PROCESS OPTIMIZATION OF GREEN AQUEOUS-BASED EXTRACTION TECHNOLOGY OF *TARAXACUM KOK-SAGHYZ* RUBBER

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ABSTRACT

Taraxacum kok-saghyz (TKS), known as Russian dandelion, can produce high-quality natural rubber. The dry weight content of rubber in the TKS roots was found to be approximately 6–9%, of which 61% and 39% were stored in the root bark and root flesh, respectively. The content of lignin and holocellulose accounted for about 40% of the total root. Two new aqueous-based rubber extraction processes were proposed and optimized, namely, the strong water shearing process and the acid–base extraction process. These two processes made the purity of rubber reach about 91% and 94%, respectively. TKS rubber was characterized as having similar composition, and molecular structure to *Hevea* NR, and TKS rubber samples did not exhibit the strain-induced crystallization (SIC) phenomenon. TKS rubber was blended into a winter tire tread formulation and tested. The results showed no significant differences in processing and mechanical properties from the other formulations. [doi:10.5254/rct.22.77883]

INTRODUCTION

As a renewable green resource, natural rubber (NR) has many excellent properties.[1] Therefore, NR is widely used in various fields and industries, such as aerospace, automotive industry, rail transit, and health care.[2,3] NR is mainly derived from *Hevea brasiliensis*, which can only grow in the tropics. As the world's demand for NR rises year by year, it is estimated that 4.3–8.5 million ha of rubber plantations will need to be added by 2024.[4] The narrow equatorial region can no longer afford excess production, and the ensuing environmental, economic, and labor issues will also bring instability to the natural rubber market. In the long run, the losses caused by sacrificing biodiversity and destroying the environment are far greater than the economic benefits brought by rubber forests.[5]

Taraxacum kok-saghyz (TKS) is a perennial herb plant that can grow in a variety of environments,[6] and its roots can produce 5%–24% natural rubber.[7,8] Studies have shown that this TKS rubber is very similar to *Hevea* NR in terms of molecular structure and performance. In particular, TKS rubber has also been developed with strain-induced crystallization (SIC) properties,[9–12] which makes it excellent in many applications, such as latex gloves and winter tires. This makes TKS rubber a beneficial supplement to NR that can effectively relieve the above problems caused by NR. In short, TKS has the potential to enter the global market like *Hevea brasiliensis*.

In fresh TKS, rubber is stored at the root in the form of latex.[13] Because of its simplicity and high purity, the TKS latex extraction process was first proposed. It is equally important to prevent latex coagulation and keep the roots fresh during the extraction process, but due to difficulties in storage conditions and transportation, the development of this process was relatively slow. Until

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now, two mature methods have been proposed.[7,14] The processing is different for the two methods. (1) Blender method: the slurry mixed with TKS latex is extruded from the root by an external force. After processing, the slurry is ground in ice-cold buffer. The latex is collected by centrifugation. (2) Flow method: this method collects latex by using a special extraction device and extraction buffer after the TKS root is cut into small pieces. Both methods have relatively low purity and latex extraction efficiency: about 50% of the rubber is extracted in the form of latex.

Because of the high sugar content of TKS roots, the fresh roots easily rot and deteriorate. Therefore, to allow for storage and transportation, the roots of TKS are dried so that the latex in the roots is condensed into rubber filaments. At present, the extraction methods of solid TKS rubber are mainly divided into three categories. The first type is based on organic solvents and is often referred to as the solvent method.[7] The advantage of the solvent method is the high purity of the extracted product, and the principle is simple. However, the solvent method produces volatile organic compound (VOC) emissions. For example, toluene and petroleum ether will cause harm to the human body, which limits its development and scope of application. With increasing public awareness of environmental protection, the extraction process of TKS rubber is developing in a diversification and pollution-free direction. The second method based on water environment and mechanical treatment can better meet this demand.[15–17] The main principle of the milling method is to use the difference in densities between rubber and plant tissue and the difference in hydrophilicity and hydrophobicity of the two to prepare the TKS rubber. Following the mechanical grinding, rubber threads are separated from finely ground plant root tissue by passing the ground plant material over a dry vibrating mesh screen and blowing away the plant root skins to leave rubber threads. The rubber threads may further be purified by stirring in warm water. Then the mixture settles, and the rubber threads are skimmed off. Optimal purification may be obtained by stirring, settling, and skimming off the rubber threads. The third type is represented by the enzymatic hydrolysis method, bringing us a new idea. Not only is the rubber obtained of higher purity, but also the natural by-products have economic benefits that deserve attention and research. For example, a fungus called *Thermomyces lanuginosus* STM was isolated from the garden soil.[18] TKS root tissue is broken down by different hydrolytic enzymes produced by the fungus. The rubber purity of TKS root can reach 71.7%. Cellulase and pectinase are used by Cornish's team to enzymatically digest TKS roots, which can significantly improve the yield (about 80%) and purity (99.4%) of rubber.[19]

This study will provide two new aqueous-based processes to prepare TKS rubber. They are the strong water shearing extraction process and the acid–base extraction process, and the purity of the rubber obtained by these two methods is above 90%. Compared with the solvent method, they have reduced the pollution and damage to the environment, providing new ideas in the large-scale industrial extraction of TKS rubber. The strong water shearing extraction process is a green and environmentally friendly treatment process, in which no solvent except water is used. The acid–base process is also a relatively environmentally friendly treatment process, in which organic solvents are not used.[20] The acidic and alkaline residues obtained by this method are mutually neutralized to obtain biomass potash fertilizer. The texture of TKS rubber is softer, and it has a lower glass transition temperature than styrene-butadiene rubber, which improves the performance of TKS rubber in snow tires.

MATERIALS AND METHODS

CHEMICAL REAGENTS AND MATERIALS

TKS (supported by Xinjiang Academy of Agricultural Sciences), H_2SO_4 (AR, 98%, Beijing Chemical Factory, China), potassium hydroxide (KOH) (GR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), toluene (AR, Aladin, USA), ethanol (AR, 99%, Beijing Chemical Factory),

NR (SCR WF, purchased from Yunnan Rubber Co. Ltd., Yunnan China), *Eucommia ulmoides* gum (EUG) (Supported by Shandong Beilong *Eucommia ulmoides* Biological Engineering Co., Ltd, Weifang, China). Isoprene (IR), butadiene rubber (BR), and styrene-butadiene rubber (SBR1500) were purchased from PetroChina Co. Ltd. Other rubber ingredients were purchased from the market.

