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A ductile and highly fibrillating PPTA-pulp and its reinforcement and filling effects of PPTA-pulp on properties of paper-based materials

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ABSTRACT: In this work, poly(para-phenylene terephthalamide) (PPTA)-pulp was investigated in view of employment in functional paper-based materials as reinforcement, bonding, and filling materials. The morphological characteristics, fibrillation degree and the role of PPTA-pulp, the ratio of PPTA-pulp to PPTA fiber on the mechanical properties, and paper formation uniformity of the functional base paper were discussed. The results showed that the ductile, rough, and highly fibrillating morphological characteristics of PPTA-pulp are helpful to give rise to some distinctive properties such as wet-machinability and reinforcement effects in composite materials. Fibrillation of PPTA-pulp significantly contributes to generating more highly dispersed slender threadlike micro-fibrils and improving the properties of base paper. This research suggested a significant reinforcement, bonding, and filling potential of PPTA-pulp for the production of functional paper composite materials. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43209.

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INTRODUCTION

As a kind of ideal replacement materials for asbestos, poly (para-phenylene terephthalamide) (PPTA)-pulp was developed and brought about industrialization by DuPont Co., in 1980s.[1,2] It has increasingly attracted the attention of both scientists and engineers worldwide due to its outstanding performance.[3,4] It is a kind of PPTA fiber derivative product with the same chemical structure, but different morphologies and properties such as highly fibrillating and easy-to-disperse in water. Due to the similarity of chemical structure, PPTA-pulp has remained the excellent properties of PPTA fiber, such as high strength and thermostability.[5] Moreover, it also exhibits distinctive properties from PPTA fiber due to its particular manufacturing method, such as superior wet-machinability, reinforcement, and filling effects in composite materials.

The ever-increasing pace in the development of technology has imposed demands on higher performance of composite materials.[6,7] Among the composite materials, the key property of paper-based functional materials in comparison with other fiber containing polymers is the cost-effective performance at reduced weight.[8] They are mainly made of high-performance synthetic fibers such as PPTA fiber, carbon fiber, and polyimide (PI) fiber through a wet forming papermaking process with a thermal calendaring process (Figure 1). Together with the different PPTA fibers, carbon fibers, and polyimide fibers show the dominant reinforcement in fiber-reinforced polymers (FRP) for demanding applications in aerospace industry where excellent mechanical properties per unit weight are required. As a kind of matrix of advanced composite materials, the base paper has exceptional specific strength, good insulating properties, low dielectric properties, and flexibility of designing.[9] Because of these favorable performances, the base paper impregnated by phenolic resin has diverse application prospects such as high-temperature insulating materials, honeycomb sandwich structure paper-based materials, and polyimide paper-based materials.[10] Nomex^{TM} paper honeycomb sandwich structures are extensively used in the aerospace and automotive industry to guarantee the aircrafts, vehicles, and trains with reduced overall-weight but higher strength and longer life-span. Examples of the applications of Nomex^{TM} honeycomb sandwich in airplane are floors, doors, wing flaps, wing-body fairings, rudders, overhead stowage bins, ceiling or sidewall panels, engine cowls, spoilers, nacelles and radomes, etc.[11,12]

In the structure of the above mentioned functional paper-based materials, the desired type of fiber (ether PPTA fiber or polyimide fiber) has distributed evenly in the matrix as a framework material, which decides the well-integrated physical structure and mechanical properties of the base paper. However, most of these high-performance synthetic fibers have little bonding behaviors among themselves, which definitely leads to poor quality formation of base paper.[13] Thus, a bonding and filling material is desirable to improve the quality of base paper. In the last few decades, the relationship between the microstructures and the mechanical properties

