted to attain better properties, Polyacrylonitrile has adequate chemical stability and could be easily functionalized [3, 4].

Acrylic fibers were modified with different methods to improve many functional properties by applying various treatments such as animation using hydroxylamine, ethanolamine and hydrazine hydrate are used to prepare ion exchangers. Acrylic/keratin composite regenerated into film was treated with hydrazine hydrate and physico-mechanical and biological properties were investigated [5-12].

Crosslinking treatments of the thermo-mechanical stability of acrylic fibers as well as the pilling resistance performance of fabrics such as Hexanediol, Pentaerythritol and keratin have been improved [13,14]. It was found that the treatment of acrylic fiber

with hydrazine hydrate and polyurethane has improved antibacterial and dyeability properties [15].

Alkaline hydrolysis of polyacrylonitrile occurs some structural changes that lead to improved dye diffusion, facilitating the interaction between the cationic dye and the carboxyl group along the polyacrylonitrile macromolecules [16-19]. The waste generated from acrylic fibers in the textile industry can have negative environmental impacts. To address this issue, various studies have been conducted to explore ways to repurpose the fiber waste after undergoing chemical treatment. [17, 18]. The study involves hydrolyzing fibers to quantify functional groups like carboxyl and amide groups, and measuring changes in nitrile content [19, 20]. The alkaline hydrolysis of polyacrylonitrile fibers was investigated for evaluation as superabsorbent materials [21-24]. Acrylic fibers characterized with, chemical stability, hydrophilicity nature low price, low-density and could be easily functionalized so it is considered the most common

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membrane material for wastewater treatment [22]. The hydrolysis conditions was affected namely, reaction temperature, NaOH concentration and reaction time, on the efficiency of the produce polyacrylonitrile-based membrane, was investigated [23].

Polyacrylonitrile containing ultrafiltration membranes were developed through chemical modifications as grafting with different monomers [25-27]. Labena et al. discussed grafted acrylic membranes, from fibers waste, using phenylenediamine the produce polyacrylonitrile-based membrane, was investigated [28].

Nano-filtration membranes based on the acrylic fibers waste were successfully prepared using the phase inversion technique, in which the membrane solutions with different concentrations of acrylic fibers waste in dimethyl formamide (DMF) were used [29]. Elsyad et al carried out the modification of acrylic fabrics with biopolymers and utilized the modified acrylic fibers in the treatment of industrial wastewater [30].

As well as known that acrylic fiber waste is difficult to degrade and create eco-pollution, the burning of these fibers creates toxic gases which pollute the environment. Many scientists have been turned to solve the problem, by recycling this waste fiber via various modifications.

In this study, treatments were conducted on acrylic fiber waste to create dye-absorbent materials through various wet processes. The common hydrolysis operation involves high temperatures and long processing times. Moreover, employing large concentrations of NaOH is demanded. However, hydrolyzing of the waste acrylic fiber using Na-ethoxid can lowering the temperature, shortening the duration, and using lower concentrations of chemicals. This method offers an environmentally friendly alternative that avoids the drawbacks of traditional hydrolysis techniques.

## 2. Experimental

### 2.1. Material

Acrylic fibers waste was collected from a local industrial Carpet and blanket of textile company; Na-ethoxide ( $C_2H_5NaO$ ) and Dimethylformamide were supplied from Sigma Aldrich. All used chemicals are of purity higher than 99%. NaOH and ethanol as solvent were supplied from El-Nasr Company Egypt.

### 2.2. Modification of Acrylic Fabrics

The exhaustion technique was used for the chemical modification of acrylic fiber waste using four different chemical treatments.

- In the first treatment, acrylic fibers were hydrolyzed with different concentrations of aqueous sodium hydroxide solution (0.1–1.0 M) using a material-to-

liquor ratio (MLR) 1:25 at different temperatures (60–95 °C) for various durations (30–120 min).

- In second method, acrylic fibers waste was treated with a binary mixture 1.0 M of NaOH/ethanol using a MLR 1:25, (30-90%,v/v)mixture ratios at temperatures (30–70 °C) for (30–120) min,
- In the third treatment, the acrylic waste fiber was modified with binary mixtures of 1 M NaOH aqueous solution of NaOH/DMF mixture ratios (90/10, 80/20, and 70/30) the treatment was at (60–95 °C) for (30-120) min.
- In the fourth trial, acrylic fibers were treated with various concentrations (0.3–1.0 M) of aqueous solution of sodium ethoxide for different interval times (30, 45, and 60 min) at (70–95 °C). In all cases, the treated samples were washed with running water and air-dried at room temperature.

## 2.3. Characterization of modified acrylic fibers waste

### 2.3.1. Fourier Transform Infrared (FTIR)

Infrared spectra were recorded on FTIR Nicolet 5 DX Spectrophotometer using a wavelength range from 400–4000  $cm^{-1}$ . The samples of modified the acrylic fibers waste were examined as 1.5% KBr pellets.

### 2.3.2. X-ray diffraction (XRD)

X-ray diffraction pattern was performed using an X-ray diffract-meter model Shimadzu 610 with a software system Dp61, CuK1, and Cu-tube radiation at 40 KV and 3 mA. The used system includes divergence and scatter slits (SS) of and receiving slit 3 mm wide [31]. X-ray diffraction from a Cu target was used at 40 KV, 30 mA and a wavelength  $\lambda = 1.540 \text{ \AA}$ . The diffractograms were recorded over  $2\theta = 5$  to 30 continuous scanning rate of scan rate of 40°C/min. All patterns were run under the same experimental conditions of instrument setting adeptness in the research services unit, National Research Centre. The crystallinity can be defined as peak area crystallinity, being the ratio of normalized scatter under the resolved peaks to the total scatter under the unresolved normalized trace. The peak resolution was described elsewhere [31]. The degree of crystallinity was calculated using EVA software based on the following equation.

$$\text{Amorphous\%} = \frac{\text{global area} - \text{reduced area}}{\text{global area}} \times 100 \quad \text{Equation 1}$$

$$\text{Crystallinity \%} = 100 - \text{Amorphous \%} \quad \text{Equation 2}$$

### 2.3.3. Scanning Electron Microscope (SEM)

The morphology of the modified acrylic fiber waste surface was characterized using scanning electron microscopy (SEM) of high resolution (Scanning electron microscopy using Bruker Nano GmbH Scanning Electron Microscope D-12489 Berlin, Germany).

