

Article

Preparation and Performance of Different Modified Ramie Fabrics Reinforced Anionic Polyamide-6 Composites

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Abstract: Anionic polyamide-6 (APA-6) composites are prepared by the VARIM process using different modified ramie fabrics to study the structure and properties of different composites. This study can not only evaluate the optimal modification method for the ramie fabrics, but also further explore the interface interaction mechanism between ramie fabrics and APA-6. In this article, the ramie fabrics are modified by a pretreatment, coupling agent and alkali modification. Different modification methods have different effects on the structure, surface properties and mechanical properties of ramie fabrics, which will further affect the impregnation process, interfacial and mechanical properties of the composites. Through the performance analysis of different modified ramie fabrics reinforced APA-6 composites, the conversion, crystallinity and molecular weight of these composites are at a high level, which indicate that the polymerization of these composites is well controlled. The coupling agent modified ramie fabrics composites and the pretreated ramie fabrics composites have higher flexural modulus, tensile strength and dynamic mechanical properties. Alkali-modified ramie fabrics composites have slightly lower mechanical properties, which however have the highest interlaminar shear strength and outperformed interface properties of the composites.

Keywords: ramie fabric; anionic polyamide-6; modification; polymerization; properties

1. Introduction

Natural fibers exhibit many excellent properties and are low-density materials, which probably lead to lightweight composites with a high specific strength and modulus. Natural fibers also offer significant cost advantages and easy processing along with being a highly biodegradable resource, as well as reducing the pollution to the environment [1–3]. Ramie fibers as one of the high-performance natural fibers [4] were selected and used in this work for the purpose of reinforcement of the resin.

Fabric reinforced composites are increasingly used to manufacture the high-performance and lightweight structures in the aerospace and automotive industry [5–7]. However, the wetting of fiber fabrics is still challenging. Thermoplastic resins usually exhibit a high melt viscosity in the range of 100–10,000 Pa·s, which made them much more difficult to impregnate into fiber. According to the previous report, the appropriate viscosity for fabric reinforced composites should normally be lower than 1 Pa·s [8]. Meanwhile, the high melting temperature of the thermoplastic resins would also have an adverse impact on natural fiber. In order to overcome these problems, a vacuum assisted resin infusion molding (VARIM) [9] was adopted by using a reactive thermoplastic polymer, i.e., anionic polyamide-6 (APA-6) [10–13]. The anionic ring opening polymerization of caprolactam is polymerized into a high

molecular weight polyamide 6 (PA6) at 130~170 °C. The melted caprolactam monomer has a water-like viscosity, which facilitated it to impregnate into fiber. In addition, this method will provide more opportunities to form a chemical bonding between the fiber and resin [5,14]. Fabric reinforced APA-6 composites processed through VARIM have been extensively investigated by many researchers. Van Rijswijk et al. [5,6,14,15] studied the choice of activator and initiator, the influence of polymerization temperature, the influence of the vacuum infusion process, and the interfacial bond formation in detail. Pillay et al. [16,17] prepared the carbon fiber reinforced APA-6 composites. Yan et al. [18] reported the mechanical properties and microstructure of continuous glass fiber reinforced APA-6 composites.

There is a layer between the fiber reinforcement and the resin matrix, i.e., the interface layer. This layer plays a role of connecting the polymer matrix and the reinforcing fibers and determines the performance of the composites [4,5,15,19]. The strong hydrogen bonding between the natural fiber macromolecular chains makes them exhibit strong polarity and water absorption [20–22]. If it is compounded with a non-polar resin, the wettability and adhesion of the interface will be extremely poor. The fiber will peel off over time, and then the performance of the composites will be deteriorated. In order to obtain the best performance composites, it is very important to modify the surface of the reinforcing fiber. A lot of research has been carried out on the modification of natural fibers [23–29]. The physical modification methods include the steam explosion treatment, heat treatment, alkali treatment, low temperature plasma treatment, laser and high energy radiation treatment and the chemical modification methods include the surface coating, graft copolymerization and interface coupling.

At present, there appears to be no research focusing on the modification of natural fibers for using in the thermoplastic reaction processing. Therefore, in this work, four kinds of modification methods were selected to modify the natural fiber. The structure and properties of the modified natural fiber were studied. The optimum modification method of the ramie fiber suitable for VARIM process for the preparation of APA-6 composites was evaluated by studying the properties of the composites.

2. Materials and Methods

2.1. Materials

Anionic polymerization grade caprolactam with a low moisture content (<400 ppm) supplied by the BASF Chemical company was used. The sodium hydroxide ($\geq 96\%$ by mass, 'NaOH', KeLong Chemical, Chengdu, China), caprolactam magnesium bromide (1.4 mol/kg concentration in caprolactam, 'C1', Brüggemann Chemical, Heilbronn, Germany) were used as initiators. The di-functional hexamethylene-1, 6-dicarbamoyl-caprolactam (2 mol/kg concentration in caprolactam, 'C20', Brüggemann Chemical, Heilbronn, Germany) was used as an activator. In this work, 1.2 mol % initiators were used together with 1.2 mol % activators. The ramie fabrics (warp/weft yarn count: 21 s \times 21 s, warp/weft density: 52 \times 36) was supplied by Chuan-dong Ramie Fabrics Corporation, Chongqing, China and the silane coupling agent KH550 was supplied by KeLong Chemical, Chengdu, China. The sodium hydroxide, sodium dodecylbenzenesulfonate, sodium carbonate and deionized water were supplied by KeLong Chemical, Chengdu, China.

2.2. Preparation of the Composites

2.2.1. Modification of the Ramie Fabric

Pretreatment: The surface of natural fiber contains many impurities, including the dust, residual pectin, hemicellulose, lignin and sizing agent. The anionic polymerization will be affected by these impurities. Therefore, the impurities need to be removed from the commercial natural fibers prior to use in the preparation of the composites. First, the commercial ramie fabric was washed by water to remove dust, which was recorded as NF-0. Then, the NF-0 was immersed in an aqueous solution containing the sodium hydroxide, sodium dodecylbenzenesulfonate, sodium carbonate and deionized water

according to a specific ratio, and the mixture was heated to 95 °C and stirred for 4 h. The pretreated fiber was recorded as NF-1.

