

Highly Improved Microstructure and Properties of Poly(*p*-phenylene terephthalamide) Paper-based Materials via Hot Calendering Process

Bin Yang^{1,2,4}, ZhaoQing Lu^{1,3,4,*}, MeiYun Zhang^{1,3,4}, ShunXi Song^{1,3,4}, RuNan Wang¹

1. College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science & Technology, Xi'an, Shaanxi Province, 710021, China

2. School of Natural and Applied Sciences, Northwestern Polytechnical University, Xi'an, Shaanxi Province, 710072, China

3. Shaanxi Provincial Key Laboratory of Papermaking Technology and Specialty Paper Development, Xi'an, Shaanxi Province, 710021, China

4. National Demonstration Center for Experimental Light Chemistry Engineering Education, Shaanxi University of Science & Technology, Xi'an, Shaanxi Province, 710021, China



Bin Yang, PhD candidate,
engineer;
E-mail: lxyangbin@126.com



*Corresponding author:
ZhaoQing Lu, PhD, professor;
research interests: high performance fibers and functional paper-based materials;
E-mail: lupaper@126.com

Abstract: In this study, the effect of hot calendering process on the microstructure and properties of poly (*p*-phenylene terephthalamide) (PPTA) paper-based materials was investigated. The microstructures of the fracture surface, crystalline structure, and single fiber strength of the PPTA paper-based materials as well as the different bonding behaviors between the PPTA fibers and PPTA fibrils obtained before and after the hot calendering process were examined. The results indicated that a high linear pressure would result in a limited improvement of the strength owing to the unimproved paper structure. The optimal values of tensile index and dielectric strength of 56.6 N · m/g and 27.6 kV/mm, respectively, could only be achieved with a synergistic effects of hot calendering temperature and linear pressure (240°C and 110 kN/m, respectively). This result suggested it was possible to achieve a significant reinforcement and improvement in the interfacial bonding of functional PPTA paper-based materials, and avoid the formation of unexpected pleats and cracks in PPTA paper-based materials during the hot calendering process.

Keywords: PPTA paper-based materials; hot calendering; interfacial bonding; crystalline structure; PPTA fiber

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1 Introduction

Poly(*p*-phenylene terephthalamide) (PPTA) is a widely used liquid-crystal polymer. PPTA fibers are well known for their outstanding properties, such as high modulus and strength, excellent high-temperature resistance, and low density, and hence, they have been extensively applied in military and civil fields^[1-2].

PPTA paper-based materials which are made of short PPTA fibers and PPTA fibrils are prepared using a wet-forming papermaking process (Fig.1). As a matrix of advanced composite materials such as high-temperature insulating materials and honeycomb structure materials, PPTA paper-based materials exhibit exceptional mechanical properties, excellent dielectric properties, outstanding heat-resistance, remarkable thermal durability, and favorable flexibility of design with a reduced overall-weight, higher strength, and longer life-span, and they have drawn increasing attention from scientists and engineers^[3-6].

After the wet-forming process, PPTA paper-based material are hot-calendered^[7]. The hot calendering process is of considerable significance in the PPTA paper-based material manufacturing, as it causes an improvement in the overall properties of the PPTA paper-based materials including the mechanical properties and microstructure^[8]. Different hot calendering parameters will lead to different microstructures, properties, bonding behaviors of PPTA paper-based materials. The interfacial bonding adhesion between PPTA fibers and PPTA fibrils will change with the different hot calendering parameters. During the hot calendering process, PPTA fibrils will extend and migrate because of their characteristics of highly ductile, supple, rough, curled, and film-like appearance, which is helpful for tuning the microstructure of PPTA paper-based materials^[9]. However, it may also lead to the superposition of local stress, thereby resulting in

