

Mechanism analysis of mechanochemical action in preparation of polymer composites¹

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Abstract. Mechanochemistry is one of the most important methods for preparing polymer composite materials, and there are not many studies on the mechanism of its preparation. Therefore, the mechanism of mechanochemical action in the preparation of polymer composite materials was analyzed in this paper. After discussing the development of mechanochemistry, the green cellulose polymer, nano cellulose, was studied as an example. The results show that in the process of preparation, mechanochemistry changes the morphology of cellulose, and also makes the molecular chain of cellulose recombine, which leads to the change of crystal structure.

Key words. Mechanochemistry, polymers, materials, preparation, cellulose.

1. Introduction

Since people began using cremation rubber as a representative of the modified natural polymer materials in nineteenth century, polymer materials have developed toward the direction of composite materials with the gradual progress of science and technology, and have played an increasingly important role in the production and life of human society [1]. The polymer composite materials are found everywhere in various kinds of plastic products which are very common in people's life and in the aerospace industry. It is precisely because of this polymer composites have had an important impact on the change in the world outlook since twentieth century. Therefore, Time Magazine has named polymer composite as the most important

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invention in human society [2]. In addition, polymer composite materials also have important influence on the cultural field and life style of human society. Therefore, the preparation of polymer materials has become the most important production activities in the society [3].

In general, the preparation of polymer composites involves many aspects, such as formula design, processing technology and processing equipment. Formulation design refers to the combination design of the properties and structure of various raw materials, which is the most important process for the preparation of polymer composite materials [4]. After the formulation design is completed, it is necessary to make use of various processing techniques and processing equipment to complete the manufacture of polymer materials. At present, due to the rapid development of science and technology, the preparation methods of polymer composites are also various [5]. Among them, mechanochemistry is one of the methods of preparing polymer composites in recent years. However, there are few studies on the application of mechanochemical methods in polymer materials. Therefore, in this paper, the mechanism of mechanochemical action in the preparation of polymer composite materials was proposed.

2. State of the art

Mechanochemistry is a technique that uses mechanical energy to stimulate chemical reactions to alter the structure and properties of materials. This technique is mainly used to prepare new materials or to modify materials. These materials are often unable to be treated or prepared by conventional chemical methods [6]. The mechanochemical method first appeared in the early part of the last century and was first proposed by German scholar W. Ostwald. He defined the mechanochemical method first and explained the two by theoretical analysis, but the basic principle was not clearly explained [7]. After nearly thirty years of silence, the golden age of development was ushered in. As time went on, mechanochemistry began to develop from the original high value-added materials to the fields of chemistry, metallurgy and alloy. Nowadays, mechanochemistry has been widely used in many fields, such as nanocomposites, minerals and waste treatment, synthesis of new materials and metal refining [8].

Mechanochemistry has been applied in more and more material fields, which has prompted scholars from all over the world to study the theory and application of mechanochemistry [9]. Takahashi used the mechanochemical process to grind the clay so that the part of the clay was dehydrated and its structure changes. China's research in this field has focused on the application of biomaterials, and has made great progress. Scholar Shi Junli once used the mechanical force to carry on the success research to the rice starch structure. In addition, some scholars have applied it in the Chinese herbal medicine treatment of traditional Chinese medicine, and it can improve the curative effect of Chinese medicine by superfine mechanical treatment of Chinese herbal medicine. It is believed that with the deepening of national research, the application of mechanochemistry will be more extensive [10].