EXTRACTION PROCESSES

Solvent Extraction Process. — A certain quality of dried roots were weighed according to different material–liquid ratios (M/L): 1:10, 1:15, 1:20, 1:25, the dried roots were put into a 5 liter Waring blender and stirred at 6000 rpm for 5 min to obtain powder. The powder was placed in a 5000 mL beaker, stirred and boiled with 2500 mL of toluene for 1 h. After centrifugation, the liquid was removed through a pipette. The remaining solids were added with 2500 mL of toluene, stirred, and boiled for 1 h, and this process was repeated three times. All the centrifuged liquid was collected, the solution was concentrated in a rotary evaporator to 30%, and then four times the volume of ethanol was used to flocculate the solution. The rubber product obtained after drying was weighed and tested for rubber content.

Strong Water Shearing Extraction Process (a) Pretreatment Process. — Three mechanical pretreatment methods (double-roll milling method, Chinese medicine milling method, and Waring blender method) were used to treat the TKS dry roots. One of them was preferred according to the treatment effect.

Double-roll milling method: A double-roll mill (Φ160×320, Shanghai Rubber Machinery Factory, Shanghai, China) was used to crush and rub the dry roots of TKS repeatedly until no more bagasse fell out after passing the roller. Chinese medicine milling method: The dry roots of TKS were put into a roller and manually rolled with a roller to continuously separate the residue and sample until there was no new bagasse falling out. Waring blender method: The dry TKS roots were placed in a blender and stirred for 2 min. The smashed samples were put into sieves with meshes of 20, 40, and 80 mesh for screening. The sieved sample was divided into four parts: less than 20 mesh, 20–40 mesh, 40–80 mesh, and greater than 80 mesh according to the particle size. Powders with a mesh size greater than 80 are defined as "residues" because the rubber content in this part was tested to be less than 1.5%. After all experiments, the mass ratio of the sample to the bagasse and rubber content ratio were tested to select the optimal pretreatment process.

Strong Water Shearing Extraction Process (b) Strong Water Shearing Process. — The strong water shearing process is a relatively gentle treatment method, which contains many principles, such as the principles of polarity difference between rubber and plant tissue, water and sugar compatibility, water and rubber incompatibility, and density difference. The specific process of strong water shearing was that the TKS root samples pretreated were put into the self-made strong shear kettle, and the stirring paddle in the equipment drives the water layer to rotate and produces laminar water flow. Under the action, the entangled state of the rubber thread, inulin, lignocellulose, and other plant tissues in the sample was gradually loosened and separated as the inulin was gradually dissolved into the hot water. Impurities on the surface of the rubber silk were gradually sheared off by this high-speed laminar water flow. The rubber gradually floated on the water surface because its density was less than that of water, and the bagasse sank to the bottom after absorbing the water fully, which allowed the rubber, inulin, and bagasse to be well separated. As shown in Figure 1, the self-made strong water shearing machine was used to further purify the rubber for the three groups of pretreated samples. The strong shear machine was composed of a high-speed motor, a stirring paddle, and a heating device. The maximum speed reached 40 000 rpm, and the temperature can rise to 90 °C. The initial conditions were: material–liquid ratio＝1:10 (g/mL); temperature＝50
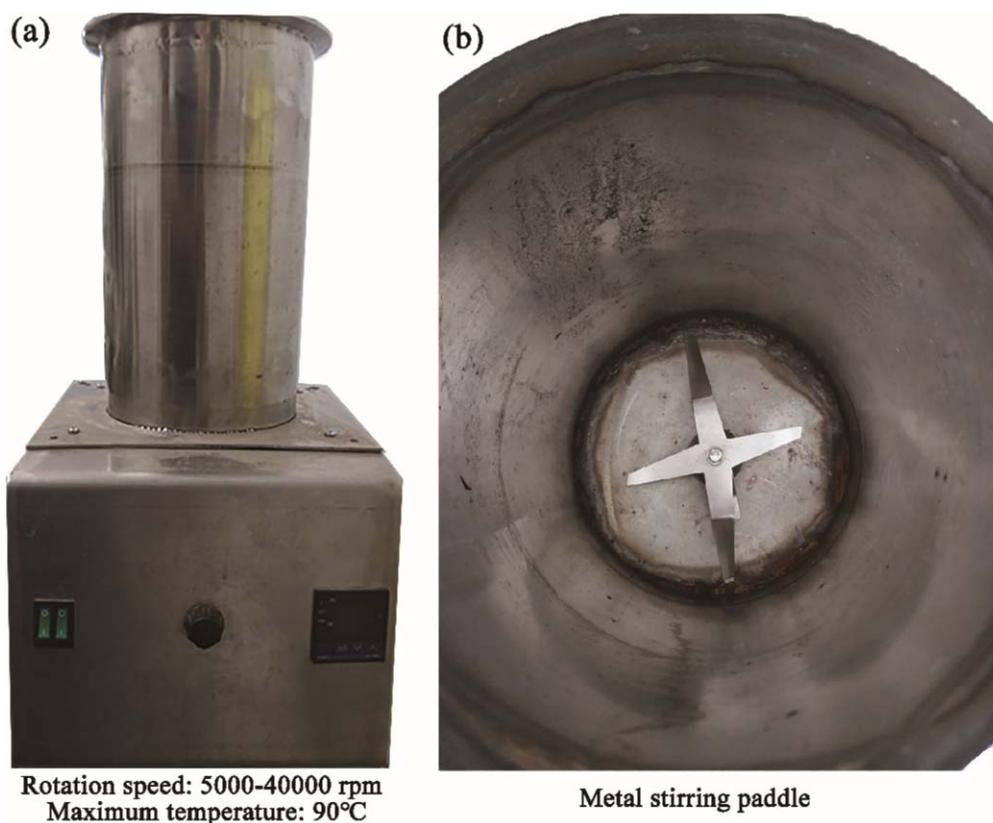
FIG. 1. — (a) High-speed strong water shearing machine and (b) internal structure.