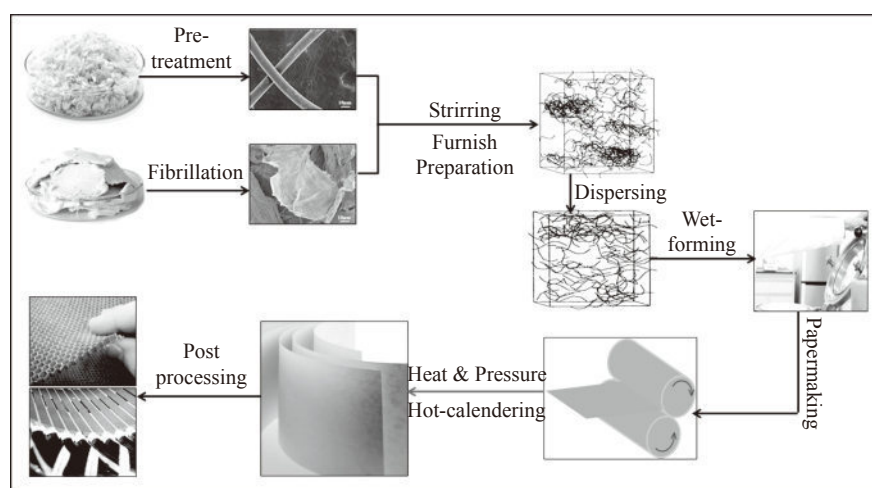
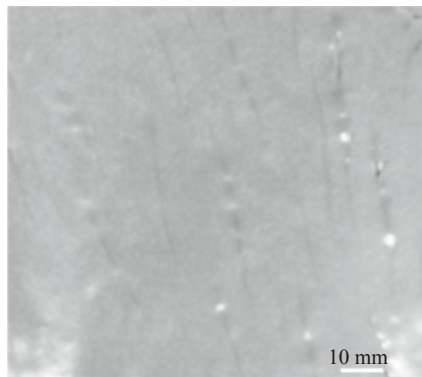


Fig.1 Schematic of the wet-forming papermaking process of PPTA paper sheets

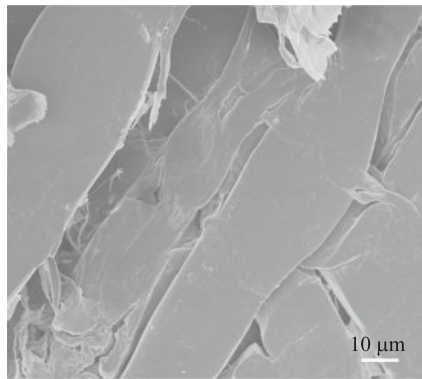
the formation of unexpected pleats and cracks on the PPTA paper surface. If the pleats and cracks occur, the thickness of the PPTA paper in the pleat position is higher than that in the other regions, then the pleat position becomes the main pressure-bearing portion. Hence, stress is concentrated near the pleat position in the PPTA fibers and PPTA fibrils, thereby increasing the crushing phenomena, as shown in Fig.2. The pleat and crack positions exhibit higher transparency and crazing, and show poor mechanical strength as compared to the other parts.

Most of previously researches focused on the PPTA fiber structure, fiber modification and the improvement of interfacial adhesion between fibers and epoxy resin matrix^[10-13]. However, only a few studies demonstrating the synergistic effect of temperature and pressure on the mechanical properties and structure of PPTA paper-based materials have been carried out, especially examining the reasons for the formation of unexpected pleats and cracks as well as the poor interfacial bonding behaviors achieved between PPTA fibers and PPTA fibrils during the hot calendering process. Zhang S F et al^[14] reported the effects of temperatures ranging from 130°C to 240°C on the structure of the paper manufactured with 100% poly(*m*-phenylene isophthalamide) (MPIA), especially on the paper sheet density and mechanical strength. They found that the surface of the paper sheet became much

smoother owing to some of the melting MPIA fibrils in the paper sheet, which resulted in a stronger adhesion between the MPIA fibers and MPIA fibrils. Nevertheless, PPTA fibrils exhibit a different chemical structure as compared to the MPIA fibrils, and they can not be melted with a rise in temperature. Therefore, they behave differently in the paper-based materials.



(a) Digital photo of the pleats



(b) SEM image showing the microstructure of the crack

Fig.2 Images of the pleat and crack phenomena on the PPTA paper-based material surface

In this study, the synergistic reinforcing effects of linear pressure and temperature employed during the hot calendering process on the microstructure and physical properties of PPTA paper-based materials were investigated. The microstructure of the fracture surface, crystalline structure, and single fiber strength of the materials as well as the difference in bonding behaviors between PPTA fibers and PPTA fibrils obtained before and after the hot calendering process were discussed. The important properties of the PPTA paper-based materials for electrical insulating applications, including

mechanical properties such as the tensile strength and tear strength as well as the dielectric strength were examined.