Coupling agent modification: First, the ethanol and water were formulated into a solvent with a volume ratio of 1:3, and then the ammonia water was added dropwise to adjust the pH of the solvent. Then, 5% KH550 was added into the solution, and the resulting mixture was ultrasonically dispersed for 20 min and preheated in an oven at 80 °C. The pretreated fiber was then immersed in the preheated solvent for 12 h. After the reaction, the fiber was taken out and washed thoroughly with ethanol, and finally placed in an oven at 80 °C to dry to a constant weight. The treated fiber was recorded as NF-KH550.

Alkali modification: First, a 10% aqueous solution of sodium hydroxide was prepared and then the pretreated fiber was placed into it. The resulting mixture was given appropriate agitation, treated at room temperature for 15 min, then regenerated with ethanol or isopropanol for 5 min. Finally, the surface lye was thoroughly cleaned by water, placed on a drying plate, and dried in an oven at 60 °C for more than 24 h. The ethanol-regenerated fiber was recorded as NF-alk-alc, and the isopropanol-regenerated fiber was recorded as NF-alk-iso.

2.2.2. Preparation of Reactive Mixtures

The caprolactam was heated to 110 °C to melt. Then, after degassing the flask (15 min at 30 mbar), the initiator was added and mixed using a static mixer. Subsequently, the activator was fed in and mixed sufficiently after degassing the flask again (15 min at 30 mbar). Since APA-6 was sensitive to moisture and easy to oxidize at this temperature, the storage and processing would be carried out under a dry nitrogen environment.

2.2.3. VARIM

A balanced and symmetrical preform consisting of ten 200 × 200 mm layers of the textile fibers was laid onto a 300 × 300 × 3 mm³ aluminum plate coated with a release agent (GS213-3, Airtech, Huntington Beach, USA). Then a layer of peel ply and a piece of resin distribution medium (Resinflow 90HT, Airtech, Huntington Beach, USA) were placed above the fibers. Two thermocouples were positioned at the surface of the top and the bottom layers of the preform to record and monitor the temperature. The inlet and outlet assembled by the springs and aluminum tubes were placed at corresponding positions. Then, the preform was bagged and sealed using a polyimide film and a heat resistant sealant tape. After degassing, the mold was rotated by 90 degrees and inserted in two infrared heating panels that were vertically placed. Then, the temperature was increased to 165 °C, and a continuous degassing (20 min at 30 mbar) were conducted to remove the moisture sufficiently. Next, the prepared reactive mixtures were infused into the preform via a heated (110 °C) silicon rubber tube. Once the resin reached the end of the preform, the inlet was clamped off. A pressure control system was used to set the infusion and curing pressure at 500 mbar precisely. After 60 min, the mold cooled down until the temperature reached below 30 °C. After that, it was de-molded directly and a composite with an average thickness of 2 mm was obtained. The diagram and specimen of ramie fabric reinforced APA-6 composites by VARIM are shown in Figure 1.

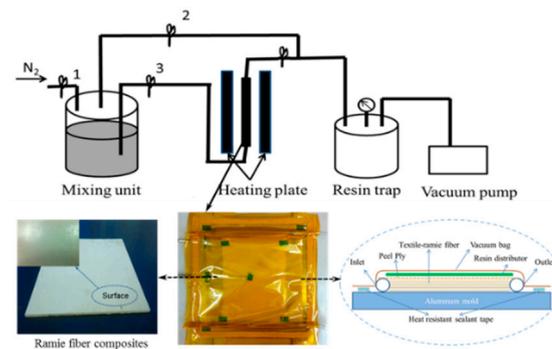


Figure 1. Diagram and specimen of ramie fabric reinforced anionic polyamide-6 (APA-6) composites by VARIM.

2.3. Characterization Methods

2.3.1. Degree of Conversion

The samples taken near the center were ground into powder, weighed (m_{tot}) and put into cellulose thimbles. A Soxhlet extraction was conducted using a heated demineralized water for 12 h at 105 °C. Then, the samples dried were in an oven at 60 °C for an additional 12 h, and weighed again (m_{pol}). The monomer caprolactam dissolves easily in water, and APA-6 is water immiscible. Additionally, the fiber weight content (m_f) of the composites was determined in a subsequent step by dissolving it into formic acid. The degree of conversion (DOC) was then calculated using Equations (1) and (2):

$$DOC = \frac{m_{pol}}{m_{tot}} \times 100\% \quad (1)$$

$$DOC' = \frac{m_{pol} - m_f}{m_{tot} - m_f} \times 100\% \quad (2)$$

where DOC is the degree of conversion for pure APA-6, and the DOC' is for the composites.

2.3.2. Degree of Crystallinity

The degree of crystallinity (X_c) of APA-6 and its composites were measured by the differential scanning calorimeter (DSC, TA Q20, New Castle, USA). The samples, approximately 5 mg, were obtained near the center of the composites and dried overnight at 50 °C in a vacuum oven. During testing, each sample was first held at 25 °C for 2 min before being heated up to 250 °C at 10 °C/min under N_2 . The X_c was then calculated using Equations (3) and (4):

$$X_c = \left(\frac{\Delta H_m}{\Delta H_{100}} \right) \left(\frac{1}{DOC} \right) \times 100\% \quad (3)$$

$$X_c' = \left(\frac{\Delta H_m}{\Delta H_{100}} \right) \left(\frac{m_{tot}}{m_{tot} - m_f} \right) \left(\frac{1}{DOC'} \right) \times 100\% \quad (4)$$

where X_c is the degree of crystallinity for pure APA-6, and X_c' is the degree of crystallinity for the composites; ΔH_m is the melting enthalpy of samples, and ΔH_{100} is the melting enthalpy of fully crystalline PA6: $\Delta H_{100} = 190$ J/g [30].