°C; rotation speed $=5000$ rpm; stirring time $=15$ min. The rubber purity under each condition was determined to decide the best process conditions.

Strong Water Shearing Extraction Process (c) Ball Milling and Centrifugal Separation. — After processing the TKS dry roots in steps a and b under the optimal treatment conditions, a freeze grinder (Tissuelyser-24, Shanghai Jingxin Industrial Development Co., Ltd., Shanghai, China) and a centrifuge (LXL-2, Shanghai Anting Scientific Instrument Factory, Shanghai, China) were used to separate the rubber filaments that were still sticky to the lignocellulose. The initial conditions were: milling frequency $=30$ Hz, milling time $=90$ s. After milling, the sample was put into a 50 mL centrifuge tube and centrifuged at 10 000 rpm for 5 min. The floating rubber was collected in the upper layer and the residue accumulated in the lower layer was discarded. Then the above processes were repeated until the residue after centrifugation no longer accumulates on the bottom of the centrifuge tube. The rubber purity, lignin content,[21] and holocellulose content[22] were determined to decide the process of rubber extraction by strong water shearing process.

Acid–Base Process. — The complete extraction process included: the bark peeling pretreatment process, acid–base treatment process, and strong water shearing posttreatment process. In addition, the remaining acid waste residue and lye waste residue could be mixed and adjusted to pH $=7$ to prepare potash fertilizer to solve the problem of liquid waste and solid waste.

The root bark could be easily removed, and the root core was pulled out by manual processing after the clean and dry TKS roots were heated and boiled in the water for 2 h. At this time, the TKS

TABLE I
EXPERIMENTAL FORMULAS FOR WINTER TIRE TREAD

Ingredient[a]	Formula, phr			
	1	2	3	4
Hevea NR	20	0	0	0
TKS rubber	0	20	16	0
EU gum	0	0	4	0
IR	0	0	0	20
BR	20	20	20	20
SBR1500	82.5	82.5	82.5	82.5
PS	45	45	45	45
CB	15	15	15	15
Oil	8	8	8	8
SCA	6	6	6	6
ZnO	2.5	2.5	2.5	2.5
SA	1.3	1.3	1.3	1.3
4010NA	3.3	3.3	3.3	3.3
TT	1	1	1	1
CZ	2	2	2	2
S	1.8	1.8	1.8	1.8
Total	208.4	208.4	208.4	208.4

[a] PS, precipitated silica (A200); CB, carbon black (N330); Oil, aromatic hydrocarbon oil; SCA, silane coupling agent HP1589C; ZnO, zinc oxide; SA, stearic acid; 4010NA, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine; TT, tetramethylthiuram disulfide; CZ, *N*-cyclohexyl-2-benzothiazole sulfonamide; S, sulfur.

root was divided into three parts: root bark, root flesh, and root core. The quality proportion of these three parts, the contents of rubber, the lignin, and holocellulose were determined as well. The root flesh part and root bark part were boiled with dilute sulfuric acid with a mass fraction of 3% and dilute potassium hydroxide solution with a mass fraction of 3%, respectively, for 2 h, and the content of holocellulose and lignin was determined to decide the optimal process for acid–base extraction of rubber.

WINTER TIRE TREAD RUBBER COMPOSITE PROCESSING

Table I showed an experimental formula for winter tire tread, in which the variable in Formula 1 is the NR component, the variable in Formula 2 is the TKS rubber component, the variable in Formula 3 is the TKS and EUG blend component (TKS 80%, EUG 20%), and the variable in Formula 4 is the IR component.

CHARACTERIZATION OF RUBBER

Rubber Purity. — The purity of crude rubber was determined by the differential weight method. Crude rubber and toluene were mixed at 70 °C and stirred at 200 rpm for 24 h. TKS rubber solution was filtered after the undissolved material reached the constant weight. The undissolved material was dried in a vacuum oven at 80 °C, and then removed for weighing (DZF-6030, Shanghai Hecheng Instrument Manufacturing Co., Ltd., Shanghai, China). The purity of TKS rubber was

calculated was as follows:

$$P = \frac{m_0 - m_1}{m_0} \times 100$$

where P is the purity of TKS rubber, m_0 is the mass of crude TKS rubber, and m_1 is the mass of undissolved material.

Microscopic Observation. — A semiautomatic frozen microtome (RM 2235, Leica Brand, Wetzlar, Germany) was used to slice the root. Then the samples were quickly freeze-dried with liquid nitrogen. An optical microscope (88-55008, Deutsche Bosch, Gerlingen, Germany) was used to directly observe the rubber distribution at the root of TKS at 100×. A scanning electron microscope (SEM) (S4800, Hitachi Co., Ltd., Tokyo, Japan) was used to observe TKS roots under microscopic conditions. The dried sample was fixed on the sample stage with conductive adhesive and sputter-coated with gold. The thickness of the gold layer was 5–10 nm, and the acceleration voltage was 5 kV. The magnification was adjusted as needed during the test.

Fourier Transform Infrared Spectrum Analysis. — Dry rubber sample was tested using the ATR program in an infrared spectrometer (Tensor 27, Bruker (Beijing) Technology Co., Ltd., Beijing, China). A series of infrared spectra were collected in the range 500–4000 cm^{-1} with a resolution of 4 cm^{-1}.

Nuclear Magnetic Resonance Spectrometer Analysis. — The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra (AV 400, Bruker (Beijing) Technology Co., Ltd.) were used to analyze the molecular structure of the TKS rubber. The test conditions were as follows: TKS rubber was dissolved in deuterated chloroform solution with a concentration of 10 mg/mL. The scan was performed 400 times with a scan pulse of 4.8 s.

Gel Permeation Chromatography Analysis. — Gel permeation chromatography (1260 Infinity, Agilent (Beijing) Technology Co., Ltd., Beijing, China) was used to analyze the molecular weight and molecular weight distribution of the TKS rubber. The sample was made by dissolving 1 mg of TKS rubber into 2 mL of chromatographic pure toluene. The toluene phase was the mobile phase, the flow rate was 1 mL/min, the injection volume was 20 μL, and the temperature of the column oven and detector was 30 °C.