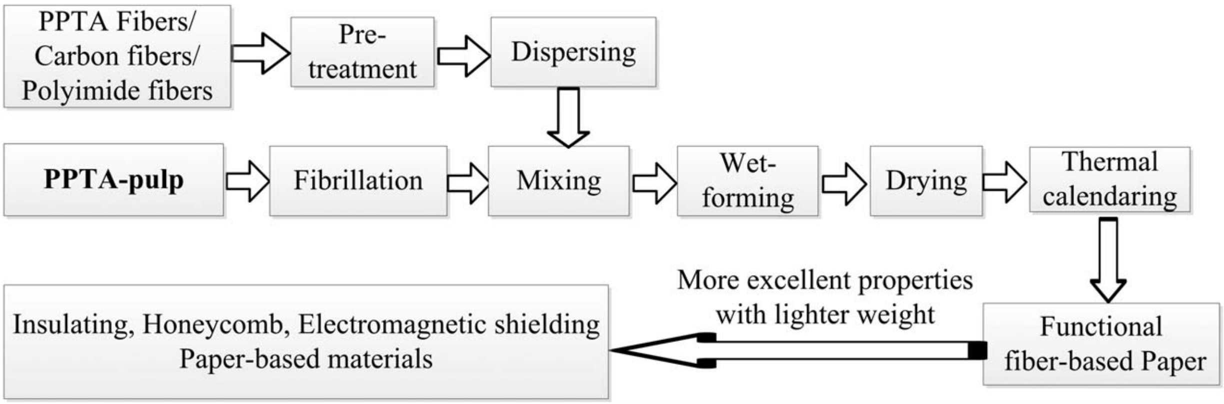

Figure 1. Basic papermaking process of functional fiber-based paper.

of PPTA fibers has been extensively studied.[14] Also, there are some studies, which have been focused on the fiber surface modification in order to improve the interfacial adhesion between fibers and resin in the structure of composite materials.[15–17]

Among all the research work reported, however, there are very few reports that have shown correlating characteristics of PPTA-pulp with its applications and the quality of paper-based materials. Only Wang reported the highly fibrillated PPTA-pulp was used for the preparation of the lithium-ion battery separator. They found that PPTA-pulp was helpful to control the pore size of the separator to less than 1 mm and improve the comprehensive performance of the lithium-ion battery separator.[18] In our previous work, three PPTA-pulps manufactured by different methods were systematically characterized. We have found that different manufacturing methods could lead to different morphological parameters and diverse crystalline structures of PPTA-pulp.[19] In this study, the morphological properties and microstructure of PPTA-pulp were investigated, and then we discussed the ratio of PPTA-pulp to PPTA fiber, fibrillation degree, and its application on the mechanical properties, uniformity, and the microstructures of different fiber-based materials such as heat-resistance insulating materials, paper-based honeycomb materials, and polyimide paper-based materials.

EXPERIMENTAL

Materials

PPTA fiber was provided by Teijin Group in Japan. Polyimide fiber was supplied by Gaoqi Polyimide Materials Co. (Changchun, China). The average length and width of them were 4–5 mm, and 10–12 μm, respectively. PPTA-pulp with the length of 0.5–1.2 mm was provided by Silicon Valley Chemical Co. (Hebei, China).

Sample Preparation

The three base papers with basis weight of 45 g m^{-2} were made using the BBS-3 handsheets former (ERNST HAAGE, Germany) according to TAPPI standard method. Insulating base papers were prepared with PPTA fiber and different contents of PPTA-pulp by the mass fraction to the whole forming slurry. Honeycomb base papers were prepared using PPTA fiber and PPTA-pulp with different degrees of fibrillation. In addition, PPTA-pulp was loaded into a valley beater (TD6-23, Tongda, China) and fibrillated at 1.0% consistency with a 5.0 kg of specific beating pressure load for times selected between 30 and 120 min, at 30 min intervals (TAPPI T 200). Polyimide fiber-based papers were prepared with polyimide fiber and PPTA-pulp. After the wet-forming process, the base paper sheets were further hot-pressed on a DT-2002 three-roller calendar (Paper Science, Finland).

Characterization

An MMDICH-30 Light microscopy (Motic), an S-4800 scanning electron microscope (SEM) (Hitachi, Japan), and an Axio Scope A1 polarized microscope (PLM) (ZEISS, Germany) were employed to analyze the morphologies of fiber, pulp, and base paper. A PAPRICAN micro-scanner (OpTest, Canada) was utilized to test the formation index of base papers. The specific

