

A NOVEL DEVELOPMENT AND APPLICATION OF SELF-CROSSLINKING STRENGTHENING FOR POLYAMIDE-EPICHLOROHYDRIN (PAE) RESIN IN POLYACRYLONITRILE (PAN) SHEET

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ABSTRACT

In this article, the mechanism of wet-strength development of polyamideamine-epichlorohydrin (PAE) resin was analyzed and applied in polyacrylonitrile (PAN) fiber sheets. PAE-containing sheets were prepared from PAN fibers with different contents by internal addition of PAE to slurries of PAN fibers. When PAN fibers form sheets, PAN fibers interwove each other, however, the interfiber bonding is weak which results in low paper strength. PAE resins are generally adsorbed on the surface of PAN fibers, which is attributed to "self-crosslinking" of PAE networks. It's like a "framework" structure in the sheets and greatly improves the interfiber bonding. Compared to the paper without PAE, the tensile index, tear index, and elongation of paper with PAE were increased by 21.0%, 25.8%, 34.3%, respectively, when 0.6% PAE (based on sheet grammage) was added. The formation of tertiary amine group in PAE-PAN films boosted by the homo-crosslinking of PAE networks were proved by attenuated total internal reflectance fourier transformed infra-red (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM), thus, the interfiber bonded more closely and the density and strength of sheets were improved.

1 INTRODUCTION

Paper-strength properties can be improved by the addition of strengthening agents to the fiber suspensions at the wet end of papermaking. Crosslinking polymers, an innovative class of strengthening agents, are obtained by the interconnecting of molecular chains together. When crosslinking polymers are applied, the macromolecular chains of fiber-fiber interactions can be intertwined, and a considerably better network structure in the paper sheets is formed [1]. Polyamide-epichlorohydrin (PAE) resin is a type of water-soluble cationic thermosetting crosslinking resins. By virtue of non-poisonous, less dosage, well wet strength, flocculation and filtration aiding [2-4], PAE is widely used in cellulosic paper strengthening. However, in recent years, the significant mechanical property impact from cellulosic-based packaging materials has become a great concern. They have garnered significant attention because of their excellent durability, reusability and mechanical properties. However, no studies have been made to date on the mechanical performance of PAE-PAN sheets. What's more, how the surface structure in carbon fibers evolved and influenced the interface formation in composites was still unclear [5]. So there is a great importance in clarifying its self-crosslinking network formation process.

At present, PAE resin almost all apply to the traditional cellulose paper, there are two views on the enhancing mechanism of PAE resin for cellulose paper strength. The former view think that the mechanisms of strength enhancement have been attributed to the formation of a covalent ester bond between carboxyl groups of cellulose and azetidinium (AZR) groups of PAE, which is attributed to “co-crosslinking” with ester bonds [3-4]. The latter view believes in the formation of “homo-crosslinking” structure between PAE internal molecules in dry paper [6-7] by which an ester bond was formed between AZR groups of PAE and carboxylate groups at the end of polyamide chains [8-10]. Takao Obokata [11] even interpreted the increase of wet-tensile strength of paper made from cotton/hardwood bleached Kraft pulp (HBKP) as the ester bond formation between carboxyl groups at the end of polyamide chains in PAE and AZR groups of PAE itself, but the effect of the network structure on the mechanical properties has not been elucidated. The reaction mechanism and reaction condition are not clear. Lots of research work considered that AZR groups and secondary amine groups of PAE molecules form tertiary amine groups, which make the networks of “self-crosslinking” or “self-covalent” [12-14]. Figure 1 shows the preparation of PAE and possible cross-linking reaction.

Therefore, PAE resin can form “self-crosslinking” networks for cellulose paper strength without any special chemical environment. Thus, PAE resin can apply to synthetic fibers sheets except cellulose paper, it can ensure the maximum recycling is achieved [15]. In this article, inspired by PAE “self-crosslinking” networks for mechanical improvement in cellulose paper, the PAN fiber sheets were prepared by internal addition of PAE and the strength mechanism was investigated. The inherent strength of PAN fiber is strong, but its inertness surface caused the loose structure of sheet which results in the low paper strength properties; by adding PAE resin and high temperature ripening, AZR groups and secondary amines of PAE develop “self-crosslinking” networks among PAN fibers, which play a vital role of “framework” structure and lead to an increase in the interfacial strength between fibers and resin [16]. In this study we will mainly explore the mechanism of mechanical strength enhancement that results from the crosslinking of PAN sheet.