### 2.3.4. Thermogravimetric Analysis (TGA) and DSC

Thermal stability of the modified acrylic waste was examined via using a SDT Q600V20.9 Build 20 instrument; firstly, the samples were heated at the rate 10 °C/min from room temperature till 700 °C in an inert nitrogen atmosphere.

### 2.3.5. Nitrogen estimation by Kjeldahl method

Nitrogen content determination was carried out by the Kjeldahl method using a Buechi (B-343) machine. Nitrogen digestion was carried out using 98% H<sub>2</sub>SO<sub>4</sub>. Two observations for each sample were taken and averaged. Two blank readings were taken before analyzing samples. Titration of the distilled ammonia was carried out against 1 mol/L hydrochloric acid. Nitrogen content was obtained as per the following equation:

$$\% \text{ Nitrogen} = (\text{volume of HCl} - \text{blank reading}) \times \frac{14}{17} (\text{fiber weight}) \quad \text{Equation 3.}$$

### 2.3.6. Zeta Potential Measurement

The measurement of surface charge on modified acrylic fiber waste was achieved by characterizing zeta potential of the fibers via a newly developed device for streaming current measurement. Low flow rates were sufficient to generate detectable streaming currents in the absence of an externally applied voltage without damaging fiber samples. Acrylic fibers waste was dispersed at 0.1 g/100 mL in ethanol using Silent Crusher S (Heidolph Instruments, GmbH & Co. KG, Schwabach, Germany) and in water by magnetic stirrer for 60 s and 180 s, respectively].

## 3. Results and discussion

### 3.1. Characterization of Modified Acrylic-Fiber waste

#### 3.1.1. Fourier Transform Infrared (FTIR)

Figure 1 and 2 show the FTIR spectrum of untreated and treated acrylic fiber waste. The peaks of modified acrylic fiber waste with pure NaOH or a mixture of NaOH/ethanol and DMF, after the hydrolysis process, show a characteristic broad band at (3000-3500) cm<sup>-1</sup> for (N-H and O-H stretching vibration). The band of the -CN group at 2245 cm<sup>-1</sup> somewhat decreased, accompanied by the appearance of a small peak at 1650 cm<sup>-1</sup>, which can be ascribed to the distinctive bands of the amide functional groups [32-33]. The peaks at 1452 cm<sup>-1</sup> and 1378 cm<sup>-1</sup> are related to CH<sub>2</sub> and CH bending, and the peak at 1234 cm<sup>-1</sup> is related to stretching C-H bonds in CH<sub>3</sub> and CH<sub>2</sub>. The peaks at 1638 cm<sup>-1</sup> and 1738 cm<sup>-1</sup> result from the appearance of C=O related to comonomers. The peaks at 1073 and 1237 cm<sup>-1</sup> correspond to C-O stretching. The FTIR of modified acrylic fiber waste shows a decrease in the intensity of the carbonyl group

compared to pure acrylic fiber at 1740 cm<sup>-1</sup> and 1735 cm<sup>-1</sup> for those treated with NaOH.

FTIR of modified acrylic fibers waste referred to the intensity of carbonyl group to pure acrylic fibers at 1740 cm<sup>-1</sup> and 1735 cm<sup>-1</sup> was obviously decreased for that treated with NaOH. There are abroad peaks more obvious for the samples treated with pure NaOH and that treated with both mix NaOH/Ethanol and that treated with NaOH/DMF.

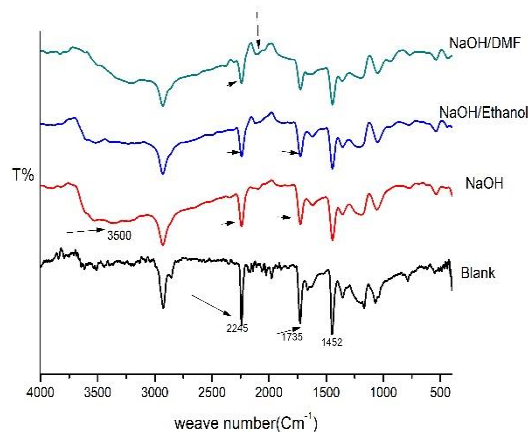


Fig.1. FTIR spectra of treated acrylic fibers waste with NaOH and its mixture

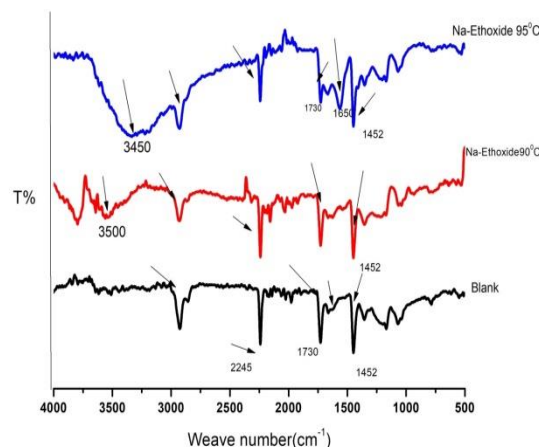


Fig. 2. FTIR spectra of treated acrylic fibers waste with Na-ethoxide

The spectra of FTIR spectroscopy for untreated and treated acrylic fibers waste with Na-ethoxide at 90 °C and 95 °C for one h respectively all peaks displayed characteristic adsorption band at 2245cm<sup>-1</sup> is assigned to the presence of nitrile group (C≡N), There are other peaks at 1073 and 1237 cm<sup>-1</sup>, which may be related to appearance of C-O and C=O. There are more obvious two intense absorption bands at 1597 cm<sup>-1</sup> and 1452 cm<sup>-1</sup> characteristic assigned to the asymmetric and symmetric stretching of carboxylate groups. An absorption band is visible in the FTIR about 1650–