2.3.3. Viscosity-Average Molar Mass

The viscosity-average molar mass was determined by the dilute solution viscometry using the Ubbelohde viscometer with a 0.6~0.7 mm capillary diameter. Dried samples (150 mg) were dissolved in an aqueous formic acid (85%, 30 mL) to obtain a transparent solution. In particular, the composites were dissolved in formic acid to remove the fibers through filtration, and then the APA-6 resin was

precipitated in deionized water. The viscosity-average molar mass (Mv) was calculated according to Equation (5).

$$[\eta] = K' Mv^\alpha \quad (5)$$

Here, K' and α is the Mark-Houwink constants which have a specific value for each polymer-solvent combination. In this particular case, $K' = 0.023 \text{ mL/g}$, $\alpha = 0.82$ [31].

2.3.4. Density and Void Content

The densities of pure APA-6 and its composites were measured using the water immersion method as specified in ASTM D-792. The rectangular specimens ($40 \times 10 \times 2 \text{ mm}$) were measured by using a MH-120 densitometer (MatsuHaku, Taiwan, China). Prior to testing, all specimens were dried at $50 \text{ }^\circ\text{C}$ in a vacuum oven. The void content of a composite sample was measured according to the ASTM standard D2734-94, which can be calculated by Equation (6):

$$V_v = 100 - D_c \left(\frac{w_r}{d_r} + \frac{w_f}{d_f} \right) \quad (6)$$

where D_c , d_r , w_r and w_f are the measured composite density, resin density, resin weight fraction (%) and fiber weight fraction (%), respectively. The density of the ramie fiber (d_f) is $1.5 \text{ g}\cdot\text{cm}^{-3}$ [1].

2.3.5. Mechanical Properties

The mechanical properties of composites and pure APA-6 were tested using the AGS-J testing machine (Shimadzu, Kyoto, Japan). Flexural properties were obtained according to ASTM D-790. The tensile properties were obtained according to ASTM D-3039. A Dynamic Mechanical Analyze (TA Q800, New Castle, USA) was used to measure the storage modulus via three-point bending at a frequency of 1 Hz with an amplitude control of $25 \text{ }\mu\text{m}$. The glass transition temperature (T_g) was obtained at the same time.

2.3.6. Morphologies

The morphologies of the fracture surfaces were observed by the polarizing microscope (BX-51, 'PLM', Olympus, Tokyo, Japan) and scanning electron microscope (JSM-5900LV, 'SEM', JEOL, Tokyo, Japan). For the SEM observation, the samples were fractured in liquid nitrogen, polished and covered with gold prior to analysis.

2.3.7. Structural Characterizations

The surface chemical groups of the KH550 modified ramie fibers was characterized by the Nicolet 6700 Fourier transform infrared spectrometer (FTIR, Thermo Fisher, Waltham, USA). The content of the elements for the unmodified and KH550 modified ramie fibers were measured by the X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos Company, Manchester, UK).

3. Results and Discussion

3.1. The Effects on Structure and Properties of Ramie Fabrics by Different Modification Methods

Different modification methods have a great influence on the structure, surface properties and mechanical properties of natural fiber fabrics, and these properties of the fabrics will affect the impregnation process, interface properties and final properties of the composites, respectively.

3.1.1. The Effects on the Structure of Different Modified Ramie Fabrics

Different modification methods can impose a different impact on the macroscopic structure of the fiber fabric. Different fabric structures have a great effect on the resin flow in the fiber, which in

turn affect the resin impregnation process. In order to characterize the changes of the morphological structure, different modified ramie fabrics were examined by the polarizing microscope, as shown in Figure 2. The fiber bundle width and void area of the above five fibers were counted according to the polarized photograph, shown in Figure 3.

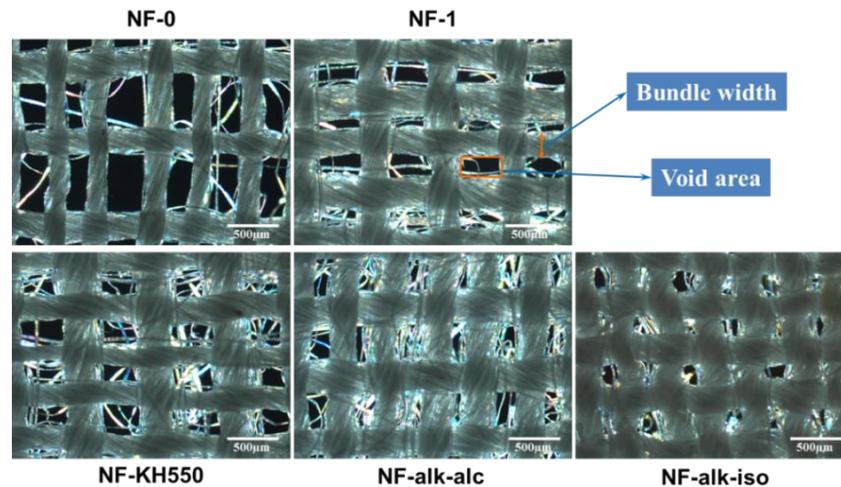


Figure 2. PLM observations of different modified ramie fabrics.

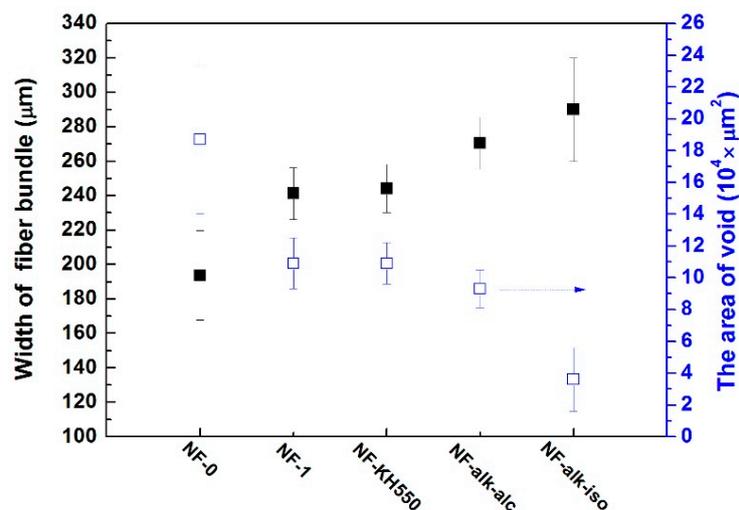


Figure 3. The variation of the fiber bundle width (black square) and the void area of different modified ramie fabrics (blue square).