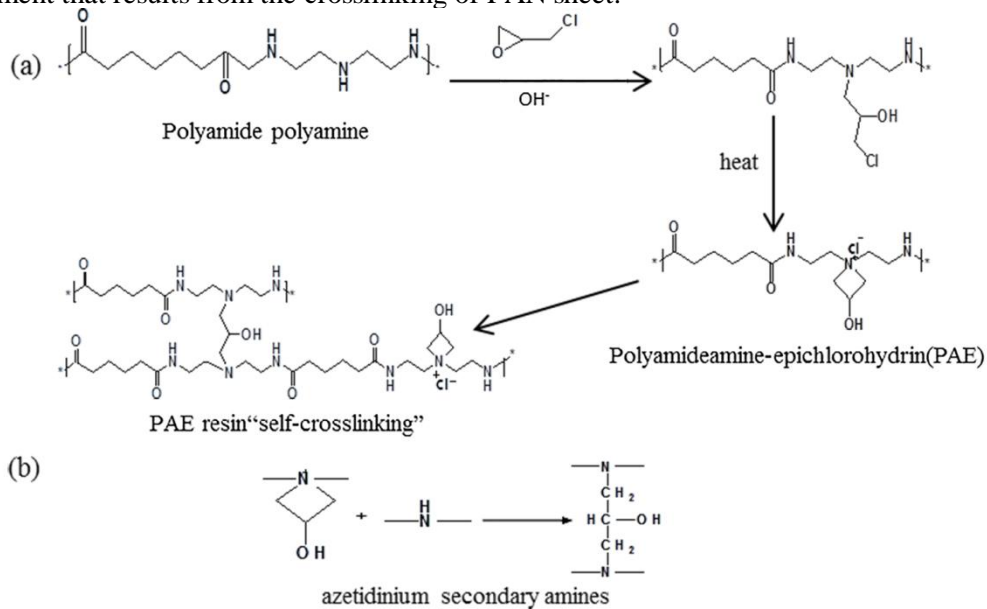


Figure 1: PAE resin “self-crosslinking” reaction process (a) PAE resin alkylation preparation and “self-crosslinking” reaction type; (b) PAE molecules “self-crosslinking” by AZR group.

2 EXPERIMENTAL

2.1 Materials

PAN fibers were supplied by Shanghai Lanbon Industrial Fiber Co. Ltd. A commercial PAE/water solution (solid content of 12.5%) was kindly provided by Tianjin Banknote Paper Co. Ltd.

2.2 PAN sheet making

An aqueous solution of one of the picked-up PAE intermediates was added to a 0.15% pulp slurry at pH 6.8–7.3 with continuous stirring at 750 rpm. The addition level of the PAE intermediates was fixed from 0.1 mass % to 1.0 mass % of the dry weight of the pulp. The pulp slurry was then subjected to handsheet making with a basis weight of 100 g/m², according to the TAPPI Test Method. PAE-PAN handsheet were prepared by drying the wet webs directly at 105 °C for 5 min using a drum dryer after pressing, followed by additional heating at 105 °C for 30 min in an oven. These handsheets were conditioned at 23 °C and 50% relative humidity for more than one day before evaluation.

2.3 Preparation of PAE film and FTIR analysis

The original PAE solution was diluted to 2.5% solid content by water, and the PAE solution was cast on a polyethylene plate. Some of the PAE films were then heated in an oven at 110 °C for 10min. FTIR spectra of PAE films and the PAE-PAN sheets were collected by the direct film method and KBr disk technique, respectively, using an FTIR (Bruker, Germany)..

2.4 Sheet strength testing

Density was measured by TAPPI Test Method T551 om-06. The dry-tensile strength and elongation of the sheets were measured according to TAPPI Test Method T494 om-01. Tear strength was measured by TAPPI Test Method T414 om-04. Ten specimen strips were measured for each sample to obtain an average strength index.

3 RESULTS AND DISCUSSIONS

3.1 Mechanical properties

In the case of internal addition, PAE content is often below 1% (relative oven dry fiber). The relationships between PAE amount used in sheets and their dry-tensile strengths are depicted in Figure 3.