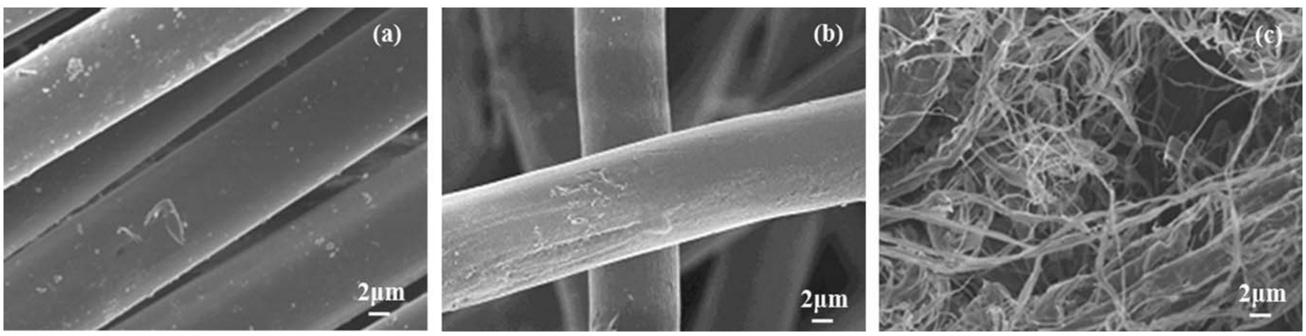

Figure 2. SEM images of fibers: (a) PPTA fiber, (b) polyimide fiber, and (c) PPTA-pulp.

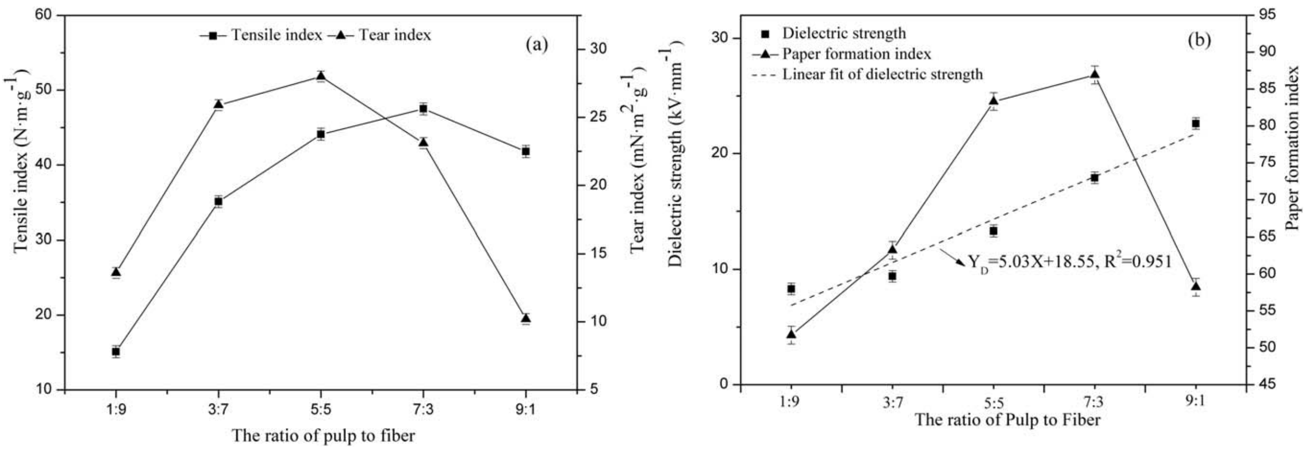

Figure 3. Effects of fiber ratio of PPTA-pulp to fiber on the properties of base paper: (a) mechanical strength and (b) dielectric strength and paper formation index.

surface area (SSA) of PPTA-pulp was determined using a Gemini 2390 BET surface area analyzer (Micromeritics).

Determination of Physical Properties

The Canadian freeness standard (CSF) was tested in accordance with TAPPI Standard Method T227 (T227 om-04). The tensile strength, tear strength and paper formation index were measured in accordance with TAPPI Standard Method T494 (T494 om-88), T414 (T414 om-88), and T563 (T563 om-03), respectively. The dielectric strength was tested according to ASTM D-149. The data in paper was averaged from three specimens of each paper sheet.