NF-0 is a kind of ramie fabric without any treatment. The unmodified ramie fabric bundle is relatively dense. The uniformity of the ramie fabric is poor and the fiber is plucked. At the same time, the void area is also extremely uneven, and the deviation is large, which will adversely affect the fluidity of the resin and the uniformity of the final product. Moreover, the unmodified fiber contains pectin, hemicellulose, dust adsorbed during storage as well as sizing agents in the weaving process, which will have a negative effect on the anionic polymerization. Therefore, the ramie fibers must be modified before being used in the reaction processing.

NF-1 is a pretreated ramie fabric that has a considerable improvement on uniformity of the fiber fabric structure compared to the unmodified ramie fabric. The fiber bundle width is significantly increased, which indicates that the compactness of the single bundle fiber reduces after modification. This will facilitate the resin impregnation to the fiber. NF-KH550 is a ramie fabric modified with a silane coupling agent, and its structural changes are similar to that of the pretreated fiber.

NF-alk-alc and NF-alk-iso represent fibers that were regenerated from ethanol and isopropanol after the alkali treatment, respectively. It is well known that the surface of natural fiber contains a large amount of hydroxyl groups, which is advantageous for resin impregnation and good interfacial adhesion to the resin. However, most of the hydroxyl groups are in the form of hydrogen bonds, and the free hydroxyl groups are limited. In addition, the strength is high due to the natural fiber that has a high crystallinity and orientation. However, the toughness is poor, and a high crystallinity is also disadvantageous for the resin impregnation. Therefore, the alkali modification (also known as the activation modification) aims to destroy the hydrogen bond structure of cellulose thereby forming more free hydroxyl groups and appropriately reducing the crystallinity and orientation of the cellulose [32]. The mechanism of the alkali modification is that the high concentration of the alkali liquid penetrates into the network structure of the cellulose to induce swelling, which increases the distance between the cellulose molecular chains gradually. This leads to a weakening of the hydrogen bonding between the molecular chains, and even breaking down the hydrogen bonds. The high concentration of the alkali solution will partially penetrate into the crystalline region of the cellulose, thereby destroying the ordered structure of the cellulose crystal region and decreasing the degree of crystallinity and orientation of the fiber. However, the swollen network structure of the fiber is easily aggregated in the subsequent process of removing alkali and drying, and intramolecular hydrogen bonds will be reformed again [24,33,34]. Therefore, the way of the regeneration of the fiber and removal of the solvent is critical to maintain the decrystallizing effect of the cellulose. In this research, ethanol and isopropanol were used to regenerate the fiber, and different methods had different effects on the alkali-treated fiber. The essence of alkali modification is to change the existing aggregate structure of the ramie fiber, by which the effect of the alkali modification can be monitored by characterizing the crystal structure of modified fiber. Figure 4 shows the X-ray diffraction curves of different modified ramie fabrics. It can be concluded that the crystal structures of the pretreatment and coupling agent treated ramie fiber are type I of cellulose, indicating that the coupling agent treatment did not change the crystal type of cellulose and only a part of the amino groups were grafted onto the surface. The X-ray diffraction curves of the ramie fiber after the alkali treatment have different degrees of variations. Among them, the diffraction peak position of the 002 crystal plane of the ramie fiber regenerated by ethanol shifts to a low angle. It means that a small amount of crystal type I of cellulose is converted to crystal type II, and the fiber has two crystal structures. Moreover, the positions of the diffraction peaks of the 101 and 002 crystal plane of the ramie fiber regenerated by isopropanol significantly shift, and the crystal structures of the ramie fiber are all expressed as type II of cellulose. The changes of the crystal structure of the fiber indicate that the crystallinity and orientation of the fiber significantly decrease.

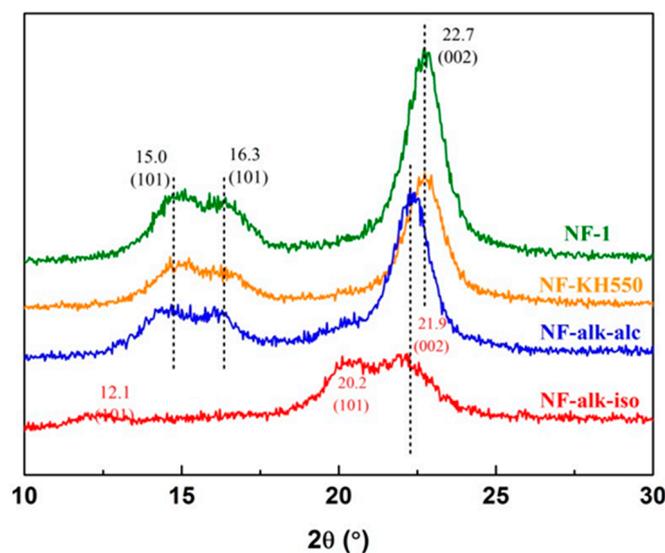


Figure 4. X-ray diffraction (XRD) curve of different modified ramie fabrics.

In summary, the alkali treatment had a great influence on the structure of the fiber, in which the fiber bundle width was further increased; the fiber void area was greatly degraded; and the surface fuzzing phenomenon was more serious. This is because the alkali has a swelling effect on the fiber. Among them, the isopropyl alcohol regenerated fiber had serious shrinkage, distortion and uniformity, which might have a negative impact on the preparation of the composites. With the ethanol regeneration, there was no serious deformation and the structure was relatively uniform.