X-Ray Photoelectron Spectroscopy Analysis. — An X-ray photoelectron spectrometer (D/Max2500 VB2+/PC, Rigaku Corporation, Tokyo, Japan) was used to detect C, O, Cl, N, and S spectra to analyze the rubber material composition. The rubber sample was cut into slices of 3 mm × 3 mm^2, dried in a vacuum for 24 h, and then fixed by conductive tape for testing. The test uses AlKα monochromatic X-ray at 150 W and 10 eV, and the spot size is 3.5 mm × 1 mm^2. Each X-ray photoelectron spectroscopy (XPS) spectrum was calibrated by the Cls external standard method.

Universal Tensile Machine Test. — According to the national standard GB/T 1688-2008, universal tensile machine (CMT4104, Shenzhen New Sansi Material Testing Co., Ltd., Shenzen, China) was used to test the mechanical properties. An 8.5 g sample of TKS rubber was put into a mold and pressed at 90°C and 15 MPa for 15 min by a flat-plate vulcanizer (XLB-350 × 350, Oriental Machinery Co., Ltd., Shandong, China). Then the sample was cold-pressed and shaped at 15 MPa by transferring it to the room temperature plate vulcanizer. The obtained sample sheet was cut into a dumbbell shape with a width of 4 mm, and a 50 N sensor was used at a rate of 50 mm/min for testing. The vulcanized sample was cut into a standard dumbbell-shaped tensile spline (width 6 mm) and a standard tear spline.

Vulcanization Curve Test. — The winter tire tread formulation selected in this paper was a sulfur vulcanization system, and a rotorless vulcanizer (MR-C3, Beijing Ruida Yuchen Instrument Co., Ltd., Beijing, China) was used to vulcanize the sample at 160 °C for 30 min. The vulcanization curve was used to analyze the vulcanization process, torque range, and optimal vulcanization time T_{90} of the rubber compound after the test is completed.

FIG. 2. — (a) Wild TKS root; (b) morphological characteristics of dry TKS roots.

Mooney Viscosity Test. — A Mooney Viscometer (M3810C, Beijing Huanfeng Chemical Machinery Experimental Factory, Beijing, China) was used to test the Mooney viscosity of the sample. The rubber compound sample was 21 g. The test conditions were: after being preheated at 100 °C for 1 min, the sample was tested for 4 min to analyze its ML (1+4).

Rubber Processing Analyzer Test. — A rubber processing analyzer (RPA2000, Alpha Technology Corporation, Howell, MI, USA) was used to test the processing performance of sample. The rubber sample was 5 g. The test frequency was set to 1 Hz, and the strain scanning range was from 1% to 400%.

Dynamic Mechanical Analysis. — A dynamic mechanical analyzer (VA3000, METRA VIB Co., Ltd, Limonest, France) was used to test the dynamic properties of rubber sample. The vulcanized samples were cut into 10 mm × 10 mm samples. The temperature ranged from −100 °C to 100 °C. The speed of temperature increase was 3 °C/min, the frequency was 10 Hz, and the strain amplitude was 0.1%.

Low-Temperature Brittleness Test. — The rubber was tested in a rubber and plastic low-temperature brittleness tester (MZ-4068, Jiangdu Mingzhu Testing Machinery Factory, Yangzhou, China) to check its storage and application properties under low-temperature environmental conditions. The vulcanized sample was cut to 6 mm × 25 mm. The initial temperature and time were set to −50 °C and 3 min, respectively, then gradually reducing the experimental temperature until the minimum temperature of −62.5 °C was reached.

RESULTS AND DISCUSSION

THE MORPHOLOGY AND CHEMICAL COMPOSITION ANALYSIS OF TKS ROOT

Figure 2a shows the morphology of TKS; the broken root was connected by the rubber filament when the fresh roots of wild TKS were broken. As shown in Figure 2b, TKS dry roots had a main root, generally 15–20 cm in size and 1–1.5 cm in diameter, the number of lateral roots was relatively small.

The root chemical composition of wild and greenhouse-grown TKS was quite different. The method of determining the composition of the TKS dry roots has been described in detail in previous research by our group.[23] The proportion of each component is shown in Figure 3, the rubber content accounted for about 6.9–8.9% of the total weight of dry roots, which was higher than those planted in the field for one year. This is because wild TKS are generally perennial plants, so
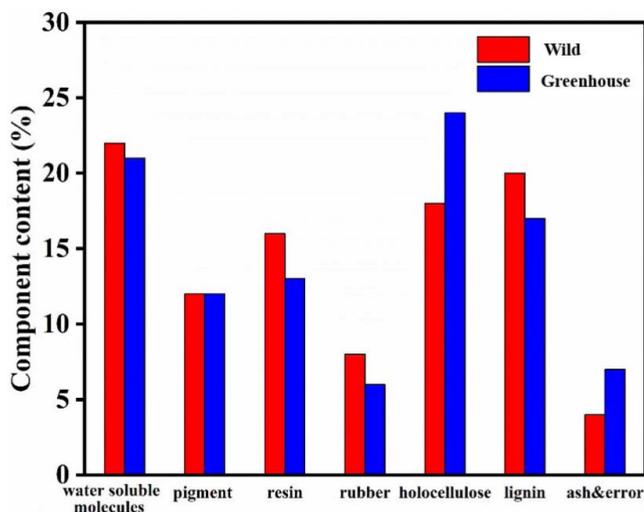
FIG. 3. — Average chemical composition of dry TKS roots grown in the wild and in the field.

the rubber content was usually higher. In terms of other ingredients, the holocellulose content of greenhouse cultivated TKS roots was significantly higher than that of wild ones. This was because the number of lateral roots was significantly greater than that of wild TKS, which led to more root bark components being grown in the same weight of roots.