1640  $\text{cm}^{-1}$  as an effect of stretching that changes some of the nitrile group into a different group. It became apparent that the stretching vibration of C-O and the C-H was reflected by absorption shoulders at 1375–1320  $\text{cm}^{-1}$  and 1047–1004  $\text{cm}^{-1}$ , respectively [34-35]. for the treated acrylic fiber waste there are new broad peaks ranging at 3000 $\text{cm}^{-1}$  to 3500 $\text{cm}^{-1}$  that refer to (NH and OH) stretching after hydrolyzing, the quantity of nitrile group that remained was less to produce either an amide group or other. It appears that the 1738  $\text{cm}^{-1}$  peak at 1738  $\text{cm}^{-1}$  and 1735  $\text{cm}^{-1}$  are related to the stretching of C-H bonds in CH<sub>3</sub> and CH<sub>2</sub>, as is the reduced strength of these peaks at 2928  $\text{cm}^{-1}$  and 2885  $\text{cm}^{-1}$ . For the fibers treated with Na-ethoxide at 95 °C, (It was found that the 1738  $\text{cm}^{-1}$  peak at 1738  $\text{cm}^{-1}$  and 1735  $\text{cm}^{-1}$  are related to the intensity of the peaks at 2928  $\text{cm}^{-1}$  and 2885  $\text{cm}^{-1}$  are related to stretching C-H bonds in CH<sub>3</sub> and CH<sub>2</sub> also the intensity of these peaks are decreased. There is a unique peak at 1650  $\text{cm}^{-1}$  for the fibers treated with Na-ethoxide at 95 °C which indicates the amide group [36].

### 3.1.2. X-Ray diffraction modified acrylic fibers waste

X-ray diffraction of unmodified and modified acrylic fibers waste was shown in figure 3. The XRD spectra of the acrylic fiber waste, and other modified under various conditions with definite characterized peak was noticed at  $2\theta = 18.45^\circ$  of fibers. The  $2\theta$ , d-values, intensity, crystal size and crystallinity of untreated and treated acrylic fibers waste were tableted in Tables 1 and 2. It was found that the treatment with NaOH or NaOH/ethanol or NaOH/ DMF as well as with Na-ethoxide led to decrease the  $2\theta$  from 18.1, 30.7 for untreated to 17.5, 25.7 for all treated fibers. Over all there are different changes in d-values between the untreated acrylic fibers waste and treated acrylic fibers waste. It was observed that high increase in the intensity for treated fibers with NaOH/ ethanol and Na-ethoxide, while there was a decrease in the case of the treatment with NaOH/ DMF.

The  $2\theta$  indicates that the high crystalline of modified fibers as a result of the high crystalline lignin. The degree of crystallinity calculated using EVA software based on the equations (1 &2) showed that the crystallinity was 52, 47.6, 41.5, 31.2, 24.5 for the untraded and 1M NaOH/DMF30% V/W at 70°C, 1MNaOH at 90 °C, 1M Na- ethoxide at 95 °C, 1M NaOH/ ethanol 50:50 for 1 hour respectively [37]. However, the intensity of the peak was decreased after modification with NaOH, and NaOH mixed with ethanol or DMF, which indicated a higher amorphous lattice than that of the unmodified one. After the hydrolysis process with either pure NaOH or mixed with ethanol or DMF has slight decrease in the

crystallinity was noticed as a result of the conversion of the nitrile groups to amide groups or hydroxyl group which has lower crystal lattice. Both solvents ethanol and DMF affected on the chains of the acrylic fibers, they may be opening up the fibers chains. It well known that the decrease in the crystallinity led to an increase in dye adsorption. Table 1 shows the data x-ray of acrylic fiber waste and other modified PAN fibers. The treatment of PAN fiber waste, and other modified fibers with NaOH, NaOH/ethanol, NaOH/DMF, as well as with Na-ethoxide, led to a decrease the  $2\theta$  from 18.1, 30.7 for untreated fibers to 17.5, 25.7 for all treated fibers. According to calculations by equation 1, the degree of crystallinity is 52, 47.6, 41.5, 31.2, and 24.5 for the untraded and 1M NaOH/DMF 30% (V/W) at 70 °C, and 1M NaOH/ethanol 50:50 at 70°C for 1 hour, respectively. Also, it was observed that there was a high increase in the intensity for treated fibers with both NaOH/ethanol and Na-ethoxide, but a high decrease in the case of treatment with NaOH/DMF [38]. Overall, there are different changes in d-values between the untreated acrylic fiber waste and the

On the other hand, the intensity of the peak was decrease after modification with NaOH, NaOH mixed with ethanol or DMF, which has higher amorphous lattice than that of the unmodified fibers. After the hydrolysis process with either of NaOH or NaOH/ethanol, there is a high decrease in the crystallinity as a result of the conversion of the nitrile groups to amide groups or hydroxyl group with higher crystal lattice. Both ethanol and DMF have effect acrylic fibers chains, this effect may be opening up the fibers chains. It well known that the decrease in the crystallinity led to increase in dye adsorption [39].

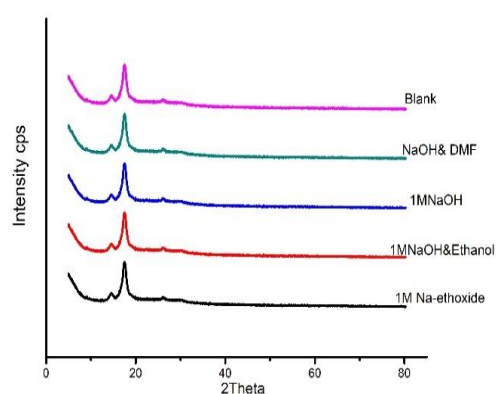


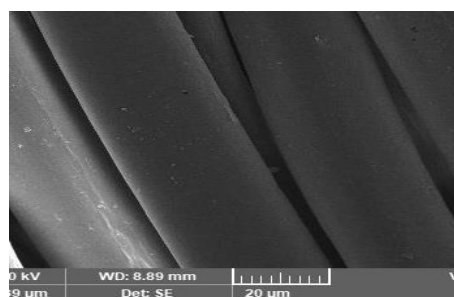
Fig. 3. X- ray of unmodified and modified acrylic fibers waste