In addition, the surface of the modified fiber has a different fuzzing phenomenon. On the one hand, it is beneficial to the interaction between the resin and the fiber surface, and the wettability and adhesion of the interface will also increase. On the other hand, the surface of the fiber becomes rough and irregular, which hinders the resin flow in the fiber, thereby affecting the wetting process. Therefore, the optimum fibers should have a good interfacial action with the resin and be beneficial to impregnate for the resin, so that the untreated fibers and isopropyl alcohol regenerated fibers after alkali treatment are not suitable.

3.1.2. The Effects on Surface Properties of Different Modified Ramie Fiber

The surface properties of the fiber have been known to affect the impregnation process of the resin, they also affect the interfacial adhesion of the resin and fiber, and further influence the properties of the composites. The scanning electronic microscopy (SEM) was used to observe the surface of a different modified ramie fiber as shown in Figure 5. The untreated fiber (NF-0) had a smooth surface, but there were obvious flow marks of the sizing agent. Most of the active groups on the surface of the fiber were covered by the sizing agent, which was not conducive to form a good interface between the fiber and the resin. The flow marks on the surface of the pretreated ramie fiber (NF-1) were found to be reduced, which revealed the characteristics of the fiber, and the surface were slightly rough. Compared with NF-1, NF-KH550 had a small amount of flow marks on the surface due to the surface being coated with a coupling agent. FTIR and XPS tests were used to confirm that KH550 was grafted onto the fiber. As the FTIR spectra shown in Figure 6, although the absorption peaks of Si-O and N-H of KH550 are in the same position with the peaks of C-O and O-H of the ramie fiber at around $1000\sim 1100\text{ cm}^{-1}$ and $3400\sim 3500\text{ cm}^{-1}$, the strength of the peaks of NF-KH550 is significantly increased during these two ranges. The C-H stretching vibration and C-H bending vibration for NF-KH550 are also more obvious at around $2850\sim 2910\text{ cm}^{-1}$ and $1365\sim 1438\text{ cm}^{-1}$. The peak at 1630 cm^{-1} is cellulose-specific and is not affected by the modifier. It can be used as a benchmark. The changes of the other peaks intensity explain the influence of modifiers to some extent. Besides, XPS was adopted to measure the changes of the elements on the surface of the fiber. It can be concluded that the intensity of N and Si peaks for NF-KH550 both increase compared to NF-1. In conclusion, it can be confirmed that the silane was grafted onto the fiber. Both the alkali modified fibers for NF-alk-alc and NF-alk-iso had rougher surfaces, which would be more conducive to resin-fiber bonding.

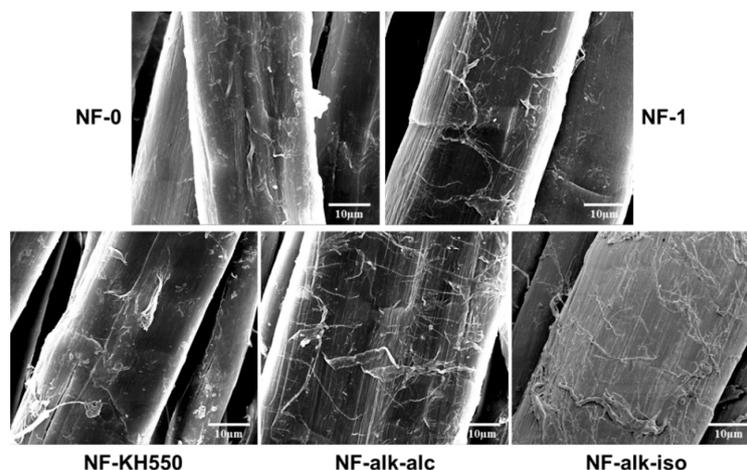


Figure 5. SEM imaging of different modified ramie fabrics.

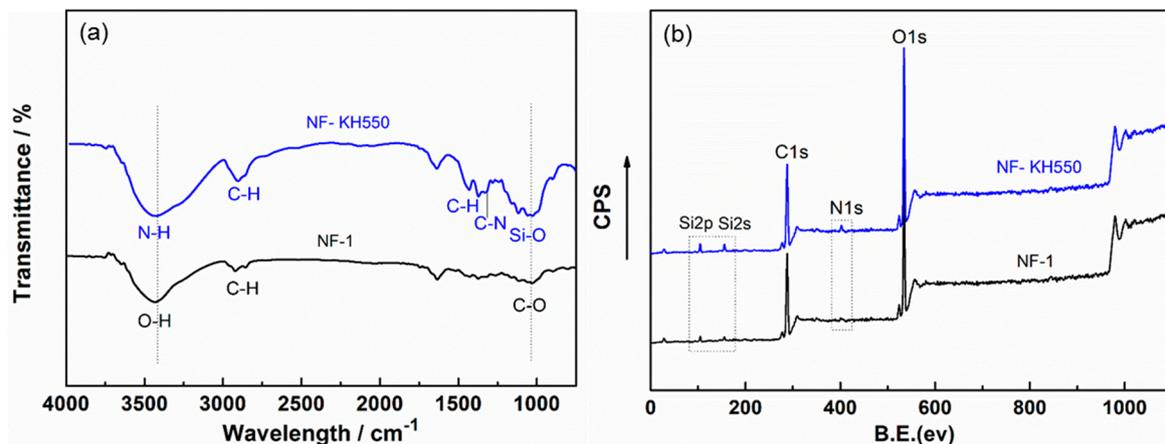


Figure 6. FTIR (a) and XPS (b) spectra of different modified ramie fabrics.