An optical microscope and an SEM scanning electron microscope were used to observe the cross section of fresh TKS root to analyze the distribution of rubber in the root. The optical photograph of greenhouse planted fresh roots is shown in Figure 4a. In the fresh roots of TKS, the rubber formed by latex coagulation exhibited irregular dense dot-like morphology. In dry TKS roots, the rubber filaments formed by the rubber and the plant tissue were entangled with each other, as shown in Figure 4b, which made the purification of rubber difficult. In addition, the three parts of TKS roots could be clearly observed in both dry and fresh roots. Figure 4c shows an SEM photograph of TKS fresh root. The complete cell structure could be clearly observed, and part of the cell wall was covered by the rubber membrane formed after the latex was frozen.

The automatic peeling machine developed by our research team could easily divide the TKS dry root into three parts: root flesh, root bark, and root core (Figure 5a). The chemical composition of each part is shown in Figure 5b. In a complete TKS dry root, the dry weight of root bark accounts for the largest proportion, reaching about 60%, and the rest were root flesh (27%) and root core (13%). Rubber was mainly stored in the root bark (61%) and root flesh (39%), while the root core did not have rubber. The vast majority (97%) of lignin in the whole root was present in the root bark, and correspondingly, the vast majority (93%) of the holocellulose was present in the root flesh. However, the content of these two in the root core was very low, replaced by some soluble substances such as inulin. The distribution characteristics of cellulose and lignin provided the theoretical basis for the following acid–base rubber extraction method. Separation treatment greatly reduced the difficulty of subsequent treatment and improves the treatment effect, while effectively reducing energy consumption.

STUDY ON EXTRACTION PROCESS OF TKS RUBBER

Two aqueous-based extraction technologies, strong water shearing and acid–base extraction processes, were used to prepare TKS rubber, which was subsequently compared in terms of quality and extraction efficiency with TKS rubber extracted by the traditional solvent process.
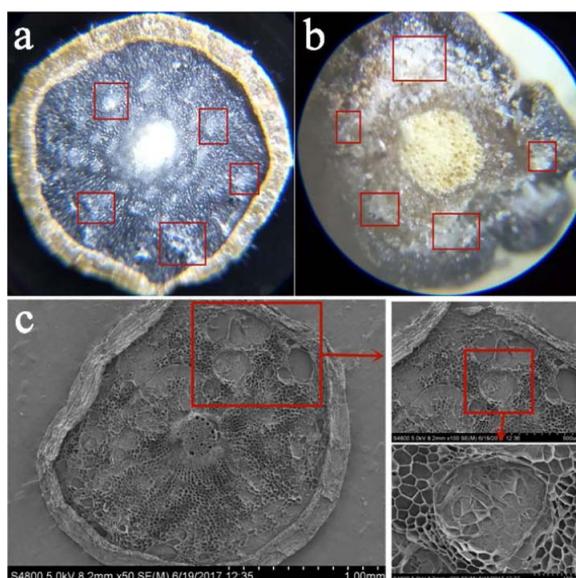
FIG. 4. — (a) Section of fresh root of TKS under optical microscope; (b) section of dry root of TKS under optical microscope; (c) section of fresh root of TKS under SEM.

Water-Based Method Process. — The water-based method was divided into four processes: mechanical pretreatment process, strong shearing process, ball milling, and centrifugal separation, as shown in Figure 6. The experimental conditions of each process would be explored and optimized.

Mechanical pretreatment process. — The detailed results are shown in Table II. The percentage rubber content in bagasse processed by the double-roll milling (D) method, the Chinese medicine milling (C) method, and the Waring blender (W) method was 41.8%, 48.9%, and 43.5%, respectively. The effects of different preprocessing methods are shown in Figure 7. The treatment principles of methods D and C were similar, but the bagasse ratio of the D method was much lower than that of the C method. This was because the squeezing force provided by the double-roll milling tends to accumulate the raw materials and was not conducive to the fall of the bagasse. So the C
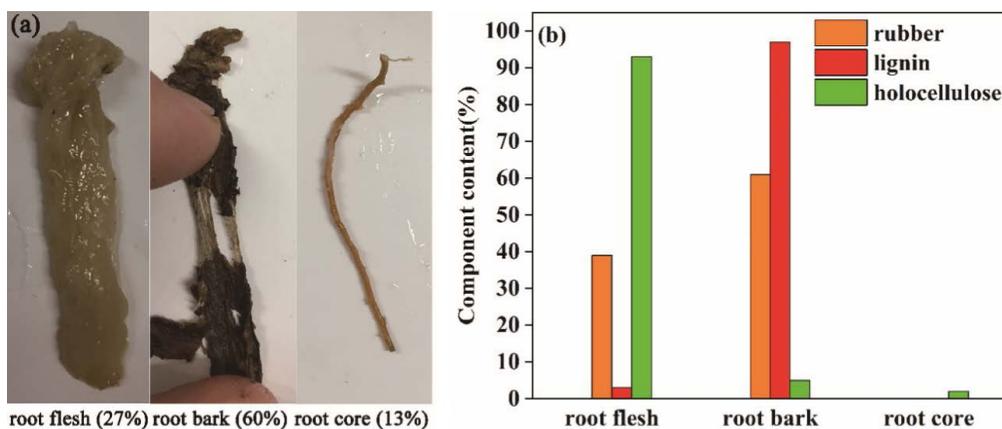

FIG. 5. — (a) Content of the three components in TKS root, (b) the chemical composition of the three parts.

FIG. 6. — Water-based overall process.

method was more effective for achieving the bagasse ratio (48.9%) and the highest rubber purity (81.0%). The residue of the W method was sieved to fine powders (>80 mesh), which included only 1.5% rubber. And it had the lowest rubber content among the three methods. However, the Waring mixer pulverized the roots indiscriminately and could not apply the squeezing and shearing forces on the TKS roots legitimately, which prevented the plant tissues from separating from the rubber threads completely, resulting in lower rubber purity (73.6%). In summary, the C method was selected as the best pretreatment method.