3. Methodology

Nowadays, with the development of science and technology, there are many kinds of polymer composite materials. Therefore, in this paper, when analyzing the mechanism of mechanochemical action in the preparation of polymer composite materials, Nano-cellulose was chosen as the object of this study, which was the most important raw material of polymer composite. Cellulose is a kind of natural biomass polysaccharide formed by glycosidic linkage of glucose units, which belongs to natural polymer materials [11]. Because of its wide range of sources, renewable nature, biodegradable nature and good biocompatibility, it has become a kind of green and environment-friendly biomass energy. Today, with the worsening of the ecological environment, the characteristics of its green environment protection will be widely used in more and more fields. Fig. 1 shows a kind of common cellulose [12]. However, cellulose as a natural polymer material, its strength and chemical resistance are relatively poor, and it is difficult to be dissolved in general solvents. These disadvantages have severely limited the development and utilization of natural cellulose [13]. Therefore, people can obtain Nano-cellulose by means of retaining the amorphous region of cellulose and decomposing the crystalline region by specific means. While retaining the advantages of cellulose degradation and broad source, Nano-cellulose has been greatly optimized for its physical and chemical properties, which makes it one of the most widely used materials in composite materials [14]. Because of its environmental protection and wide application, it is the important reason that Nano-cellulose is chosen as the object of this study.

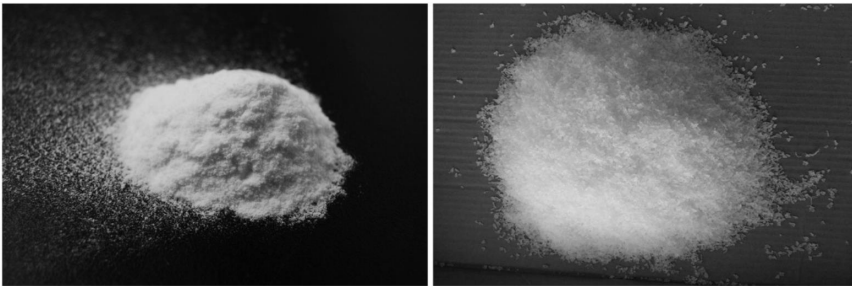


Fig. 1. Currently more common cellulose

In the analysis and study of Nano cellulose, Nano cellulose was firstly prepared by mechanochemical method. Then, the mechanism of the preparation of cellulose by mechanochemical method was analyzed. First of all, the experimental materials and methods involved in the experiment were described in detail. The raw material of this experiment is rayon grade pulp, phosphotungstic acid, and anther. α -cellulose content of rayon grade pulp exceeded 94 %, which was the main raw material in this experiment and purchased from Nanzhi Limited by Share Ltd. in F province. Phosphotungstic acid and ether were purchased from the National Pharmaceutical Group Chemical Reagents Co., Ltd. Phosphotungstic acid is a kind of solid heteropoly acid with mild conditions. It has high catalytic activity, low toxicity, easy recovery, good

thermal stability and so on. It belongs to the green environmental protection catalyst [15]. It is widely used as catalyst in condensation, esterification and oxidation reactions, and this is also an important factor in the use of phosphotungstic acid in this experiment. The related instruments and equipment involved in the test are shown in Table 1.

Table 1. The related instrument and equipment used in the test

Instrument	Model	Manufacturer
Standard fiber breaker	GBT-A	Changchun on small test machine limited liability company
Variable frequency planetary ball mill	BXQM-0.4L	Nanjing special wheel new instrument Co., Ltd.
Heat collection type constant temperature heating magnetic stirrer	DF-101S	Gongyi Hua Hua Instrument Co., Ltd.
Numerical control ultrasonic cleaner	KQ-250DB	Kunshan Ultrasonic Instrument Co., Ltd.
Electrothermal constant temperature blower drying box	DHG-9246A	Shanghai precision experiment equipment Co Ltd.
TGA	STA449C	NETZSCH
Vacuum freeze drying apparatus	TB-1B-50	Beijing boyikang experimental instrument factory
Fu Liye transform infrared spectrometer	NICole80	Thermo electron, USA
High speed freezing centrifuge	GL-20G-I	Shanghai Anting Scientific Instrument Factory
Transmission electron microscope	JEM-1010	JEOL
X-ray diffractometer	MiniFlex	Japan Science Corporation
Fiber analyzer	Morfi Compact	French Techpap