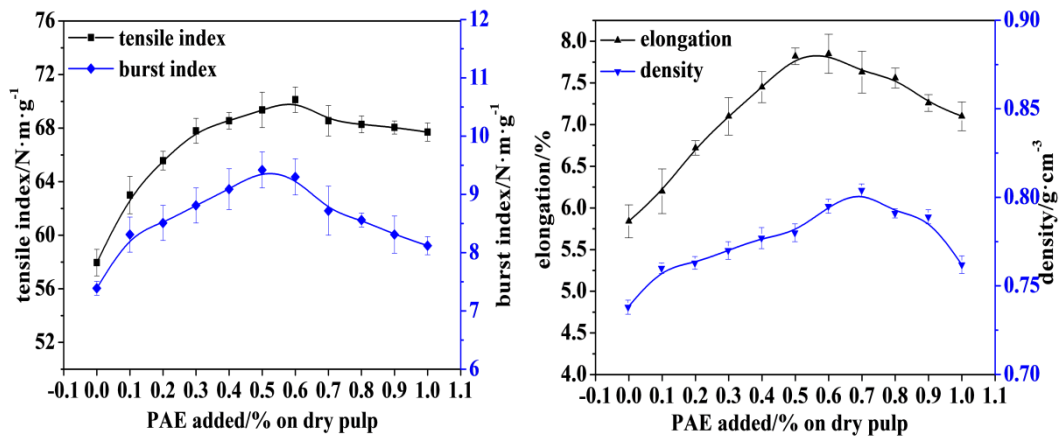


Figure 3: Relationships between PAE content in sheets prepared with different PAE addition levels and strength properties of the sheets.

As shown in Figure 3, the tensile index, burst index, and elongation of PAN sheets without PAE were 57.9 N m g⁻¹, 7.4 N m² g⁻¹, 5.8%, respectively. After PAE application, the strength properties of PAN sheets increased. At low PAE dosage, the PAN fiber's surface was unsaturated and all polymers adsorbed and deposited onto the PAN fibers. Obviously, the paper properties were significantly increased when the PAE dosage increasing. The tensile index, tear index, elongation and density of the paper can reach a maximum value when the dosage was 0.6%, in which the tensile index, tear index, and elongation were 70.1 N m g⁻¹, 9.3 N m² g⁻¹, 7.9%, respectively. This is because that by adding PAE resin and high temperature ripening, AZR groups and secondary amines of PAE developed a

“self-crosslinking” networks among PAN fibers, which play a vital role of “framework” structure and improve the density and strength properties; moreover, PAE has positive charge and the fibers have negatively charge, PAE is easy to combine with fiber, then they form a cross-linked structure.

When continue to increase the amount of PAE above 0.6%, the strength properties of PAN sheets decreased, but still stay a higher level than that of original sheet without PAE. This is because the absorbing decreasing of the small molecular PAE mass on the PAN fiber, which may affect the formation of the networks and the strength properties. Additional, the viscosity of PAE resin was provided by PAE molecular and few PAE cross-linking structure, an excessive cross-linking may cause gel and pitch trouble.

There are lots of research work about PAE resin for enhance paper properties. They think the density of sheet may increase and the binding force between PAE and fiber become stronger. Jielong Su [17] added PAE resin to bleached eucalyptus Kraft pulp. When 0.2% PAE was added, the maximum tensile index reached $15.2 \text{ N m}^2\text{g}^{-1}$ and the density become higher. As PAE amount increased more, fiber flocculation induced by PAE becomes significant and counteracted the strength improvement. Jianlin Luo [18] improved the loose soy protein molecules were cross-linked, together and formed dense cross-linking network structure. By SEM images, the cross-section of original paper was thick, and the fiber combination was loose. The cross-section of paper with PAE was thin. PAE could improve the bonding between the fibers, which is in agreement with the increased paper density after addition of PAE. As shown in Figure 4(a) and 4(b), there were pores on the surface of the original PAN sheet and sheet with PAE, and no great differences between them. Figure 4(c) and 4(d). also displays the SEM cross-section images of PAN sheets. As shown, the cross-section of sheet with PAE was thin, PAE resin could increase the binding of fibers in paper with the density increased by 9.6%.

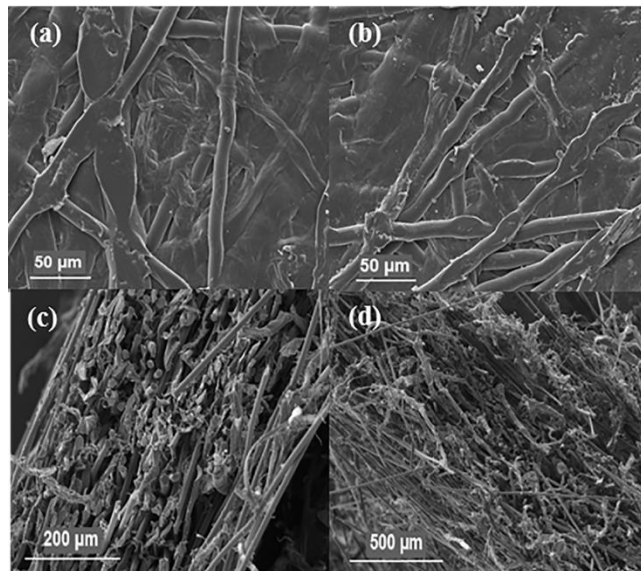


Figure 4: SEM images of PAN sheets (a) and (c) with PAE resin (b) and (d) without PAE resin.