Strong water shearing process. — During the process, parameters such as material–liquid ratio (M/L) [root weight (g):water volume (mL)], temperature (T), rotation speed (RS), and stirring time (St) were analyzed and optimized to achieve the best condition. The initial conditions were: M/L = 1:10, T = 50 °C, RS = 5000 rpm, and St = 15 min, and the M/L was set as a variable. The rubber purity under each condition was determined to decide the best process conditions. Figure 8a shows that, with the amount of water increasing, the rubber purity first increased slightly and then decreased until flat. When the ratio of M/L = 1:15, the rubber purity reached the highest value of 83.5%. This was because the shearing force of the water decreased as the amount of water further increased, which reduced the rubber extraction effect. Therefore, M/L = 1:15 was selected as the best process parameter. Figure 8b shows that the experimental conditions were changed to: M/L = 1:15, T = 50 °C, RS = 5000 rpm, and St = 15 min, and the T was set as a variable. The rubber purity increased with increasing temperature. When the temperature was higher than 50 °C, The inulin in the TKS roots could be dissolved in water easily with increasing temperature. The plant tissue became looser and could be easily separated from the rubber. When T = 60 °C, the rubber purity

TABLE II
COMPARISON OF THE EFFECTS OF THREE PRETREATMENT PROCESSES

Method	Sample, %		Bagasse, %		
	Weight ratio	Rubber content ratio	Weight ratio	Rubber content ratio	Rubber purity, %
D	58.2	93.7	41.8	6.3	79.6
C	51.1	92.8	48.9	7.2	81.0
W	56.5	98.5	43.5	1.5	73.6

FIG. 7. — Comparison of the effects of different pretreatment methods.

peaked at 84.3%, and 60 °C was selected as the optimal temperature parameter. Figure 8c shows that the experimental conditions were changed to: M/L = 1:15, T = 60 °C, RS = 5000 rpm, and St = 15 min, and the RS was set as a variable. The purity of the rubber increased with the increased rotation speed of the stirring paddle. When RS = 6000 rpm, the rubber purity peaked at 85.1%, and 6000 rpm was selected as the optimal rotation speed parameter. Figure 8d shows that the experimental conditions were changed to: M/L = 1:15, T = 60 °C, RS = 6000 rpm, and St = 15 min, and the St was set as a variable. The rubber purity increased with increasing stirring time. When the stirring time was longer than 20 min, the purity of the rubber hardly increased. Therefore, in consideration of time cost, the optimal extraction time was determined to be 20 min.

Temperature and rotational speed had a greater impact on the purity, because the solubility of inulin increased with the increase of temperature and rotational speed, which increased the degree of damage to the overall structure of rubber silk–inulin–plant tissue. The upper part of Figure 9 showed that at the same rotation speed (5000 rpm), an increase in temperature would cause more rubber threads to be freed. The lower part of Figure 9 shows that at the same temperature (60 °C), the increase of the rotation speed caused the shear force on the samples to become larger, which made the separation of the rubber thread and the bagasse easier, and increased the rubber purity. This indicated that the influence of the rotating speed of the stirring paddle was the largest among these four factors. Because at the same temperature, if the shearing force was not strong enough, the rubber filaments were still not easily separated from the plant tissues, even if the inulin was partially dissolved. In summary, the above four influencing factors would make the rubber obtained purer under synergistic effect conditions.

The highest purity of TKS rubber optimized by the strong shearing process can only reach approximately 85%. The rubber was observed under an optical microscope, and the photos are shown in Figure 10. Brown plant tissue bagasse was still distributed in the enlarged rubber. The
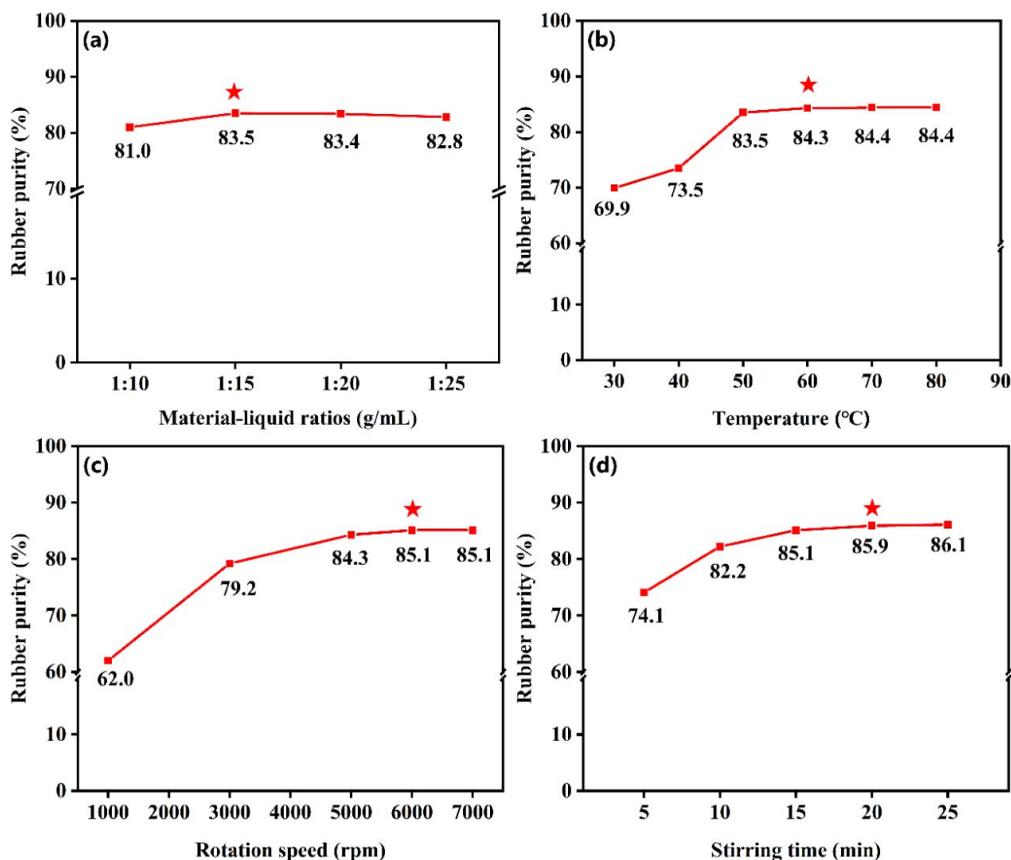
FIG. 8. — (a) RP VS M/L curve; (b) RP VS T curve; (c) RP VS RS curve; (d) RP VS ST curve.

edge part of the rubber block has a relatively simple color distribution and a pure appearance (Figure 10a). This was because the rubber and plant tissue bagasse in this part were more likely to be separated by strong water shear. There were many impurities inside the rubber block (Figure 10b). This was because the bagasse inside the rubber was wrapped by the rubber and was protected from the shearing force, so the rubber and bagasse were not easily separated.