Before the test, the mill was used to break the raw material, rayon grade pulp, so as to obtain cellulose pulp and dry it at the temperature of 60 °C. 2 g cellulose slurry and 40 ml phosphotungstic acid were dissolved in two ball milling tanks of 90 ml in volume. Each pot used 20 agate balls with a radius of 3 mm for ball milling in 0.5 h to 2.5 h. The 600 r/min of agate ball speed was appropriate. After completing the above procedure, the sample was transferred to a round bottomed flask with a volume of 200 ml for a certain period of time with a temperature of 90 °C. After cooling, the sample was centrifuged several times until the reactants were neutral. The obtained acid solution was treated with ethyl ether to obtain phosphotungstic acid and recovered. The reactant suspension was subjected to ultrasonic treatment for 1 h, and the ultrasonic treated suspension was centrifuged using a centrifuge.

After treatment, the upper layer of white latex suspension was collected to obtain Nano-cellulose. Cellulose powder was obtained by drying with a vacuum freeze drying apparatus.

0.03 g rayon grade pulp was extracted and diluted to 1000 ml. The morphology of the fiber was observed with an instrument, and the length and width of the fiber were analyzed. The projection electron microscope was used to observe the morphology and size of Nano-cellulose to disperse the situation. Subsequently, cellulose suspensions with a content of 0.01 % were disposed and adsorbed by copper nets. After the use of phosphotungstic acid solution for dyeing 1 min or so, it was naturally dried. The 100 kV accelerated voltage was used in this paper. The rayon grade pulp was blended with Nano-cellulose to form powder and then mixed with KBR at a ratio of 1:100 to be fully ground and pressed. Fourier transform infrared spectroscopy was used to analyze the chemical structure of cellulose. The crystallinity analysis of cellulose was carried out by X-ray diffractometer. The cellulose sample was to be powdered in the experiment. Using Ni filter and Cu K α ray, the range of scan and step scan was 6–900. The cellulose crystallization strength was calculated using the crystalline index CrI, and the cellulose type I was calculated as follows

$$C_{rI} = \frac{I_{002} - I_{Iamorph}}{I_{002}} \times 100\%, \quad (1)$$

where, I_{002} represents the maximum diffraction intensity of the main crystallization peak 002 with a value of 22.60 and $I_{Iamorph}$ indicates the diffraction intensity of the scanning range of 180.

The formula for cellulose type II is as follows:

$$C_{rII} = \frac{I_{101} - I_{Iamorph}}{I_{101}} \times 100\%, \quad (2)$$

where, I_{101} in the formula represents the maximum diffraction intensity of the 101 peak with a scanning range of 20.8 °C, and $I_{Iamorph}$ indicates the diffraction intensity of the trough at the scanning range of 160.

The thermogravimetric analysis of nanofibers was carried out by thermogravimetric analyzer. The experimental condition was that the temperature under argon protection rose to 550 °C at a rate of 5 °C/min, and the gas flow rate was 30 ml/min.

4. Result analysis and discussion

Firstly, morphological analysis of nanofibers was carried out. Fig. 2 shows the fiber morphology of the rayon grade pulp. As can be seen from the diagram, the fiber state of the raw material was elongated, and some short fibers were mixed. Fiber length and width were measured by fiber morphology. The final results showed that the length of the fiber was between 0.68–5.31 mm and the width of the fiber was between 15–60 nm.

After observing the fiber morphology of the rayon grade pulp, the morphology of cellulose jelly and nanofiber was observed by transmission electron microscopy. First



Fig. 2. Fiber morphology of the rayon grade pulp

of all, the aqueous solution of nanofiber paste was mainly white in appearance. A transmission electron microscope was used to observe cellulose jelly, and it could be seen that the length of the fiber was between 200–300 nm and the width was between 20–40 nm. In terms of length and width, nanofibers underwent a mechanochemical process, and their fiber length and width underwent significant physical changes. The fibers presented a microfibril state, and the structure was a network of intertwining structures. Under transmission electron microscopy, the length and width of nanofibers were shorter than those of the gel. The length was about 100–300 nm, and the width was between 10–40 nm. The nanofibers were in the shape of bars, and they were also intertwined with each other into a network. The results show that the fibers of the nanofibers become finer and shorter under ultrasonic action, but their structure is not destroyed, as shown in Fig. 3.