**Table 1:** Crystal size and crystallinity of unmodified and modified acrylic fiber waste

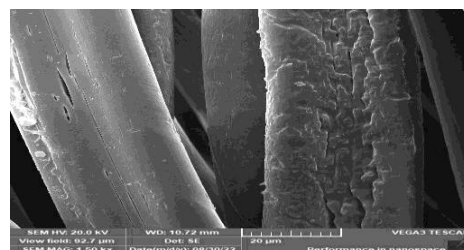
Treatment conditions	2 $\theta$	d-Values	Crystallinity %
Untreated	18.1	4.8	52
1 M NaOH, 95 °C, 1h	18.1	4.8	41.8
1M NaOH/DMF30 %, 70°C, 1h	17.4	5	47.6
1M NaOH/Ethanol 50:50, 95°C, 1h	17.5	5	31.1
1M sodium ethoxide, 95°C, 1h	15	5	24.9

### 3.1.3. Scanning Electron Microscope (SEM)

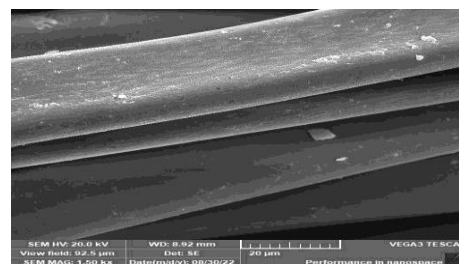
The surface morphology of the acrylic fiber waste was evaluated by scanning electron microscopy as shown in figures 4(a-f). It can be seen from Figure 4a that the untreated fibers have a smooth surface and homogenous structures [40]. Figures 4b, 4c, 4d and 4f show the surface morphology of hydrolyzed acrylic fibers with different conditions. Hydrolysis makes the surface nonhomogeneous; Hydrolysis is not only changing the chemical structure of macromolecular fibers but also forming a porous structure because of the partial dissolution of the phenomenon of the fiber surface. This made the strength of hydrolyzed fiber decrease. The roughness is more pronounced for the samples that treated with NaOH mixed with other solvents. Regardless of the hydrolyzed fiber waste has obvious signs of etching and there are more uneven defects and cracks, which may be returned to the effect of solvents. The hydrolysis loosens the compact structure of acrylic fibers, by leading to higher penetration of dye molecules into the fibers structure. The effect is more pronounced at a higher degree of hydrolysis. The presence of more voids/amorphous regions in the hydrolyzed fibers led to increase the dye uptake.



a) Untreated



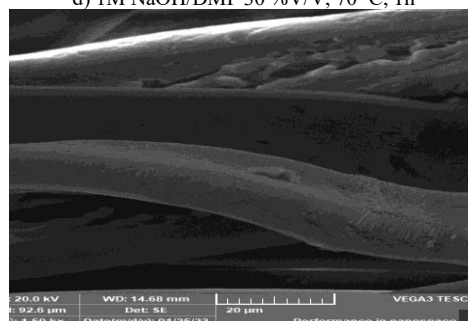
b) 1 M NaOH, 120 min, 95°C



c) 1M NaOH/Ethanol 50:50, 90 °C, 1h



d) 1M NaOH/DMF 30 %V/V, 70 °C, 1h

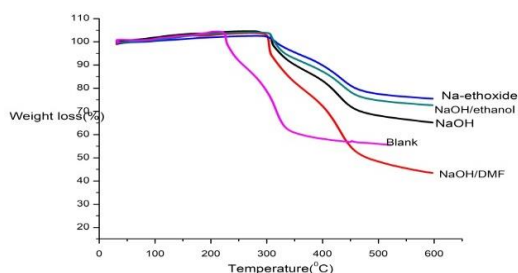


f) 1M Na-ethoxide, 95°C, 1h

**Fig. 4.** Scanning Electron Microscope (SEM) of unmodified and Modified acrylic fiber waste

### 3.1.4. Thermogravimetric analysis (TGA) and DSC

TG and DSC diagram indicates the thermal behavior of the untreated and treated acrylic fiber wastes under various conditions, the thermogravimetric analysis is a powerful tool to follow chemical changes during heat treatments refer to The three reactions occurring during the Thermo-oxidative stabilization of polyacrylonitrile in air atmosphere are cyclization of nitrile groups, dehydrogenation, and oxidation. The rate of heating from 10- 650 °C of treated and hydrolyzed acrylic fibers under different circumstances. The results of this study are shown in Table and as shown in Figure 5&6 of untreated acrylic fabric indicates that there is weight loss occurs in two steps first one about 15% at temperatures 223°C and 279°C, followed by further weight loss ~of 25 % at initial temperature 299°C and 301°C, which can be related to evaporation reactions such as evaporated some gases such as NH<sub>3</sub> and CO<sub>2</sub> as well as water vapour [41].



**Fig. 5.** TGA diagram of unmodified and modified acrylic fibers waste

The sample just lost 35% of its weight and the remaining weight is 50% as shown in Table 3 Fragmentation of polymeric chains at elevated temperatures may be related to weight loss [42]. The amount of fibers residue remaining at 650°C was 40%, containing the main element in skeleton of acrylic fibers is carbon atom, [43]. In the case of the hydrolyzed sample, there was loss in weight in the range of 291–441 °C, may be related to thermal decomposition of the monomers that present in acrylic fibers(ester, sulphonic, hydroxyl, ...so...on) and the liberation of CO<sub>2</sub> gas [41]. In the case of the hydrolyzed sample, there was a remarkable loss in weight in the range of 291–441 °C, presumably due to the thermal decomposition of the carboxylic groups and the liberation of CO<sub>2</sub> gas [41]. This confirms the successful transformation of cyano groups into carboxylic groups inside the polyacrylonitrile macromolecular chains during alkaline hydrolysis. It has been reported that the number of carboxylic groups in the hydrolyzed PAN fabric can be estimated quantitatively by determining the weight loss at these temperatures [43].

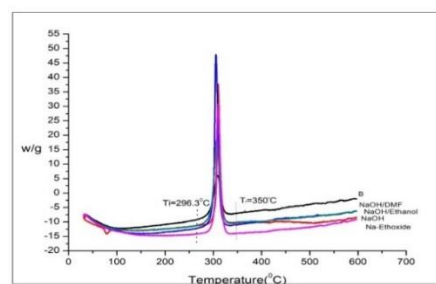
**Table2:** Initial decomposition temperature (IDT) of treated and untreated acrylic fabrics waste and remaining weight (at weight loss 15%, 25%, and 35%).