Ball milling and centrifugal separation. — Figure 11a shows that as the frequency of ball milling increases, the rubber purity showed an upward trend. After the frequency reached 30 Hz, the rubber purity stabilized at 88.9%. Therefore, MF = 30 Hz was selected as the best ball milling frequency. Keeping MF = 30 Hz, the ball milling time was changed sequentially. Figure 11b shows that with the increase of the ball milling time, the rubber purity did not change after 180 s. This meant that prolonging the ball milling time would not have a beneficial effect on rubber extraction. Therefore, for the consideration of time cost, MT = 180 s was selected as the best ball milling time. After milling, the sample was placed in a 50 mL centrifuge tube and centrifuged at 10 000 rpm for 5 min.

The above-mentioned rubber was prepared using whole TKS roots as raw materials, and its color was brownish-gray due to more lignin pollution. The cellulose content in the root part was relatively high, and the inulin mainly existed in the root flesh and root core, and the root core could be directly removed by mechanical means. In summary, the root flesh was selected as the raw material, and the best parameters of this process (ML = 1:15, T = 60 °C, RS = 6000 rpm, Ts = 20
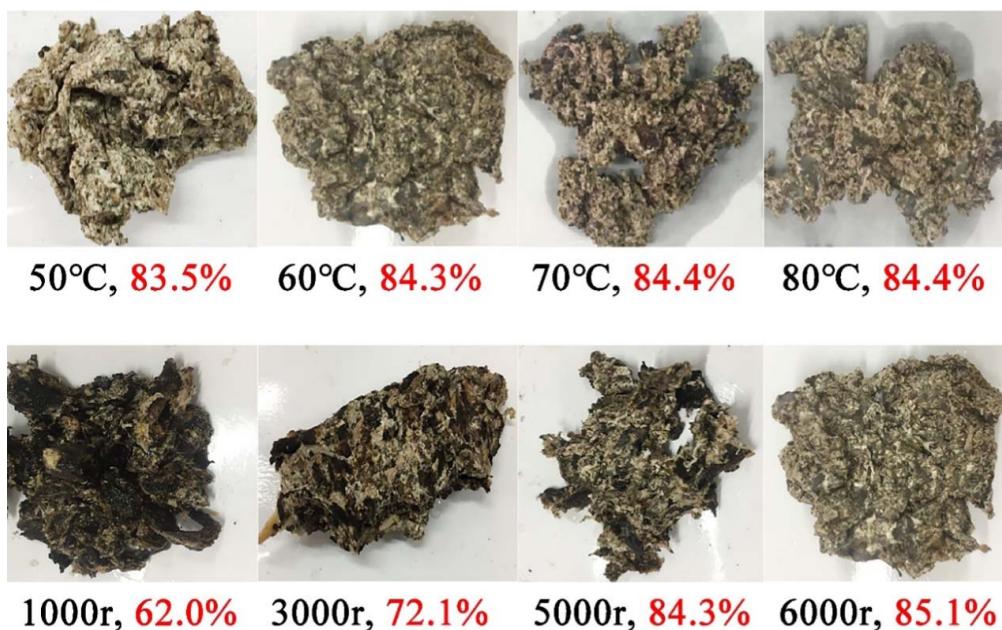
FIG. 9. — The effect of rotation speed and temperature on the extraction effect under the same conditions (RS = 5000 rpm, upper) and (*T* = 60 °C, lower).

min) were used to prepare TKS rubber with higher purity and lighter color. Figure 12 shows that the root flesh obtained after peeling has a density close to that of water, and was suspended in water. After standing for 3 days, the root flesh floated on the water surface. The strong water shearing process was used to treat the roots to prepare TKS rubber. Rubber purity reached 89.5% when tested, which was higher than the purity of the rubber prepared with the whole roots as the raw material after the ball milling process. Since there was little lignin pollution, the overall color of this rubber was white.
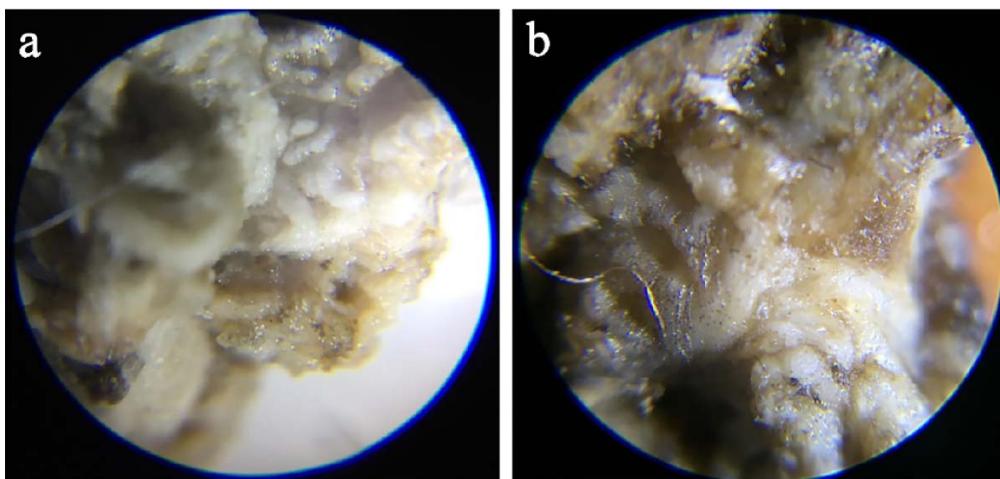
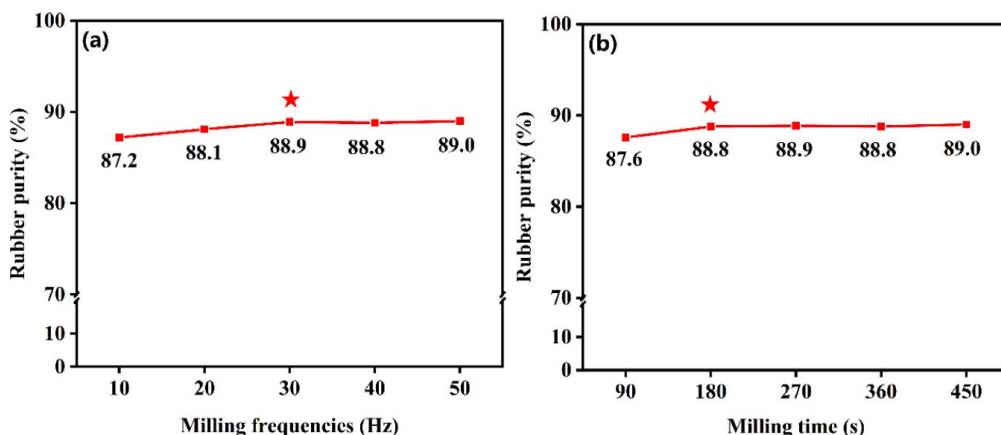FIG. 10. — Optical micrograph of (a) the edge and (b) center of the rubber block.