Fig. 4 shows the infrared spectra of the rayon grade pulp, jelly, and Nano-cellulose in Fourier infrared spectrometer. It can be seen from the infrared spectrum that the characteristic peaks of the rayon grade pulp, jelly and Nano-cellulose were basically the same, and three of them had the basic structure of cellulose. This spectrum showed that acid hydrolysis did not change the basic structure of cellulose during the preparation of Nano-cellulose. There was a broad and strong hydroxyl absorption peak at the 3445/cm position in the three, and the absorption peak belonged to the stretching vibration of -OH. The characteristic peak around 2900/cm was the C-H symmetric stretching vibration of -CH₂-. The peak around 1640/cm was formed by water absorption of the cellulose samples, and the emergence of this characteristic peak showed that the water absorption capacity of cellulose samples was very strong. The absorption peaks around 1382/cm belonged to the C-H symmetric stretching vibration. The C-O stretching vibration around 1060/cm and the rocking vibration around 897/cm belonged to cellulose alcohol. The only big difference between the

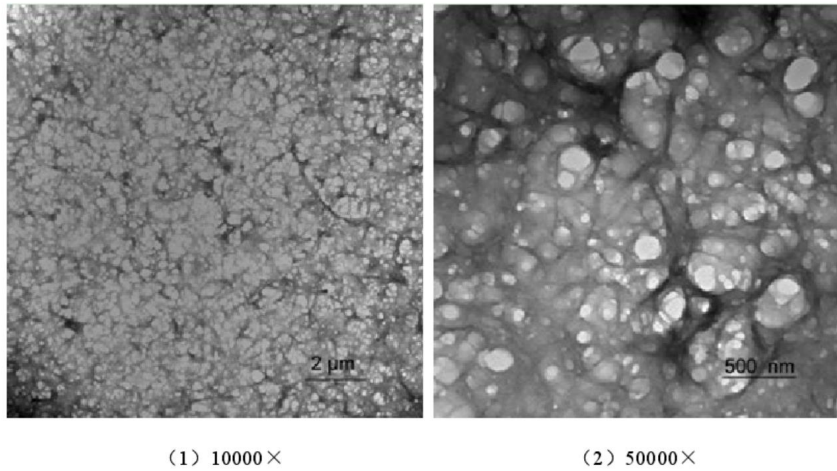


Fig. 3. Nanofiber under transmission electron microscope

three infrared spectra was the peak around 1429/cm. There was a small absorption peak in the human plasma, which was due to the $-\text{CH}_2-$ symmetric bending vibration. The peak intensity of the other two in this position was obviously weakened, which was accompanied by a slight blue shift. The reason for this may be that the mechanochemical action leads to fracture and reconstruction of hydrogen bonds around C_6H_6 in cellulose molecules. The appearance of this phenomenon indicates the emergence of cellulose II crystalline variants.

Fig. 5 shows a diffraction diagram of raw material, the rayon grade pulp, and the finished product of Nano cellulose under X-ray diffractometer. First of all, from the diffraction curve of the rayon grade pulp, the diffraction peaks were located around 14.50, 160 and 22.50 of the scanning range. This result indicated that the fibrous crystal belonged to the fiber type I. The analysis of the diffraction peaks of Nano cellulose showed that the position of the nanofibers was within 12.10, 19.50 and 220 of the scanning range. This result showed that the crystal of cellulose belonged to the fiber type II. From the diffraction of X-ray diffractometer, it indicated that in the process of mechanochemical preparation of nanometer cellulose, phosphotungstic acid was used as reagent to promote the dissolution of natural cellulose, and then to regenerate. Mechanochemical changes led to changes in the crystal type of cellulose. The crystallinity of the rayon grade pulp and Nano cellulose was calculated by crystallization index CrI. The final calculation results showed that the crystallinity of the rayon grade pulp was 66.44 %, and the crystallinity of Nano cellulose was 59.62 %. The results showed that the crystallinity of Nano cellulose was less than that of human cellulose. In the preparation of Nano cellulose by mechanochemistry, the crystallinity of cellulose decreased. The reason was probably that during the mechanochemical process, the small molecular chains of cellulose underwent the reorganization when the rayon grade pulp was dissolved and reconstituted.