Acrylic fabric	IDT (°C)	Decomposition temperature at weight loss(°C)			
		15%	25%	35%	Remaining weight% at 650 °C
Untreated	223	279	299	319	50
NaOH	291	350	401	441	60
NaOH/DMF	285	322	353	369	40
NaOH/ethanol	299	388	426	-----	65
Na-ethoxide	301	434	439	-----	70

The results in Table 2 show that there is an increase in the thermal stability of treated acrylic fabrics waste (indicated by the decomposition temperature at different weight loss percent and the remaining weight at 650 °C), whether with amino acids or amid or carboxylic group, i.e. new bonds are formed (e.g., ester and amide bonds) and cross-links with the appropriate active groups in the modified acrylic fabrics, higher thermal stability.

The DSC diagram of untreated and treated acrylic fiber waste shows exothermic thermal peaks associated with the thermal behaviour of fibers. The DSC curve of the untreated waste displayed a sharp single exothermic peak at 350°C, which is referred to as a cyclization reaction of the acrylic via a radical mechanism [44].

The average temperature of the initiating exothermic cyclization reaction was 350°C, and the average range of peak temperature was 296–350 °C. The results show the peak maximum and offset temperature of exothermic peaks, the heat of fusion, and the peak height of untreated and treated acrylic fabrics, which were found to be very close to each other. This is confirmed that there is a limited enhancement in the thermal stability treated compared to the untreated sample.



**Fig. 6.** DSC diagram of untreated and treated acrylic fiber waste

The reduction of the peak temperature ( $T_{pk}$ ) from 308°C for untreated acrylic fibers waste and for that treated with to 310°C, 309°C and 308.8°C for that treated with 1 M NaOH at 95 for 120min, the other treated with 1M Na-ethoxide at 95C for 1 h and 1MNaOH/ethanol 50:50 respectively. This indicates new crystals are formed, and the exotherm and heat liberated during the scan are strongly dependent on the morphology and physical changes occurring during the fiber process. Melting of acrylic fiber waste could not be observed under the normal set of conditions as it undergoes cyclization and degradation well before the melting point [45].

**Table 3.** Onset, maximum and offset temperatures, heat of fusion, and peak height of untreated and treated acrylic fabrics

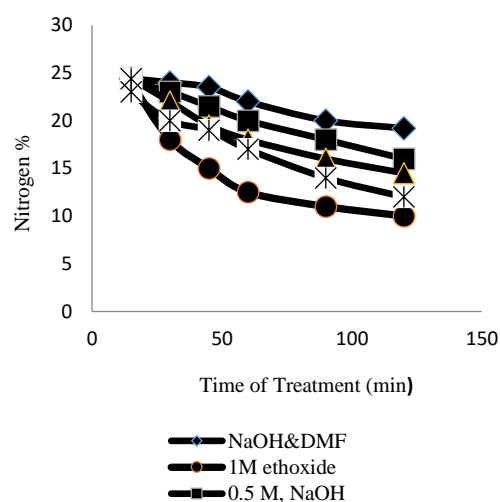
Acrylic fabric	Degradation process			Heat of fusion ( $\Delta H$ ) (J/g)	Peak Height (mW)
	$T_{onset}$ (°C)	$T_{peak}$ (°C)	$T_{offset}$ (°C)		
Untreated	292.8	298.6	305	-374	55.6
NaOH	304.9	311	317	-234	48.4
NaOH/DMF	300	307.7	313	-327	58.9
NaOH/ethano l	295	307	316	-154	28.8
Na-ethoxide	303	310.7	316	-178	44.7

Table 3 show onset, peak maximum, and offset temperature of exothermic peaks, heat of fusion, and peak height of untreated and treated acrylic fabrics, which were found to be very close to each other. This emphasized that there is a limited enhancement in the thermal stability of modified fabrics compared to the unmodified sample.

The nitrogen content of untreated and treated fibers is shown in Figure 7. From the figure 5 the nitrogen contents of untreated fiber waste, there is an obvious decrease in nitrogen contents of treated acrylic fiber waste in comparison to untreated one. As the concentration of sodium hydroxide increases there is a decrease in nitrogen content for example the fibers treated with 1MNaOH at interval time have nitrogen content lower than one treated 0.5 M NaOH at the same times this may occur due to some structural change in the nitrile group present in acrylic fibers due to hydrolysis process. The most likely groups are amide or carboxyl groups [46]. As observed. There is a higher decrease in nitrogen content for the samples treated with Na-ethoxide in compression for that treated with sodium hydroxide may indicate that there

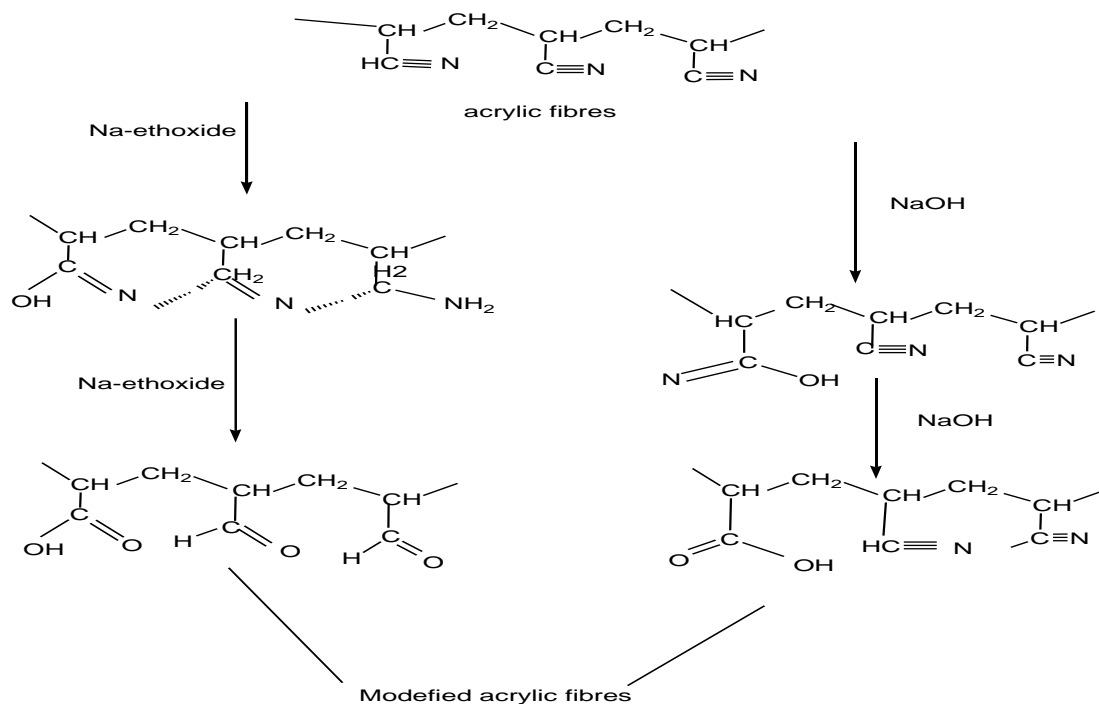
is the degree of hydrolysis in this treatment higher and the functional groups that converted are higher. It was found that the decrease in the values of nitrogen content depended on the concentrations of both sodium ethoxide and sodium hydroxide.