3.1.3. The Effects on the Mechanical Properties of Different Modified Ramie Fabrics

The above studies have showed that the different modification methods have different effects on the morphological structure, surface properties and aggregation structure of ramie fabrics, which will inevitably affect the mechanical properties of fabrics and eventually affect the properties of composites. Figure 7 showed the strength values of different modified ramie fabrics, as well as the fabrics strength and elongation curves during stretching. The strength of the pretreated fabrics and silane coupling agent modified fabrics were both higher than that of the untreated sample, because the relative content of cellulose in the modified ramie fabrics was slightly increased after pretreatment. The strength of the two fabrics after the alkali treatments decreased significantly, but also accompanied by a significant increase in elongation at break. This is because the crystallinity and orientation of the fiber after the alkali modification decrease. Therefore, the alkali treated fabrics have an adverse effect on the strength of the composites and are advantageous for the toughness and interfacial adhesion of the composites. In conclusion, the different modified ramie fabrics can be used to prepare composites with different properties to meet the different environmental requirements.

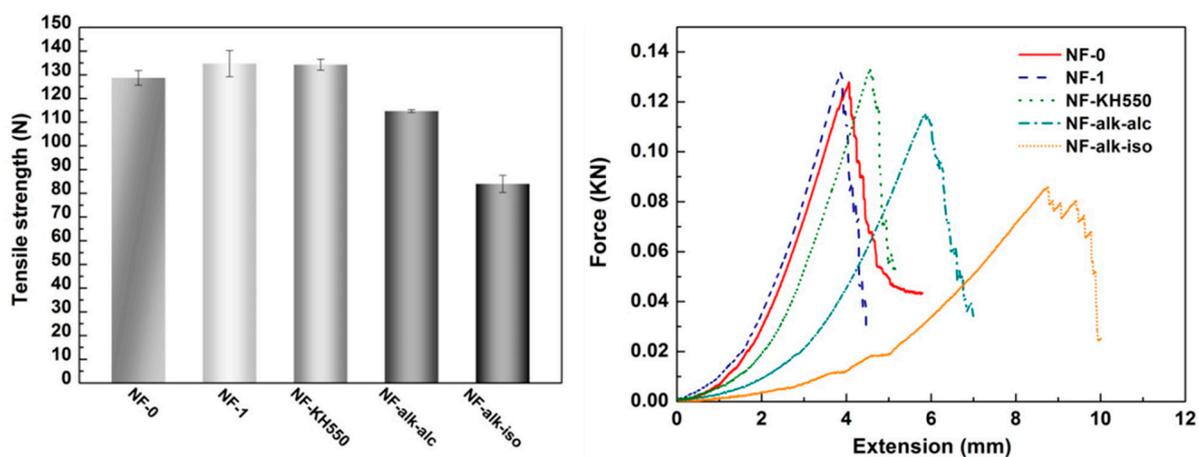


Figure 7. The mechanical properties of different modified ramie fabrics.

3.2. The Properties of APA-6 Composites Reinforced by Different Modified Ramie Fabrics

3.2.1. Physical Properties

The five modified ramie fabrics mentioned above were used as the reinforcing materials and these composites were prepared by the VARIM process accordingly. It was found that not all modified

ramie fabrics were suitable as reinforcing materials in this study. First, the untreated ramie fabrics impeded the anionic polymerization, because the surface of the untreated fiber contained some sizing agents, hemicellulose, lignin, pectin and other impurities, which hindered the occurrence of anionic polymerization. Second, the fabrics regenerated by isopropanol after the alkali modification could not be prepared to obtain composites with uniform wetting and perfect polymerization. The reason was that the alkali treatment seriously changed the morphological structure of the fabric, and the uniformity was deteriorated. The fiber bundle was even severely distorted thereby hindering the impregnation process of the resin.

The composites prepared by NF-1, NF-KH550 and NF-alk-alc all showed a well uniformity. In order to further characterize the polymerization properties of these composites, the conversion, crystallinity and viscosity-average molecular weight were analyzed as shown in Figures 8 and 9. First, the degree of conversion of these three composites showed a different degree of decline compared to the pure APA-6. It meant that the addition of natural fibers had a certain effect on anionic polymerization. Moreover, the effect of the alkali-modified fiber on the anionic polymerization conversion was more obvious. Since the alkali-modified fiber carried more reactive groups, the consumption of the initiator in the polymerization system was increased. On the other hand, the reaction probability of the surface of the fiber with the activator was increased. Therefore, the active center of the polymerization system was also consumed to some extent. The degrees of crystallinity of these three composites were significantly higher than that of the pure APA-6, which is due to the fact that the natural fiber easily induced polymer crystallization. The viscosity-average molecular weights of composites were not much different from that of the pure APA-6, and were much higher than that of nylon 6. However, there were slight differences among these different composites, which related to the reaction between the hydroxyl groups on the surface of the fiber and the activator in the polymerization system. Besides, the degree of conversion and viscosity-average molecular weight of the untreated ramie fabrics reinforced APA-6 composites were also measured, only 18% and 3600 respectively, which demonstrated the inhibition to the anionic polymerization by the unmodified fibers (NF-0). In this system, only a small amount of oligomer was produced, and the polymerization was not reached.

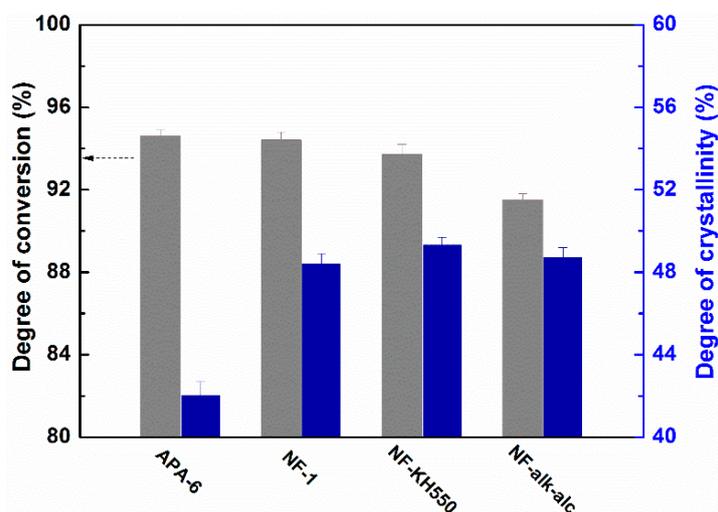


Figure 8. The degree of conversion (gray columnar) and crystallinity of different modified ramie fabrics reinforced APA-6 composites (blue columnar).