Fig. 6 shows a thermogravimetric diagram of the nanofibers prepared from raw material, rayon grade pulp, and mechanical power. Firstly, the raw material and

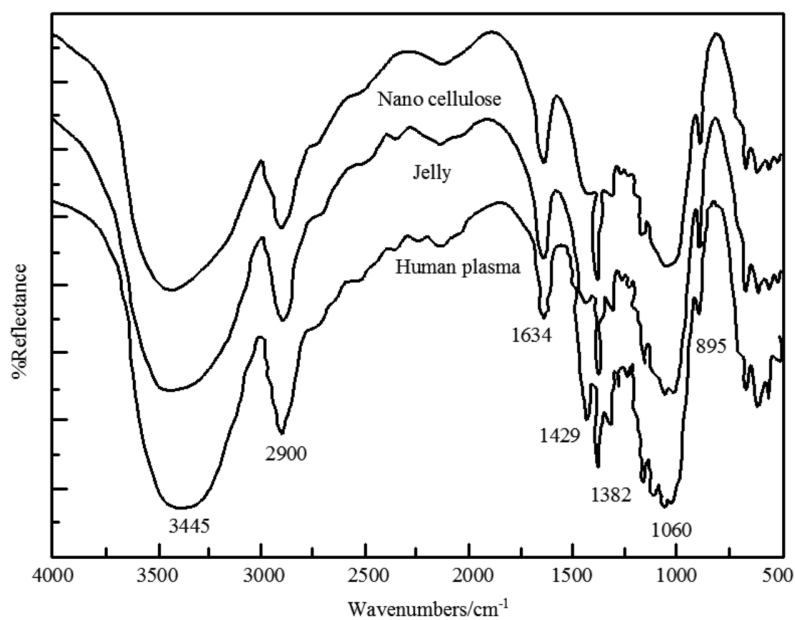


Fig. 4. Infrared spectra of different cellulose samples

pulp were analyzed.