RESULTS AND DISCUSSION

Morphological Characteristics of PPTA-Pulp

The properties of base paper are closely related to the morphological characteristics of fibers.[20,21] PPTA fiber is known to have poor interfacial adhesion due to its highly crystalline with a rigid molecular chain oriented along the fiber axis.[22] It shows a smooth surface [Figure 2(a)], lacking of functional groups which are indispensable for the adhesion between fibers and the matrix such as epoxy resin.[23] Similar to PPTA short fibers, polyimide fiber also appears to be smooth and chemically stable [Figure 2(b)], which makes it difficult in forming strong bonding among particles in base paper. In contrast, PPTA-pulp, which is made from PPTA chopped fiber through mechanical refining in the water, exhibits a supple, ductile, rough, being curled, and branched appearance [Figure 2(c)]. It can be visualized as a soft, flexible, highly fibrillating threadlike microstructure with high SSA of 6.0–11.0 m^2 g^{-1}. Such special characteristics of PPTA-pulp might provide great opportunities for better bonding among the particles such as fibers, pulp, and resin matrix, improving the properties of paper-based composite materials accordingly.[24]

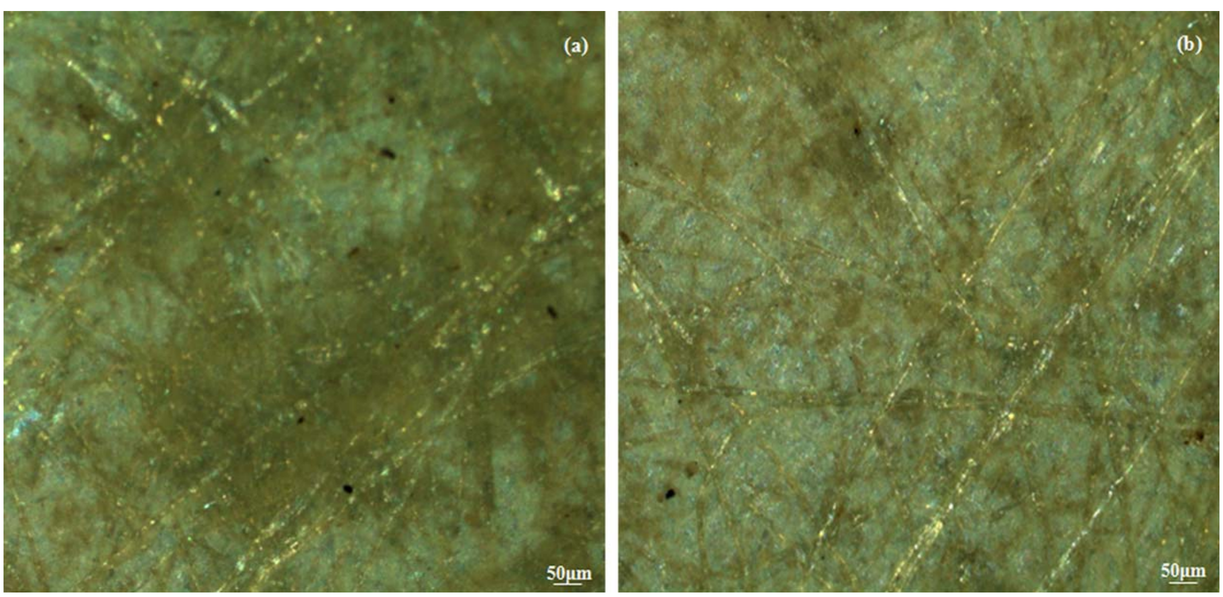

Figure 4. The PLM images of base paper: (a) poor uniformity at the ratio of 3:7 and (b) good uniformity at the ratio of 7:3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