2 Experimental

2.1 Materials

PPTA fibers and PPTA fibrils were provided by the Teijin Group in Japan. The average length and width of the PPTA fibers were 4.0 mm and 12.0 μm , respectively. The average length and the Canadian freeness standard (CSF) of the PPTA fibrils were 0.95 mm and 250 mL, respectively.

2.2 Sample preparation

The PPTA base paper sheets with a basis weight of 45 g/m^2 were made using a BBS-3 handsheets former (ERNST HAAGE, Germany). The mass ratio of the PPTA fibers to PPTA fibrils in the slurry was 3 : 7. After employing the wet-forming process, the PPTA paper-based materials were further hot-calendered using a DT-2002 three-roller calender (Paper Science, Finland) under different conditions. (1) PPTA base paper sheets I were hot-calendered at the ambient linear pressure with the temperature changing from room temperature to 120°C, 160°C, 200°C, 240°C, and 280°C. (2) PPTA base paper sheets II were hot-calendered at room temperature with a linear pressure changing from 0 to 50 kN/m, 80 kN/m, 110 kN/m, 140 kN/m, and 170 kN/m. (3) PPTA base paper sheets III were hot-calendered under a temperature of 240°C and linear pressure of 110 kN/m. In addition, PPTA base paper sheets not subjected to the hot calendering process were used as the control samples.

2.3 Characterization

A KH8700 digital microscope (HIROX, Japan) and S-4800 scanning electron microscope (SEM) (Hitachi, Japan) were employed to analyze the morphologies of PPTA fibers, PPTA fibrils, and PPTA paper-based materials. A micro tension tester (JSF08, China) was used to investigate the strength and modulus of a single PPTA fiber.

2.4 Determination of physical properties

The physical properties of PPTA paper-based materials were measured in accordance with the TAPPI Standard. The dielectric strength was tested according to ASTM D-149. The data were averaged by testing three specimens of each PPTA paper-based material.

3 Results and discussion

3.1 The effect of temperature or linear pressure on the properties of PPTA paper-based materials

PPTA fiber exhibits a smooth surface without any active functional groups present, which makes it chemically inactive and thus exhibits poor interfacial adhesion^[13]. This hinders the adhesion between PPTA fibers and a matrix, such as epoxy resin^[15]. PPTA fibrils, which are produced by precipitation caused by rigorous stirring of PPTA copolymer solutions at low temperatures, can be visualized as having a soft, ductile film-like structure with a high specific surface area. In the PPTA base paper sheet, PPTA fibers are evenly distributed in the matrix as a framework material with the PPTA fibrils wrapped and interlocked among the PPTA fibers acting as the building block materials, which determines the initial physical structure and mechanical properties of the PPTA base paper sheet. However, the structure of the PPTA base paper sheet was so loose that it exhibited poor mechanical strength.

As shown in Fig.3(a), the mechanical strength and dielectric strength of the PPTA paper-based material hot-calendered

under a high temperature of 240°C and ambient linear pressure remained almost the same to those of the PPTA base paper sheet not subjected to the hot calendering process. The PPTA fibers exhibited a cylindrical morphology, which was same as that of the PPTA fibers not subjected to the hot calendering process. PPTA fibrils only overlapped and wrapped around the surface of the PPTA fibers, indicating that the hot calendering process with a high temperature and ambient linear pressure did not result in any bonding between the PPTA fibrils and the PPTA fibers. PPTA monofilament fibers were prone to be pulled out from the matrix because of the sliding and translation of PPTA fibers under stress. Moreover, the PPTA fibrils softened and shrank with an increase in temperature in the absence of any oriented driving force, which resulted in the formation of larger pores and voids in the PPTA paper-based materials. In addition, the high ductility of PPTA fibrils did not significantly affect the formation of a compact structure with a high bonding force.