Alkaline hydrolysis of acrylic fiber waste in alkaline media using either Na-ethoxide or NaOH is the hydrolysis process both in terms of resulting product formation and the mechanism involved. Generally, alkaline hydrolysis of nitrile groups in polymer was performed by 1 M of NaOH at 95°C for one hour. The hydrolysis reaction was slower than that treated with 1M Na-ethoxide at 95°C for 1 hour. This reaction leads to the formation of hydroxyl or amide groups along with small amounts of acrylic acid groups as shown in scheme 1. It was found that the hydrolysis of acrylic fiber waste resulted in the formation of a multi-block copolymer of acrylonitrile and acrylamide units. The theory of neighbouring group effect was applied to explain the formation of this particular product [47].



**Fig. 7.** Nitrogen content of unmodified and modified acrylic fiber waste

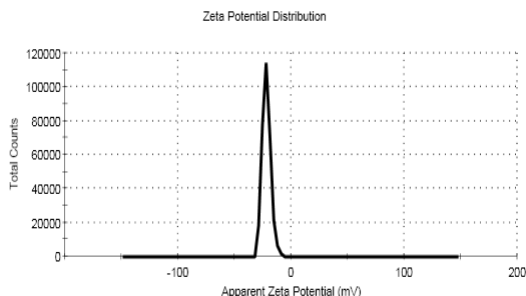
Alkaline hydrolysis of acrylic fiber waste in alkaline media using either Na-ethoxide or NaOH is the hydrolysis process both in terms of resulting product formation and the mechanism involved. Generally, alkaline hydrolysis of nitrile groups in polymers is performed by 1 M of NaOH at 95°C for one hour the hydrolysis reaction is slower than that treated with 1M Na-ethoxide at 95°C for 1 h. This reaction leads to the formation of hydroxyl or amid groups along with small amounts of acrylic acid groups as shown in scheme 1.



**Scheme 1.** The chemical reactions of acrylic fibers with sodium ethoxide and sodium hydroxide.

### 3.1.5. Zeta potential measurement

The zeta potential distribution curves of the modified acrylic fiber waste are shown in Fig. 8, indicating a negative charge on the surface based on the recorded zeta potential values of -21 for the sample treated with 1 M Na-ethoxide at 95°C for 1 hour. The negative zeta potential is likely due to the presence of amide or hydroxyl groups as indicated by FTIR analysis of the modified acrylic fiber waste. Additionally, the hydrolysis reaction carried out in a basic pH environment (in the presence of Na-ethoxide) leads to the hydrolysis of the nitrile group ( $C\equiv N$ ) in the reaction. This may result in the presence of ionizable  $-COOH$  or  $-COONa$  groups in the product. Therefore, an increase in the feeding concentration leads to an increase in the zeta potential value.



**Fig. 8.** Zeta potential of modified acrylic fiber waste with Na-ethoxide

### 4. Conclusion:

Alkaline hydrolysis using Na-Ethoxide and NaOH has been shown to effectively modify acrylic fiber waste, resulting in structural changes and improved dye removal capabilities. This study highlights the potential of Na-Ethoxide as a valuable hydrolysis agent and offers insights into optimizing conditions for sustainable waste treatment in the textile industry.

Nitrogen content analysis indicates a significant decrease, suggesting structural changes, particularly in amide or carboxyl groups. Zeta potential measurements confirm the development of negatively charged surfaces as a result of hydrolysis. Dye removal experiments demonstrate higher dye concentrations in treated fibers, attributed to the extent of hydrolysis. Different NaOH mixtures further enhance dye removal, underscoring the importance of functional groups.

Overall, alkaline hydrolysis using Na-Ethoxide and NaOH effectively modifies acrylic fiber waste, impacting nitrogen content, zeta potential, and dye removal capabilities. The observed structural changes and increased functional groups contribute to enhanced dye adsorption. This study establishes the potential of Na-Ethoxide as an effective hydrolysis agent and underscores the need to optimize conditions for maximum efficacy in treating acrylic fiber waste. These findings advance knowledge in textile waste



management and lay the groundwork for future research and applications.

By utilizing this research, filters can be produced from modified acrylic fiber waste, enabling dye removal from wastewater through sustainable methods. This approach contributes to environmentally friendly preservation and economic benefits. Therefore, this research is considered to have an environmental and economic impact.

##### 5. Declaration:

The authors declare that they have no conflict of interest."