3.2 FTIR spectra

According to the above mentioned, PAE resin can greatly improve the strength properties of PAN sheets and form “self-crosslinking” networks, which makes fibers bind more tightly. Figure 5 shows the FTIR spectroscopy of PAN sheets with or without PAE resin. PAE film and PAN sheets were subjected to FTIR analysis to explain whether any structural changes of PAE molecules occurred by adding PAE resin and the “self-crosslinking” specific reaction process.

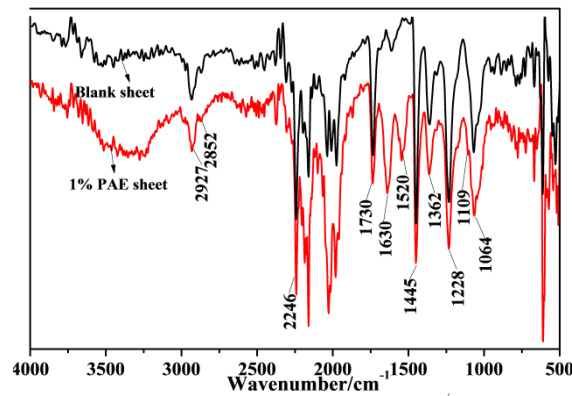


Figure 5: FTIR spectrogram of PAN sheets with PAE (red line) and without PAE (black line).

Characteristic absorption peak of PAN sheets are cyan group (-CN) 2246 cm^{-1} ; methene group (-CH₂-) 2852 cm^{-1} in PAN fiber; second amine (-NH-) 1630 cm^{-1} ; carbonyl (C=O) 1520 cm^{-1} ; -CH- 1064 cm^{-1} in PAE resin, as shown in Table 1.

By using PAE resin, the absorption peaks of PAN sheets at 1109 cm^{-1} occurred, indicating the tertiary amine groups increased, which is probably due to C-N covalent bond during PAE molecules “self-crosslinking”. In addition, the hydrogen bonding association absorption peak of PAN sheets at 3000-3500 cm^{-1} become slightly strong, implying that more hydrogen bonding formed. As shown, PAE resin can greatly improve the paper strength properties.

Wavenumber / cm^{-1}	Vibration type	Wavenumber/ cm^{-1}	Vibration type
2927	-CH ₂ - asymmetrical	1520	amide C=O
2852	-CH ₂ - symmetrical stretching vibration	1445	-CH ₂ - -CH ₃ flexural vibrations
2246	-CN stretching vibration	1109	tertiary amine flexural vibrations
1630	amide -NH-	1064	-CH stretching vibration

Table 1: The absorption peaks in PAN sheets.

3.2 XPS analysis

In order to directly prove the covalent bonds in the adding PAE resin PAN sheets, XPS were used to analyze the differences by adding PAE resin and “self-crosslinking” PAE resin. Table 2 shows the elements contents changes in PAN sheets by adding PAE resin. It can be seen, the contents of C and O elements slightly increased and the N elements content decreased greatly. These changes indicate that the N elements relative amount in PAE resin is lower than PAN fiber. Aiming at big changes in N elements, the N1s XPS spectrogram was main analyzed.

Elements content	C/%	O/%	N/%
Blank sheet	78.43	11.61	9.95
PAE-containing sheet	80.94	13.57	5.49

Table 2: PAE resin element' contents changes by "self-crosslinking"