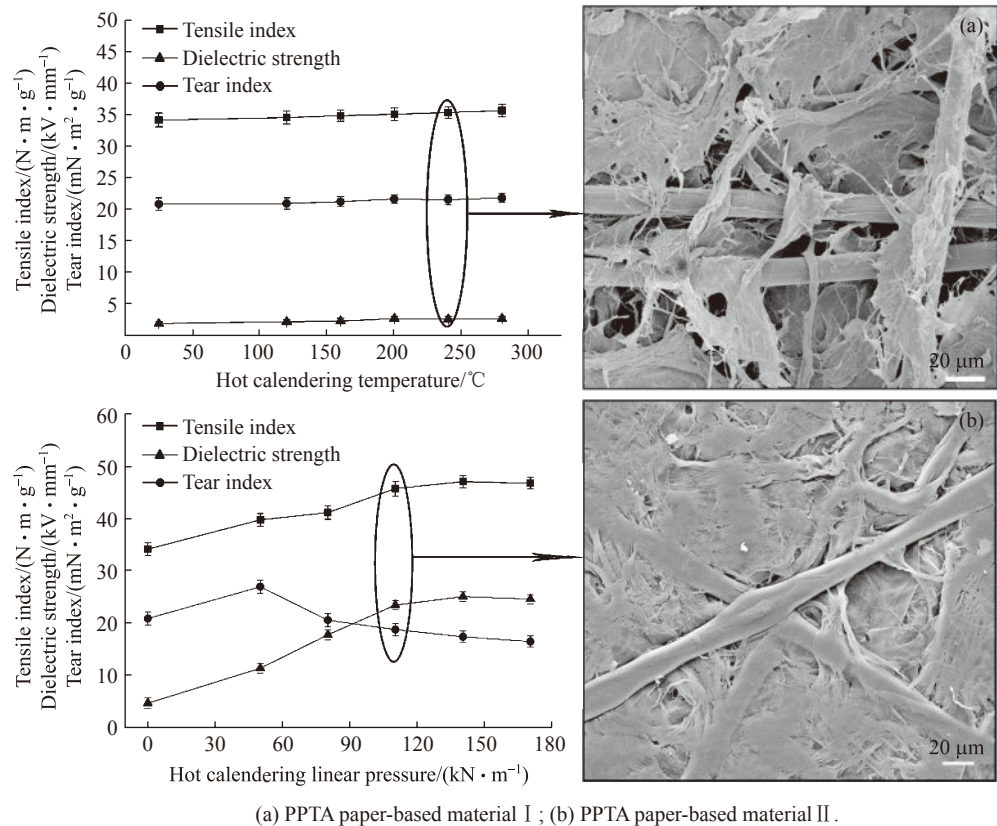


Fig.3 Performances and microstructures of the PPTA paper sheets hot-calendered only with an increase in temperature or pressure

On the other hand, as shown in Fig.3(b), the performances of the PPTA paper-based material hot-calendered with a high linear pressure and room temperature could be remarkably enhanced as compared with those of the control samples, especially in terms of the tensile strength and dielectric strength. At a hot calendering linear pressure of 110 kN/m and room temperature, the tensile index and dielectric strength of the PPTA paper-based material were 47.0 N · m/g and 23.8 kV/mm, respectively, resulting in an increase of 34.0% and 408.7% as compared with those of the control samples, respectively. Although a high hot calendering temperature was helpful in softening the PPTA fibrils, a high hot calendering linear pressure could effectively drive the mutual integration of the PPTA fiber and PPTA fibrils. The PPTA paper-based materials exhibited a compact structure with a lower thickness, resulting in a decrease in the porosity and making the pulling out of the PPTA fibers from the matrix to be more difficult. The proper deformation of the PPTA fibers under a high hot calendering linear pressure resulted in the enhancement of mechanical interlocking with PPTA fibers and PPTA fibrils, causing an improvement in the mechanical strength. However, the higher hot calendering linear pressure resulted in a poor tear strength of the PPTA paper-based materials. The high hot calendering linear pressure (>140 kN/m) resulted in not only decreasing the original strength and modulus of the PPTA fibers, but also increasing the brittleness and accelerating the tendency of parchmizing of the PPTA paper-based materials.

3.2 The synergistic effects of temperature and linear pressure on the performances of PPTA paper-based materials

Compared to the control samples, the mechanical properties and structure of the PPTA paper-based

materials II improved significantly via hot calendering process under a high linear pressure at room temperature. However, the limitations of the PPTA paper-based materials II include their weak internal bonding strength, rough surface, high porosity, and the tendency of parchmizing deformation, which cause the degradation of their integrated properties, thereby confining the applications in high-end fields.