##### 6. References

1. El-Gabry L. K. "Modification of Acrylic Fibers improve many physical and chemical properties" 3rd Conference for Industrial, Textile Research, "Manpower Development, Manufacturing Technologies and Management in Textile Industries" NRC, Cairo, Egypt, 9-10 March (2015).
2. El-Gabry L. K.; Abou El-Kheir A.; Salama M.; Mowafi S. and El-Sayed H.; "Functional Finishes of Acrylic Fibers Using Different Technologies" *Journal of Applied Sciences Research*, 10, (3) March; pages 218-229 (2014).
3. Lee J.Y., Huang T.Y., Belle M., Marie Yap Ang, Huang S.H., Tsai H.A., Jeng R.J., *J. Memb. Sci.* 657, 120702, (2022).
4. Hashem A. ; Nasr M. F. ; Fletcher A. J. and Mohamed L. A. "Aminated Acrylic Fabric Waste Derived Sorbent for Cd (II) Ion Removal from Aqueous Solutions: Mechanism, Equilibria and Kinetics" *Journal of Polymers and the Environment*, 29:175–186 (2021).
5. Zhongyu Fu.; Baijun L.; Lihao S.; and Huixuan Z.; "Study on the thermal oxidative Stabilization reactions and the formed structure in Polyacrylonitrile during thermal treatment" *Journal of polymer degradation and Stability* 140, pp 104-0113 (2017).
6. El-Gabry L. K.; Abou El-Kheir A.; Salama M.; Mowafi S. and El-Sayed H.; "Acrylic/keratin composite of enhanced dyeability towards cationic and anionic dyes" *Coloration Technology*, 132, 83–91 (2016).
7. Wang qiang, Feng yan:" Modification Technology for Polyacrylonitrile, Fiber and its Application, *Synthetic Fiber in China J. Vol. 1*, p.1,(2010).
8. El-Gabry L. K.; Ezzat M.; Abou El-Kheir A. and Abdel-Megied Z. M.; "Physical and Mechanical properties of Treated Acrylic Fabrics using nano-Bentonite" *Egypt. J. Egypt. J. Chem.* 62, Special Issue (Part 2, 63), pp. 467 - 490 (2019).
9. El-Gabry L. K.; Bendak A.; El- Hossamy M. and Abo Hamr M.S.; "Effect of Some Acids and Metal Salts Pretreatments on Acrylic Dyeability" *Research Journal of Textile and Apparel* 15, 4, 1-9 (2011).
10. El-Sheikh M.A.; El-Gabry L.K. and Ibrahim H.M; "Photosynthesis of carboxymethyl starch-stabilized silver nanoparticles and utilization to impart antibacterial finishing for wool and acrylic fabrics" *Journal of Polymers*, Volume 2013, Article ID 792035, pages 1-9 (2013).
11. Kamel M.M.; Allam O.G.; El-Gabry L. K. and Helmy H.M.; "Surface Modification Methods for Improving Dyeability of Acrylic Fabric Using Natural Biopolymer" *Journal of Applied Sciences Research*, 9, 6, 3520-3529 (2013).
12. Salama M.; Mowafi S.; Abou El-Kheir A.; El-Gabry L. K.; and El-Sayed H."Preparation and Characterization of Polyacrylic/ Keratin Composites: Physico-Mechanical and Biological Properties" *Life Science Journal* 11(8) (2014).
13. Brown, P. J., Sultan, M. and Nobbs, J. H. (2002), "Crosslinking Acrylic fibers with Hexanediol and Pentaerythritol", *AATCC Vol. 2*, No. 3, pp.46-50.
14. K. M. Seddik; L. K. El-Gabry and M. Atfe; "Improving Some Utility and Functional Properties of Cross-linked Acrylic Fabrics as garment" on line in *Research Journal of Textile and Apparel* March (2023).
15. El-Sayed A. A. ; El Gabry L. K.; and Allam O. G.; "Preparation of waterborne polyurethane extended with chitosan and its application on acrylic fabrics" *J. Mater Sci: Mater Med*, 21, 507-514 (2010).
16. Wang qiang, Feng yan:" Modification Technology for Polyacrylonitrile, Fiber and its Application, *Synthetic Fiber in China J. Vol. 1*, p.1, (2010).
17. El-Gabry L.K. and Bendak A.; "Dyeing Characterization of Alkoxide Pretreated Acrylic, Polyester Fibers Blend Using Cationic Dyes" *Polish Journal of Applied Chemistry*, L, no. 3-4, 83-94 (2006).
18. Pi Zhi Yu, Modification of waste polyacrylonitrile fiber and its application as a filtrate reducer for drilling, *Journal, Petroleum Science*, 12, 325-329, (2015).
19. Wenjun Long and Zhongjin Wei and Fengshan Zhou and Shaohua Li and Kang Yin and Yu Zhao and Siting Yu and Hang Qi ,Alkaline Hydrolysis of Waste Acrylic Fibers Using the Micro-Water Method and Its Application in Drilling Fluid Gel Systems, *Gels*(2023)
20. Basuoni A. and El-Sayed H., Developing durable antistatic hydrophilic acrylic fabrics with