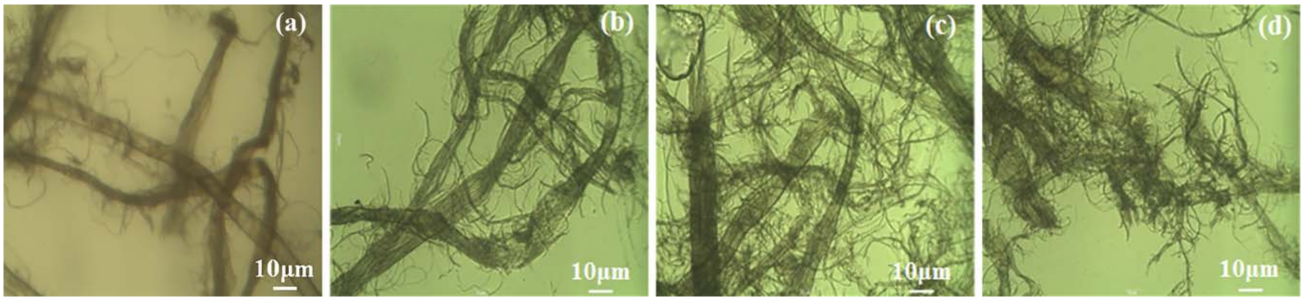

Figure 5. Effects of fibrillation of PPTA-pulp on its morphologies: (a) 475 mL, (b) 375 mL, (c) 275 mL, and (d) 175 mL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Contribution of PPTA-Pulp Contents to the Properties of Insulating Base Paper

PPTA fiber and PPTA-pulp have distinctive sheet forming performances and great differences of paper properties due to their different morphological characteristics.[25] The ratio of PPTA-pulp to PPTA fiber has a significant effect not only on the integral mechanical properties, also on the dielectric strength and sheet forming uniformity. The effect of fiber ratio of two particles on mechanical properties and uniformity of base paper are shown in Figures 3 and 4, respectively.

As shown in Figure 3(a), PPTA-pulp with the contents of 10%–50% showed a significant increase in the tensile index and tear index of base paper. The results implied that it was the characteristics of PPTA-pulp, such as highly fibrillating and high SSA that made a great difference to the bonding of the PPTA fiber and PPTA-pulp. On the other hand, the higher contents of PPTA fibers, the higher occurrence of fiber flocculation. Fibers flocculation can cause difficulties in paper forming and poor uniformity of fiber distribution during the paper forming process.[26] As shown in Figure 4, the uniformity of the base paper improved remarkably with the decrease of PPTA fiber contents. Compared to the paper formation index at ratio of pulp to fiber 3:7, it raised from 63.2 to 86.9 when the ratio of pulp to fiber was 7:3. The increase of the paper formation could significantly improve the insulating properties and solve the problems of uneven breakdown point of insulating paper-based materials.

With respect to the dielectric strength of base paper, it exhibited an obvious trend of rising with the increase of PPTA-pulp contents. Also, Figure 3(b) showed a linear relationship between the dielectric strength and the contents of PPTA-pulp. This might indicate higher PPTA-pulp contents in the matrix, more easily could it extend due to its properties of ductility and flexibility during the hot-calendaring process, making the structure of base paper denser, and the insulating properties better.

Effects of PPTA-Pulp Fibrillation Degree on Properties of Honeycomb Base Paper

Compared to the heat resistance insulating paper-based materials, honeycomb sandwich paper-based materials have higher requirements on the mechanical properties, because the base paper could bear higher compressive and shear strength.[27] It is well known that the interfacial adhesion plays a crucial role on the mechanical performance of composite materials.[15,28–31] Because the material failure always occurs at the weakest interfacial bonding areas, the interfacial bonding between the PPTA fiber and PPTA-pulp has a tremendous influence on the comprehensive performance of the final honeycomb materials. Taking the advantage of the pleat structure of PPTA fiber,[32] PPTA fiber has proven to be more prone to