The paper performances can only be optimized by employing the synergistic effects of the temperature and linear pressure in the hot calendering process. Under a high linear pressure at room temperature, the bonding behaviors between the PPTA fibers and PPTA fibrils increase to a relatively high level, resulting in the formation of a compact structure. By employing the synergistic effects of high temperature and linear pressure in the hot calendering process, PPTA fibrils softened dramatically and stretched with heating owing to its excellent ductility, which was helpful in filling and covering the pores of the PPTA paper-based materials. Furthermore, owing to the soft, flexible film-like structure with a high specific surface area of the PPTA fibrils, they can easily wrap the PPTA fibers and increase the bonding points among PPTA fibers, accordingly enhancing the mechanical interlocking and reinforcing effects.

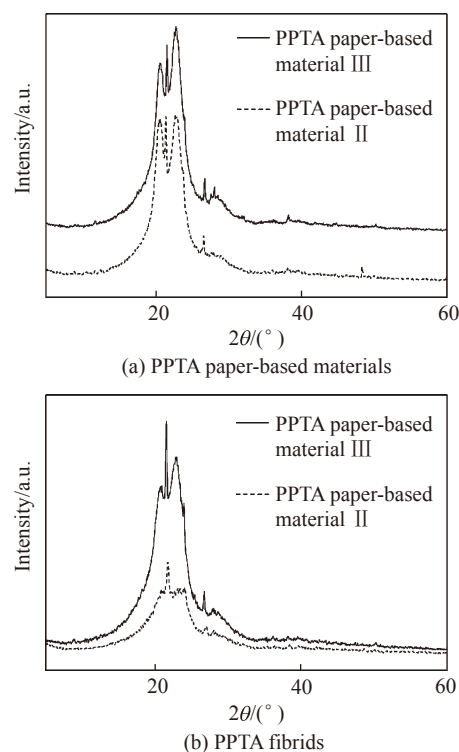
As shown in Table 1, the mechanical strength and dielectric strength, especially the internal bonding strength of the PPTA paper-based material III hot-calendered under the synergistic effects of temperature and linear pressure (240°C and 110 kN/m, respectively) exhibited evident advantages over the PPTA paper-based material II hot-calendered under a higher linear pressure (110 kN/m) at room temperature. As compared to the PPTA paper-based material II, the tensile index and dielectric strength of the PPTA paper-based material III exhibited optimal values of 56.6 N · m/g

Table 1 Comparisons of the properties of PPTA paper-based materials hot-calendered under different conditions

PPTA paper-based materials	Temperature /°C	Linear pressure /(kN · m ⁻¹)	Tensile index /(N · m · g ⁻¹)	Tear index /(mN · m ² · g ⁻¹)	Internal bonding strength /(J · m ⁻²)	Dielectric strength /(kV · mm ⁻¹)
II	25	110	47.0	15.0	16.5	23.8
III	240	110	56.6	16.4	32.1	27.6

and 27.6 kV/mm, respectively, indicating an increase of 20.4% and 16.0%, respectively. The internal bonding strength increased to 32.1 J/m², indicating an increase of 94.5%. The internal bonding strength of the paper is determined by the intrinsic strength of fibers and the amounts of bonding points among the fibers. The more the bonding points, the higher would be the internal bonding strength of PPTA paper-based materials. The highly ductile and film-like structural characteristics caused an increase in the bonding areas with the synergistic effects of temperature and linear pressure in hot calendering process.

As shown in Fig.4(a), the crystallinity of the PPTA paper-based material III increased from 60.6% to 77.3% as compared to the PPTA paper-based material II. This is mainly because the distances of the molecular chains of fibers shortened and orientated along the crystalline orientation under the driving forces achieved with the high linear pressure and temperature. Hence, the mechanical strength of PPTA fibers could be optimized further, thereby improving the properties of the PPTA paper-based material. As shown in Fig.4(b), only on hot calendering under a high pressure, the PPTA fibrils exhibited broadened and low-intensity diffraction peaks, which were characteristics of amorphous states. However, the crystalline structure of the PPTA fibrils improved significantly after hot calendering the samples under the synergistic effects of temperature and linear pressure. It caused a significant improvement in the intensity and orientation of diffraction peaks observed at $2\theta=20.6^\circ$ and 23.1° , corresponding to (110) and (200) lattice planes in PPTA, respectively. PPTA molecules are highly oriented in the axial direction in the PPTA fibers^[16]. The molecular chains can be more perfectly arranged owing to the oriented-crystallization of the PPTA fibrils, resulting in an enhancement of the mechanical properties and thermal stability of the PPTA fibrils. The improvement in the crystalline structure of the PPTA fibrils is of great significance for improving the properties of the PPTA paper-based materials. In addition, the bonding points of the fibers increased, and the hydrogen bonding strength improved.