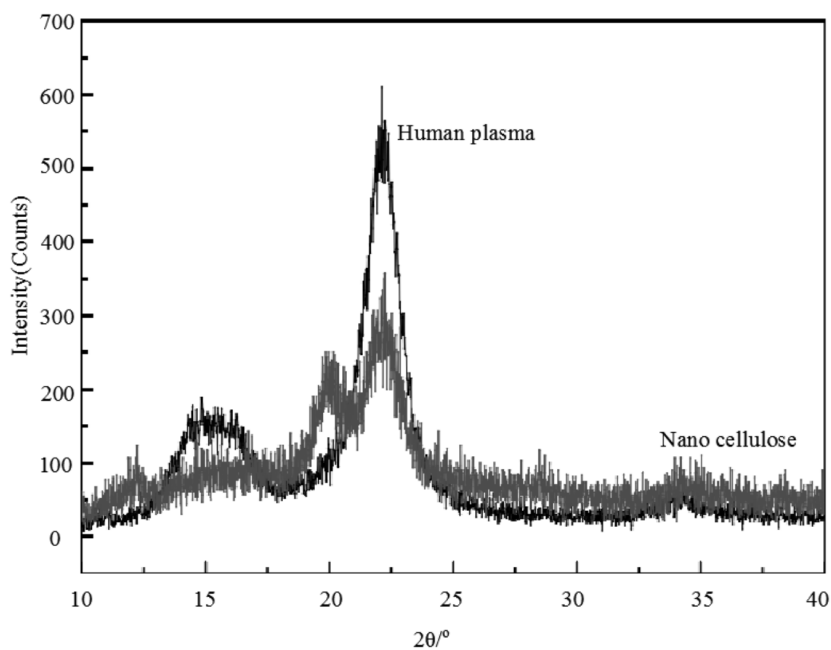


Fig. 5. X-ray diffraction patterns of human plasma and Nano-cellulose

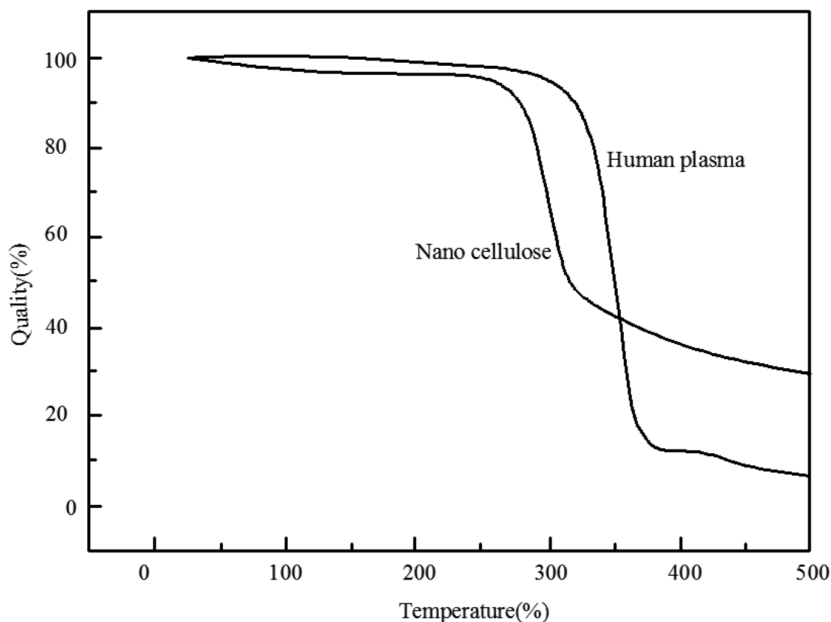


Fig. 6. Thermogravimetric diagram

It could be seen from Fig. 6 that there was no weightlessness in the rayon grade pulp at about 150°C, which showed that the water in the pulp contained less water. Starting from 200°C, the thermogravimetric curve of the sample began to decline rapidly until slowly at 375°C. At the temperature of 200–375°C, the total mass loss of the sample was about 85%. From 375 to 500°C, the rate of thermal degradation decreased very slowly, and the total mass loss was about 90%. Thermogravimetric analysis of Nano cellulose showed that the thermogravimetric curve of Nano-cellulose decreased slowly at 35–150°C. The main reason was that there was a slow evaporation of water at this stage, and the total mass loss was about 3%. The thermal gravimetric curve of the cellulose decreased rapidly at 200°C and slowed down at 325°C. The total mass loss was 49% mainly because of the decomposition of Nano-cellulose. When the temperature reaches 500°C, the total mass loss was about 70%. By comparing the thermogravimetric curves of two samples, it could be seen that the thermal decomposition temperature of Nano-cellulose was lower than that of the rayon grade pulp. The results showed that the stability of Nano-cellulose was less than that of human plasma. The main reason was that the size of the Nano-cellulose became much smaller than the size of the raw material through mechanochemical action. In addition, the surface area increased considerably, and the exposed active group changed more.

5. Conclusion

Nowadays, with the rapid development of science and technology, all kinds of industrial products made of polymer composite materials have become one of the most important factors in the production and life of human society. In this context, the mechanism of mechanochemical action in the preparation of polymer composite materials was proposed in this paper. Nano-cellulose, a green and environmentally friendly polymer material, was chosen as the object of this study. Firstly, Nano-cellulose was prepared and analyzed by mechanochemical method. It can be seen from the analysis that the fiber morphology of the human fiber changed under the action of mechanochemistry. The main reason is that the length and width of the fiber become smaller, but the whole structure is not destroyed. However, the crystal structure of cellulose was changed, and the crystallinity of cellulose was reduced. The reason is that the small molecular chains of the cellulose undergo recombination when the rayon grade pulp is dissolved and reconstituted by mechanochemical action.

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