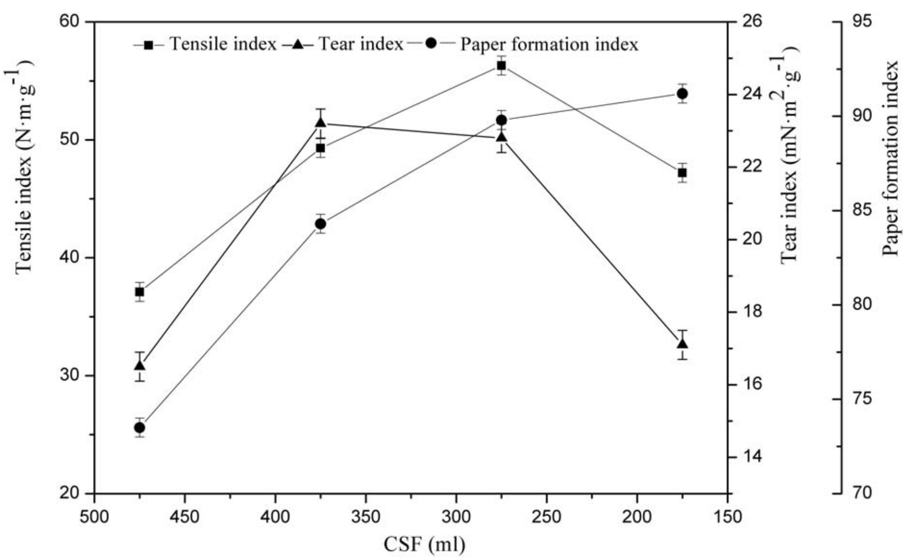

Figure 6. Effects of fibrillation degrees of PPTA-pulp on physical properties of paper sheets.

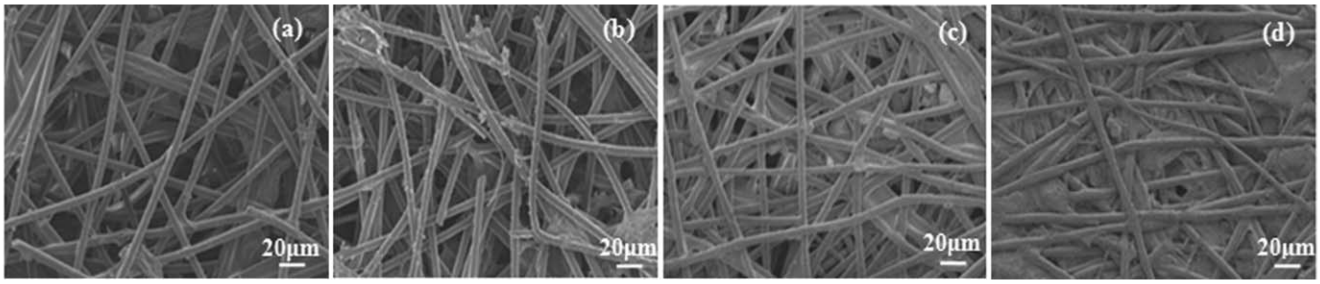

Figure 7. Effects of PPTA-pulp contents on the microstructure of polyimide fiber-based paper: (a) 0%, (b) 2%, (c) 4%, and (d) 8%.

fibrillate alone the length of the fiber by the mechanical refining.[33] The Canadian freeness standard (CSF) was utilized to characterize the degree of fibrillation. The morphologies of PPTA-pulp with different CSF and their effects on the physical strength of base paper are shown in Figures 5 and 6, respectively.

As shown in Figure 5, PPTA-pulps were more longitudinally dilacerated as the fibrillation degree increasing. This could contribute more highly dispersed slender microfibers in slurry system, which could help to enhance the SSA of PPTA-pulp (the SSA of PPTA-pulp was 5.23 $m^2\ g^{-1}$ at the CSF of 475 mL, 9.85 $m^2\ g^{-1}$ at the CSF of 275 mL, respectively), and thus strengthen the formation of particles bonding, and greatly improve the properties of the base paper accordingly (Figure 6). Compared to the base paper prepared with PPTA-pulp of 475 mL, the tensile index, tear index, and paper formation index of the base paper prepared with PPTA-pulp of 275 mL, increased by 51.8%, 38.2%, and 22.2%, respectively. The molecular chains in radial orientation of PPTA fiber are linked by hydrogen bonds. Mechanical fibrillation of PPTA-pulp leads to generating freer hydroxyl group and combination points, and produces significant improvements in bonding between fibers and pulp. The research shows that the mechanical properties of PPTA paper is of great significance to performance of honeycomb sandwich structures material.[34] Accordingly, it could improve the crushing strength and tensile modulus of honeycomb sandwich structures material when used in aerospace and automotive industry. However, more PPTA-pulp fines will generate when the PPTA-pulp further fibrillated and past a certain point, which resulted in lowering the overall retention rate of the pulp slurry system and decrease the drainage speed in paper forming process. This might be the reason why the strength showed a downward trend after the CSF was less than 275 mL.