* PPTA paper-based material II was hot-calendered at 25°C and 110 kN/m; PPTA paper-based material III was hot-calendered at 240°C and 110 kN/m.

Fig.4 XRD patterns of the PPTA paper sheets hot-calendered under different conditions

3.3 The influences of hot-calendering on the fracture surfaces and bonding behaviors of PPTA paper-based materials

Hot calendering caused a noticeable improvement in the performances of the PPTA paper-based materials, mainly because the application of heat and linear pressure provided driving force to prompt the bonding between the PPTA fibers and PPTA fibrils. As shown in Fig.5(a), many intact PPTA fibers with a homogeneous diameter were pulled out in the fracture surfaces of PPTA paper-based materials before being hot-calendered. It suggested that the PPTA fibers and PPTA fibrils not subjected to hot calendering were only mechanically stacked, resulting in a poor interfacial bonding force and loosened paper sheet structure. The PPTA fibers could be completely extracted from the fiber networks and the intrinsic strength was maintained when the PPTA paper sheet fractured owing to the force. However, as shown in Fig.5(b), only a few

PPTA fibers could be pulled out in the fracture surfaces of PPTA paper-based materials with a flattened and transformed structure. It was mainly because the PPTA fibers became deformed and accordingly transferred the stress on cracking. PPTA fibrils softened and deformed under the effects of heat and linear pressure, which filled among the pores owing to its high ductility.

In the fiber-reinforced composite material (FRP), the interface between the reinforcement and matrix is the bridge, which transfers deformation and stress. The structure and strength crucially affect the properties of FRP. The PPTA fibers distributed evenly in the matrix acted as framework materials in the PPTA paper-based materials, which adjusted the stress transferring direction and route, as determined by the well-integrated mechanical strength. The bonding behaviors between the PPTA fibers and PPTA fibrils in the samples obtained from different hot calendering processes differed diversely.

As shown in Fig.5(c), the PPTA fibrils covered or wrapped the surfaces of PPTA fibers in the paper-forming process because of their highly ductile nature

and film-like structure, which increased the bonding areas and adhesive strength between the PPTA fibers and PPTA fibrils. The bonding behaviors could probably result from the specific morphologies of the PPTA fibrils and the friction force among PPTA fibers. This suggests why the PPTA base paper sheet needed to be hot-calendered after paper formation. Fig.5(d) shows the bonding behaviors between the PPTA fibers and PPTA fibrils achieved after the hot calendering process. The PPTA fibers deformed and rearranged dramatically, and exhibited compressed and tortile morphologies, resulting in more adhesive points for the PPTA fibers and PPTA fibrils^[17]. This could be attributed to the remarkable improvement in the mechanical strength of the PPTA paper-based materials after the hot calendering process.

3.4 The influences of linear pressure on the mechanical strength of PPTA fibers

Along with the factors such as the interfacial bonding strength, fiber length, and combination of fibers, the intrinsic strength of individual fiber also plays an important role in the comprehensive performance of PPTA paper-based materials. The conditions employed in the hot calendering process, especially the use of the high linear pressure caused the PPTA fibers to be flattened and transformed status, resulting in an improvement in the interfacial bonding strength of PPTA paper-based materials. Different linear pressure values led to different transformation extents of the PPTA fibers. As shown in Fig.6, the modulus and strength of the PPTA fibers decreased with a rise in linear pressure. When the hot calendering linear pressure increased, the PPTA fibers became compressed and non-isodiametric, resulted in achieving