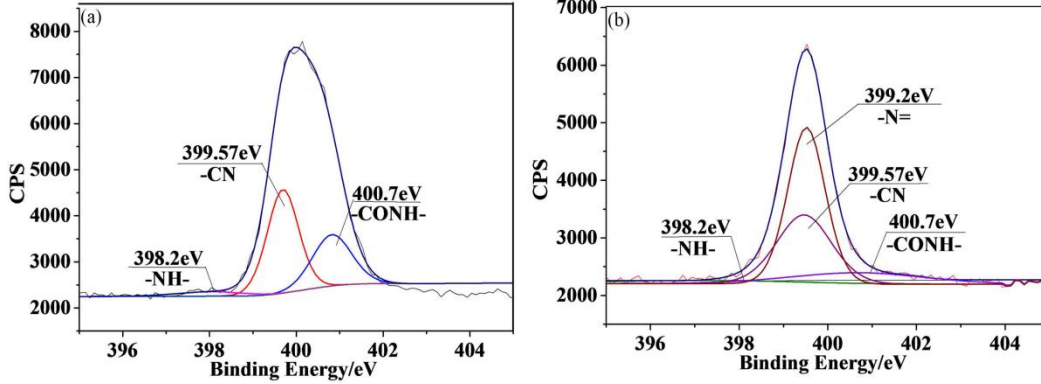


Figure 6: PAN sheets N1s XPS spectrogram:(a) without PAE resin; (b) "self-crosslinking" PAE resin.

The groups binding energy /eV	400.7	399.57	399.4	398.2
without PAE resin PAN sheets	-CONH-	-CN	none	-NH-
"self-crosslinking" PAE resin PAN sheets	-CONH-	-CN	-N=	-NH-

Table 3: The groups binding energy in PAE resin changes before and after "self-crosslinking"

It can be seen from Figure 6, the binding energy of the without PAE resin at 400.7eV is due to the N in -CONH-; the binding energy at 399.57eV is originated from the N in -CN, and 398.2eV is ascribed to the N in -NH-. While the "self-crosslinking" PAE resin PAN sheets occurred 399.2eV binding energy, which arises from the N in tertiary amine groups. It is proved that PAE molecules form tertiary amine groups each other. According to paper strength theory, once the networks structure developed, though the amount of "self-crosslinking" PAE molecules is few, the crosslinking greatly attributed to the strength enhancement of paper, which can enhance the inter-fiber bonding and stimulate the fiber itself to keep their inherent strength. The reaction process of "self-crosslinking" PAE molecules in PAN sheets is shown in Figure 7.

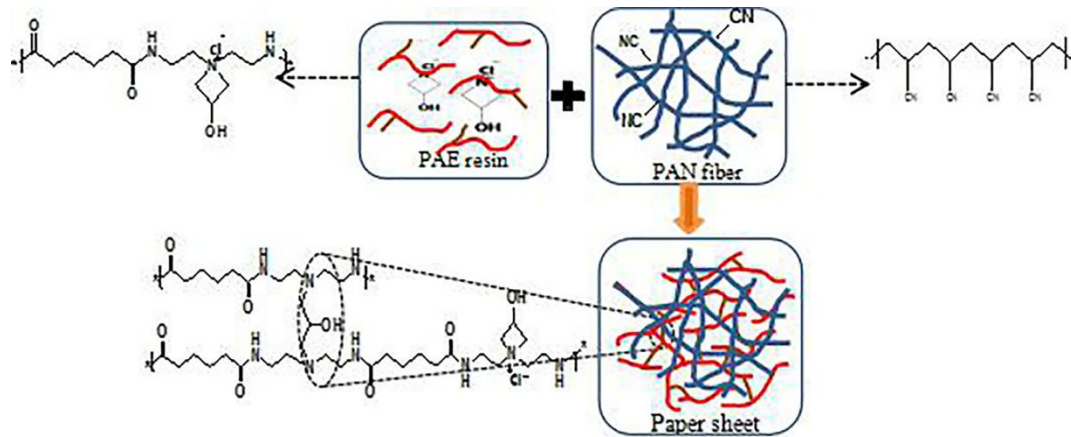


Figure 7: The process of PAE resin “self-crosslinking”

When adding PAE resin in wet end, it can quickly absorb on the PAN fiber. In the medium alkaline chemical environment of paper-making, the heated resin forms “self-crosslinking” by the inherent hot setting property, this achieves the good water-insoluble cross-linked networks and improves the strength. When concerning the materials selection and sustainability engineering [19-20], the PAN sheet can be good materials for material packaging.

4 CONCLUSIONS

It can achieve good paper strength improvement of PAN sheets by using PAE resin. Compared to the untreated paper, the tensile index, tear index, and elongation were increased by 21.0%, 25.8%, 34.3%, respectively, when 0.6% PAE was used. What's more, it will improve the density. By using ATR-FTIR and XPS, we can analyze the occur of tertiary amine groups, which is due to the “self-crosslinking” of PAE resin deposited between or absorbed on the PAN fiber; From SEM, the surface images between the blank sheet and the PAE-containing sheet have no great differences. But the binding energy at 399.2eV is ascribed to the N in tertiary amine groups, which indicates that the “self-crosslinking” is good for fiber combination and density improvement. That's why the paper strength can greatly improve.

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