Effects of PPTA-Pulp on Polyimide Fiber-Based Material

Compared to Kelvlar-49, which is the most representative fiber product with high modulus and strength, polyimide (PI) fiber possesses higher strength and modulus, better thermal property, and fatigue durability.[35] However, when polyimide was applied to manufacture polyimide fiber-based paper by wet-forming papermaking method, it flocculated dramatically and resulted in poor paper quality because of lacking of adhesive fibers. Moreover, it cannot fibrillate even though by dramatic refining. Certainly, highly fibrillating polyimide pulp with high SSA is unavailable for the methods of mechanical refining.[36] Therefore, PPTA-pulp, which has the similar properties with polyimide such as strength and thermostability, was utilized to play the role of bonding fiber among the polyimide fibers.

As shown in Figure 7, without PPTA-pulp, the polyimide fibers in base paper were merely mutually overlapping in a loose structure with holes. In addition, the properties of the base paper were poor enough, and hardly had a good forming performance. We can see in Figure 8, the PI fiber-based paper without PPTA-pulp worked as bonding and filling materials has very poor physical strength. However, the structure was shown

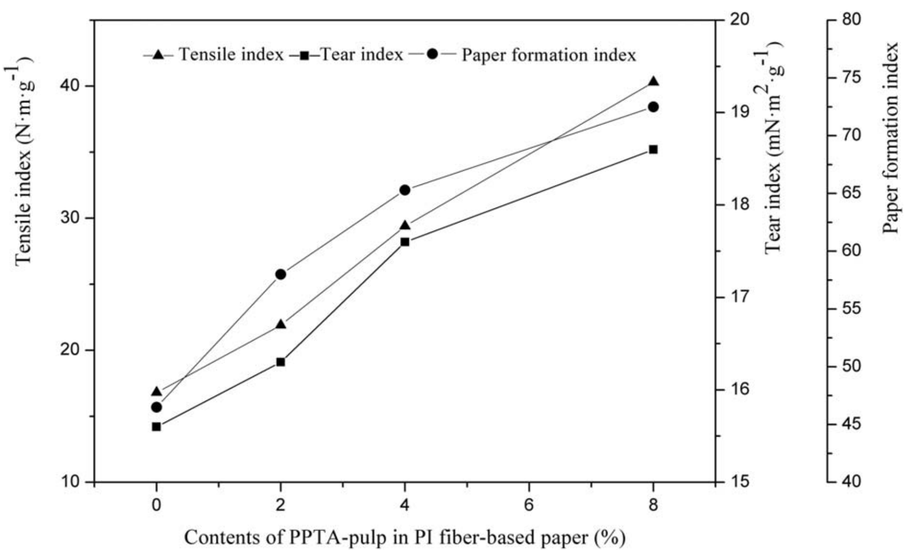

Figure 8. Effect of PPTA-pulp on physical strength of PI fiber-based paper.

to be more compact and dense with the addition of PPTA-pulp. The physical strength improved remarkably, especially the tensile strength and the paper formation index. Schmied *et al.*[37] reported that fibrils or fibril bundles in paper structure play a crucial role in fiber–fiber bonding because they act as bridging elements. This might indicate that PPTA-pulp fibrils wrapped the polyimide fibers, filled in the holes formed, and got better extending and softening in the hot calendaring process due to its properties of ductility. It finally showed a filling and reinforcement effects on the polyimide fiber-based paper, which suggesting a significant performance-reinforcing potential for the production of honeycomb sandwich composite materials with higher heat-resistance and more excellent properties.

CONCLUSIONS

In this article, the properties and microstructure of PPTA-pulp and its application on functional paper-based materials were investigated. PPTA-pulp shows ductile, rough, flexible, and highly fibrillating threadlike micro-fibrils with high SSA, which gives rise to some distinctive properties such as wet-machinability, reinforcement, and filling effects in composite materials. The ratio of PPTP-pulp to PPTA fiber reaches 70% to obtain the optimal properties of the insulating base paper. The dielectric strength of dielectric base paper shows a linear relationship to the contents of PPTA-pulp. Fibrillation of PPTA-pulp significantly contributes to generating more highly dispersed slender micro-fibrils and enhancing the SSA of PPTA-pulp, which improves the properties of base paper. By the employment of PPTA-pulp into the polyimide fiber-based paper, notable improvement in mechanical strength and structure are achieved.

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