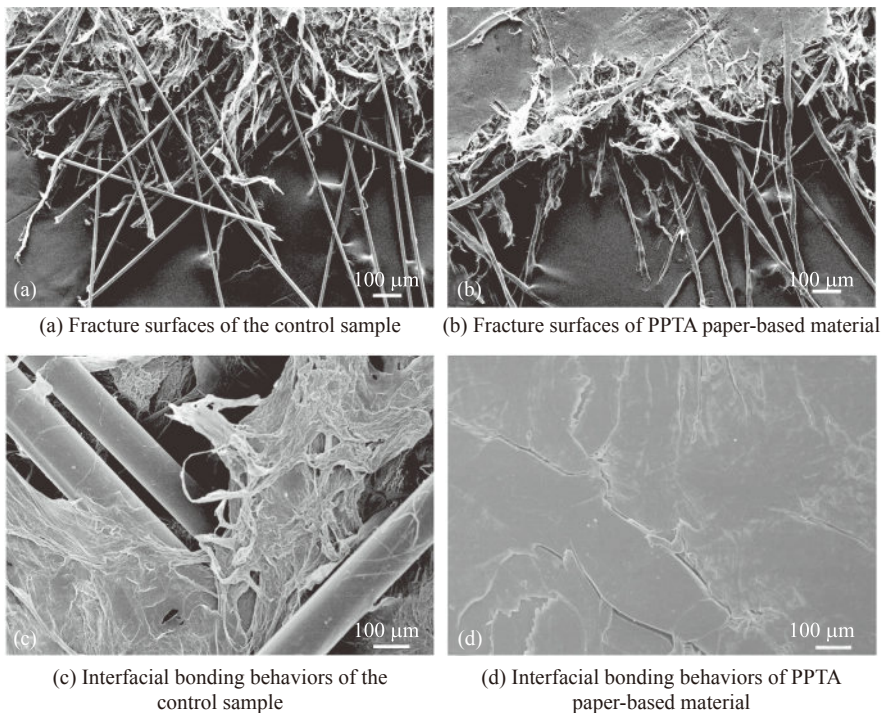


Fig.5 SEM images of fracture surfaces and bonding behaviors of the control sample and PPTA paper-based material hot-calendered at 240°C and 110 kN/m

more bonding points with the PPTA fibrils. In addition, some fibrillated fibrils were observed on the surface of PPTA fibers to some extent, which contributed to the reinforcement of the friction force and bonding among PPTA fibers. Schmied et al.^[18] reported that fibrils or fibril bundles present in the paper structure played a crucial role in fiber–fiber bonding because they acted as bridging elements. However, when the linear pressure increased further (e.g., 170 kN/m), some cracks were formed on the PPTA fibers, which damaged the structure and molecular chain, accordingly lowering the intrinsic strength of the individual PPTA fiber.

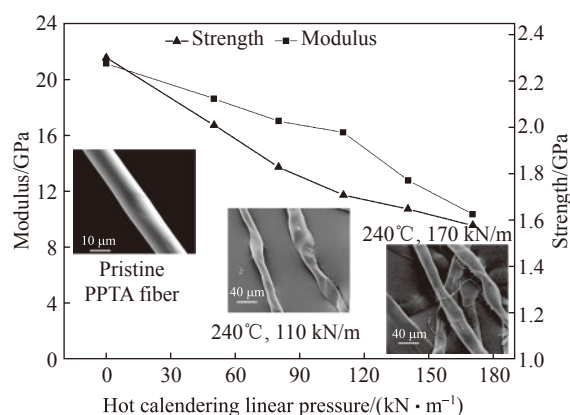


Fig.6 Effect of linear pressure on the mechanical strength of individual PPTA fiber

4 Conclusions

In this study, the microstructure of the fracture surface and different bonding behaviors between the PPTA fibers and the PPTA fibrils, as well as the synergistic effects of temperature and linear pressure on the mechanical properties of PPTA paper-based materials were investigated. Only with the synergistic effects of high temperature and linear pressure (240°C and 110 kN/m, respectively), the tensile index and the dielectric strength of PPTA paper-based materials achieved the optimal values, 56.6 N · m/g and 27.6 kV/mm, respectively. As compared to the structure of the PPTA base paper not subjected to hot calendering, the structure of PPTA paper-based materials remarkably improved after hot calendering, resulting in a compact microstructure and smoother surface. The improvement of the crystalline structure of the PPTA fibrils was

of great significance for improving the properties of the PPTA paper. The high linear pressure caused the formation of some cracks on the PPTA fibers and lowered the intrinsic strength of the individual PPTA fiber. The bonding behaviors between the PPTA fibers and PPTA fibrils could be attributed to the specific morphologies of PPTA fibrils and the friction force among PPTA fibers. This study suggests the potential for significant reinforcement and interfacial bonding improvement of the hot calendering process for the production of functional PPTA paper-based composite materials.

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