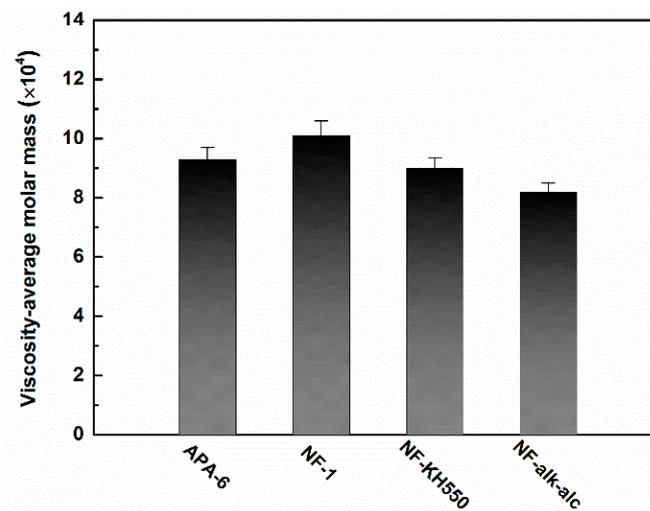


Figure 9. Viscosity-average molecular weight of different modified ramie fabrics reinforced APA-6 composites.

Figure 10 showed the fiber content and void content of these three composites. These composites were prepared by the same process, so that the fiber content was the same. The void content of these composites was lower, and the NF-alk-alc composites were the best. The difference in void content indicated that the resin had different wetting effects on different modified fibers, and the alkali-modified ramie fabric had better wettability.

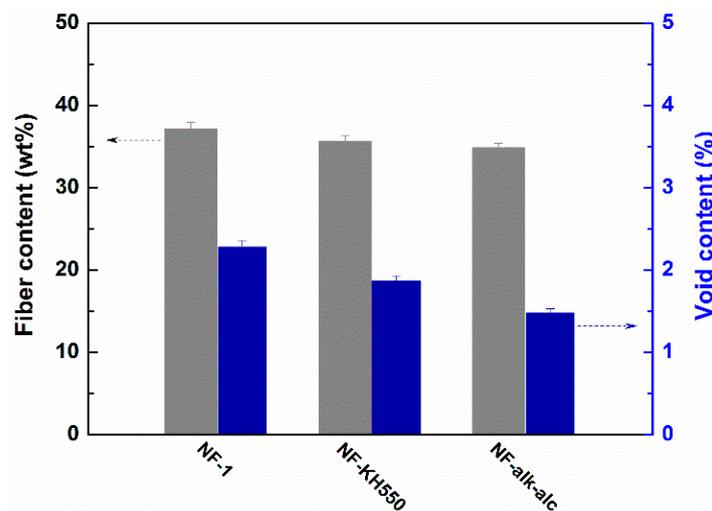


Figure 10. The fiber content and the void content of different modified ramie fabrics reinforced APA-6 composites.

3.2.2. Mechanical Properties

Figure 11 showed the flexural modulus, tensile strength and elongation at the break of APA-6 and different composites. The flexural modulus of NF-1 and NF-KH550 composites were better than that of the other samples. The tensile strength and elongation at the break of the NF-KH550 composites were larger than that of NF-1 composites, which indicated that the coupling agent modified ramie fiber fabric increased the strength and plastically deform under tension of the composites. The reason may be that the interfacial interaction between the fiber and the matrix becomes better after coating a layer of coupling agent. However, the NF-alk-alc had a great decrease in the mechanical properties, so that the flexural modulus and tensile strength of the composites were much lower than that of other two

composites. In addition, the elongation at the break of NF-alk-alc composites was found significantly increased, which indicated that the plastically deform under tension of the NF-alk-alc composites was improved. Their trends are closely related to the changes in the mechanical properties of different modified ramie fabrics. The reasons have been stated in 3.1.3 in this paper.

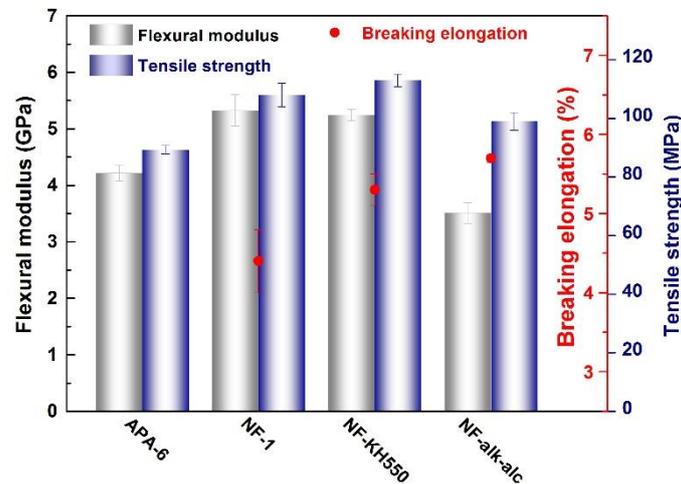


Figure 11. The mechanical properties of different modified ramie fabrics reinforced APA-6 composites.

The storage modulus is an important parameter to characterize the resistance to thermal mechanical deformation of the materials. The larger the modulus, the less deformed. Figure 12 showed the results of dynamic mechanical properties of different materials. The NF-1 and NF-KH550 composites had the same variations under the low temperature, but the storage modulus of the NF-1 composites was larger than that of the NF-KH550 composites under the high temperature. Under the high temperature, the chain segments began to move, and the NF-1 composites had a slightly larger molecular weight. NF-alk-alc composites had a lower modulus over the entire temperature range than the other two composites. The reason was that the degree of crystallization and orientation of the fiber decreased during the alkali treatment. In the loss factor curve, the peak at 75 °C represents the α transition of nylon 6, which meant that the values of glass transition the temperature of the composites. It relates to the molecular weight and crystallinity of the materials. The peak at around -60 °C indicates the β relaxation of nylon. This transition peak is related to the moisture and motion units of small-sized chain unit.