- improved dyeability towards cationic and anionic dyes. *Emergent Materials*, 6:1339–1350 (2023).
21. Murari La Gupta, Bhuvanesh Gupta, Wilhelm Oppermann, Gabriele Hardtmann, "Surface Modification of Polyacrylonitrile Staple Fibers via Alkaline Hydrolysis for Superabsorbent Applications", *Journal of Applied Polymer Science*, Vol. 91, 3127–3133 (2004).
  22. Anup Tuladhar, ac Horng-Bin Pan and Inna Popova, "The use of acrylic yarn modified with amidoxime and carboxylate-containing polymer for lead removal from drinking water", *RSC Adv.*, 12, 27473–27482, (2022).
  23. Kaur H., Sharma G. "Removal of Dyes from Textile Industry Effluent": A Review. *SSRG Int J Humanit Soc Sci.*, 59–63, (2015).
  24. Keleş, Mustafa & Uysal, Yagmur, "Production of a microfiltration membrane from acrylic fiber(AF) and low-density polyethylene (LDPE) shrink film wastes", *Clean Technologies and Environmental Policy*, 23,1-12,(2021).
  25. Jinwen Wang, Zhongren Yue, Jeffrey Scott Ince, James Economy "Preparation of nanofiltration membranes from polyacrylonitrile ultrafiltration membranes" *Journal of Membrane Science* 286 ,333–341, (2006).
  26. Zhi-Ping Zhao, Jiding Li, Ding Wang, Cui-Xian Chen, "Nanofiltration membrane prepared from polyacrylonitrile ultrafiltration membrane by low-temperature plasma: 4. grafting of N-vinylpyrrolidone in aqueous solution", *Desalination* 184 37–44, (2005).
  27. Zhongyong Qiu, Xiaofei Ji, Chunju He, Fabrication of a loose nanofiltration candidate from Polyacrylonitrile/Graphene oxide hybrid membrane via thermally induced phase separation,360,122-131,*Journal of Hazardous Materials*,(2018).
  28. Labena, A., Abdelhamid, A. E., Husien, S. T. Youssef , Azab E., A. Gobouri, A. A., Safwat, G. Grafting of Acrylic Membrane Prepared from Fibers Waste for Dyes Removal: Methylene Blue and Congo Red. *Separations* 2021, 8(4), 42.
  29. Deng, S.; Bai, R.; Chen, J.P. "Aminated polyacrylonitrile fibers for lead and copper removal". *Langmuir*, 19, 5058–5064, (2003).
  30. H. El-Sayed; L. El-Gabry; H. S. Ibrahim; A. A. El-Sayed; E. M. Abou Taleb; N. S. Ammar; M. Salama; A. Abou El-Kheir; S. Mowafii and M. Abou Taleb "Treatment of Selected Man-made Fabrics with biopolymers and Their Utilization in Removal of Copper II Cations Industrial Waste Water" 9th Inter. Conf. Textile Achen-Dresden., Dresden., Germany, 27-28 November (2015).
  31. Park, S., Baker, J.O., Himmel, M.E. Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnol Biofuels* 3, 10 (2010). <https://doi.org/10.1186/1754-6834-3-10>
  32. Majid Abdoussa, Ahmad Mousavi Shoushtarib, Ahmad Majidi Simakania, Somaye Akbarib & Aminoddin Haji, Citric acid-modified acrylic micro and nanofibers for removal of heavy metal ions from aqueous media, *Desalination and Water Treatment*, 52 7133–7142 November (2014) doi: 10.1080/19443994.2013.827776
  33. El Gabry; L. K. "Effect of mineral acids on the properties of acrylic fabrics" *Coloration Technology*, 120, 5, 236-240 (2004).
  34. Ashrafi F. and Firouzzare M., Preparation of Forcespun Amidoximated Polyacrylonitrile-graphene Oxide Nanofibers and Evaluation of Their Uranium Uptake from Aqueous Media, *Fibers and Polymers*, Vol.22, No.12, 3289-3297 (2021).
  35. Orabi A.H., Abdelhamid A.E.S., Salem H.M., Ismaiel D.A., New adsorptive composite membrane from recycled acrylic fibers and Sargassum dentifolium marine algae for uranium and thorium removal from liquid waste solution, *J. Radioanal. Nucl. Chem.* 326 1233–1247(2020). <https://doi.org/10.1007/s10967-020-07403-2>.
  36. Wang, B.; Chen, P.-Y.; Zhao, R.-X.; Zhang, L.; Chen, Y.; Yu, L.-P. "Carbon-dot modified polyacrylonitrile fibers: Recyclable materials capable of selectively and reversibly adsorbing small-sized anionic dyes". *Chem. Eng. J.*, 391, 123484, (2020).
  37. Kainan Liu and Liqin Cao, ZIF-67-based Composite Membranes Generated from Carboxymethyl Chitosan and Nylon Mesh for Separation Applications, *Fibers and Polymers*, Vol.22, No.12, 3261-3270 (2021) DOI 10.1007/s12221-021-0044-8
  38. Dang W., Liu J., Wang X., Yan K., Zhang A., Yang J., Chen L., Liang J., Structural Transformation of Polyacrylonitrile (PAN) Fibers during Rapid Thermal Pretreatment in Nitrogen Atmosphere, *Polymers*, 12, 63 (2020).
  39. Kenawy E.-R., Tenhu H., Khattab S.A., Eldeeb A.A., Azaam M.M., Highly efficient adsorbent material for removal of methylene blue dye based on functionalized polyacrylonitrile, *European Polymer Journal*, 169, 111138, (2022).
  40. El-Gabry L. K., Abou El-Kheir A.; El-Sayad H. S., and El-Kashouty M. A., Ecofriendly Modification of Acrylic Fabrics for Enhanced Transfer Printability, *Fibers and Polymers*, 22, .2, 421-429 (2021).
  41. Shahram Arbab, Joseph D. Menczel, Thermal analysis of acrylic and carbon fibers, Editor(s): Michael Jaffe, Joseph D. Menczel, In *The Textile Institute Book Series, Thermal Analysis of*

- Textiles and Fibers, Woodhead Publishing, Pages 297-323, (2020).
42. Bendak A.; El-Gabry L. K; and Allam O. G.; "Chemical / Thermal Modifications of Acrylic Fabric as a Precursor of Quasi -Carbon Fibers" 10 the Inter. Conf. Textile Res. Div., NRC, Cairo, Egypt, Decamped 17-19 (2009).
  43. Jin, So & Kim, Min & Jeong, Young & Yoon, Young Il & Park, Won Ho. "Effect of alkaline hydrolysis on cyclization reaction of PAN nanofibers" Materials & Design. (2017).  
<https://doi.org/10.1016/j.matdes.2017.03.0>
  44. Khattab T. A., Rehan M., Abdelmoez Aly S., Hamouda T., Haggag K. M., Thomas M. Klapötke, Fabrication of PAN-TCF-hydrazone nanofibers by solution blowing spinning technique: Naked-eye colorimetric sensor, Journal of Environmental Chemical Engineering,5, 2515-2523, (2017).  
<https://doi.org/10.1016/j.jece.2017.05.001>.
  45. 27] Dang W., Liu J., Wang X., Yan K., Zhang A., Yang J., Chen L., Liang J., Structural Transformation of Polyacrylonitrile (PAN) Fibers during Rapid Thermal Pretreatment in Nitrogen Atmosphere, Polymers, 12 (2020) 63.
  46. Perez, Leyre , Ruiz-Rubio, Leire , Moreno, Isabel, Vilas, J. Characterization and Optimization of the Alkaline Hydrolysis of Polyacrylonitrile Membranes. Polymers. 11. (2019). 1843.  
[10.3390/polym11111843](https://doi.org/10.3390/polym11111843)
  47. Murari Lal Gupta, Bhuvanesh Gupta, Wilhelm Oppermann, Gabriele Hardtmann, Surface Modification of Polyacrylonitrile Staple Fibers via Alkaline Hydrolysis for Superabsorbent Applications Journal of Applied Polymer Science, Vol. 91, 3127–3133 (2004).