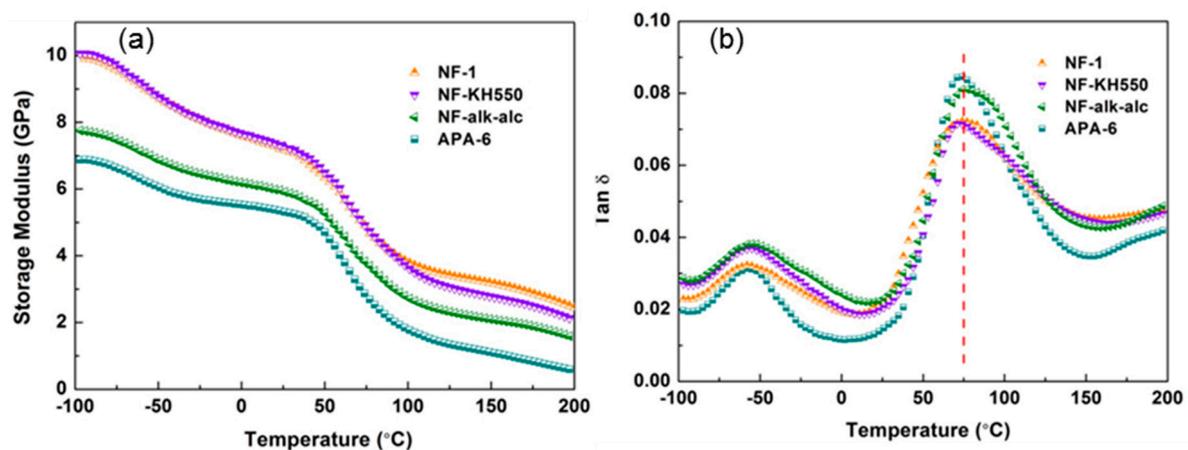


Figure 12. The dynamic modulus (a) and Tan δ (b) for different modified ramie fabrics reinforced APA-6 composites.

The interfacial properties for the ramie fiber reinforced APA-6 composites is better than the glass fiber reinforced APA-6 composites measured by SEM [35]. In this study, the fractured surfaces of the three composites were also characterized by SEM. All composites showed good fiber-to-matrix bonding expectedly, but there was no obvious difference. So the SEM images were not given in this article, instead of the interlaminar shear strength test. The interlaminar shear strength refers to the maximum load that the composites can bear per unit area parallel to the bonding surface. It mainly reflects the bonding properties of the composites under the applied load, which is very important for the safety and stability of the materials during applications. The interlaminar shear strength (ILSS) of these three composites prepared by the pretreated fiber, the coupling agent modified fiber and the alkali-modified fiber was found sequentially increased as shown in Figure 13. The NF-alk-alc composites had the worst mechanical properties but had the highest interlaminar shear strength. It indicated that the hydrogen bond on the surface of the cellulose was opened after the alkali treatment, and the content of free hydroxyl groups increased. Thus, it was very helpful to improve the interface interaction between the fiber and the matrix. The interlaminar shear strength of NF-KH550 composites was higher than that of NF-1 composites, which indicated that the interfacial interaction between the fiber and the matrix became better after coating a layer of coupling agent.

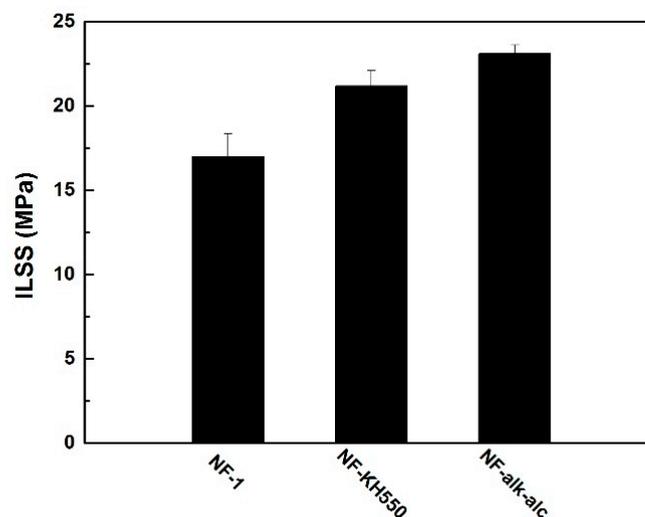


Figure 13. Interlaminar shear strength of different modified ramie fabrics reinforced APA-6 composites.

4. Conclusions

First, it was included that different modification methods had different effects on the structure of ramie fabrics. The uniformity of the structure was improved for the pretreatment and the coupling agent modified fabrics. The structure of the alkali-modified fabrics was greatly changed and the fabrics regenerated by ethanol tended to be uniform. The uniformity of the fabrics regenerated by isopropanol was found seriously degraded. Then, different modification methods also had different effects on the surface roughness of ramie fabrics. The strengths of the ramie fabrics modified by the pretreatment and silane coupling agent were improved compared with that of the untreated fabrics. The strength of the fabrics after the alkali treatments were severely reduced, but the elongation at break was greatly increased. The performance analysis of different modified ramie fabrics reinforced APA-6 composites was carried out, and the conversion, crystallinity and molecular weight of these three composites were found to be at a high level, which indicated that the polymerization of these three composites was well controlled. The coupling agent modified ramie fabrics composites and the pretreated ramie fabrics composites both had higher flexural modulus, tensile strength and dynamic mechanical properties than that of the alkali-modified ramie fiber composites. Alkali-modified composites had slightly lower

mechanical properties, which however had the highest interlaminar shear strength and outperformed interface properties of the composites.

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