FIG. 11. — (a) RP VS MF curve; (b) RP VS MT curve.

Overall process optimization. — A complete water-based rubber extraction process has been established. The purity of rubber was also significantly affected by the number of process cycles. The overall process includes optimized mechanical pretreatment, strong shearing, ball milling, and centrifugal separation. The overall process was cyclically tested up to five times; the effect of rubber extraction is shown in Table III.

The rubber purity reached 91% after the overall process was performed three times. As the number of times further increased, the rubber purity stabilized. Therefore, three cycles is the best process parameter. The rubber obtained by the water-based method was subjected to the determination of the content of lignin and holocellulose. And under the best process cycles, the lignin content and the holocellulose content were greater than 3% and 2%, respectively. This showed that the water-based method cannot completely remove the lignin and the holocellulose in the rubber, because the lignocellulose is wrapped in rubber, and they are entangled with each other. Figure 10 shows that the impurities inside the rubber block were more difficult to remove than on the outside. Based on this, an improved method for removing lignocellulose using the water-based method was proposed.

Acid–Base Method Process. — When the rubber purity was not high enough, excessive impurities would become the stress concentration points, which would adversely affect the performance of the TKS rubber. The cellulose and lignin were very easily degraded in acidic and alkaline environments, respectively. The acid–base technology that cooperates with strong water
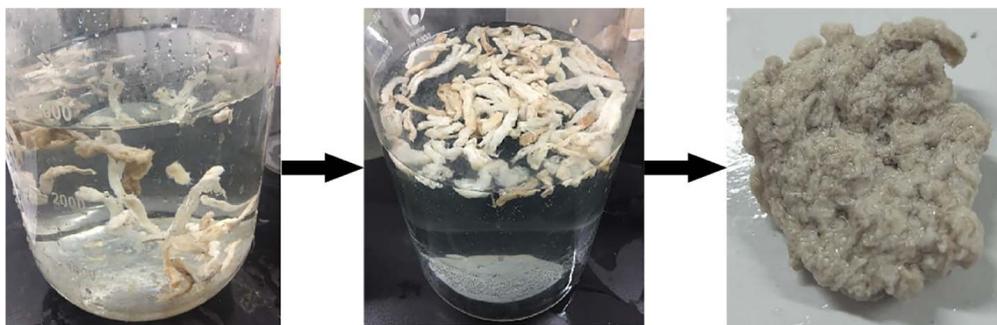

FIG. 12. — The process of preparing TKS rubber from root flesh.

TABLE III
RUBBER PURITY IN DIFFERENT PROCESS CYCLES AND IMPURITY CONTENT UNDER OPTIMAL CYCLE TIMES

Sample	Cycle times, %					Lignin content, %	Holocellulose content, %
	1	2	3	4	5		
1	89.1	90.0	91.4	91.4	91.4	3.4	2.1
2	88.5	89.9	90.9	91.0	91.0	3.7	2.6
Average	88.8	90.0	91.2	91.2	91.2	3.6	2.4

shearing technology was first proposed to further purify the TKS rubber by removing the holocellulose and lignin, respectively.

Bark peeling pretreatment process. — The pretreatment process is shown in Figure 13. The TKS roots were boiled in water for 1 h and were divided into three parts by the self-made peeler. The different parts showed different colors: from light to dark, they were root flesh, root core, and root bark. The proportion of three parts and component content of each part after pretreatment had been discussed above, as shown in Figure 5. The results show that most of the rubber was distributed in the root bark, and the remaining rubber was in the root flesh. In summary, it was considered effective to use this preprocessing method for peeling.

Acid–base treatment process. — Figure 5b shows the composition distribution of dry TKS root, wherein 97% of the lignin was in the root bark, and 93% of the holocellulose was in the root flesh. Therefore, H_2SO_4 and KOH were used to deal with root flesh and root bark, respectively. Figure 14a shows that the concentration of dilute acid was very important for the degradation of cellulose inside the root flesh. As the concentration of dilute acid increased, the cellulose content in the rubber decreased rapidly. When the mass fraction of H_2SO_4 is 4%, the content of holocellulose in root flesh was only 0.8%. When the mass fraction of H_2SO_4 was greater than 4%, its content was stable, so the 4% H_2SO_4 solution was selected as the best H_2SO_4 mass fraction. Figure 14b shows that the boiling time in dilute acid also had an important effect on the decomposition of cellulose, and the cellulose content steadily decreased as the treatment time increases. After boiling in the H_2SO_4 solution for 3 h, the content of holocellulose in the root flesh decreased to the lowest percentage, 0.6%, so boiling for 3 h was selected as the optimal H_2SO_4 boiling time. Figure 14c shows that the concentration of dilute alkali was very important for the decomposition of lignin in the root bark. As the concentration of dilute alkali increased, the lignin content in the rubber decreased rapidly. When the KOH mass fraction reached 3%, the lignin content in the root bark was 1.2%, so the 3% KOH solution was selected as the best KOH mass fraction. Figure 14d shows that the boiling time in dilute alkali also had an important effect on the degradation of lignin, and the lignin content steadily decreased with the increase in treatment time. After boiling in KOH solution
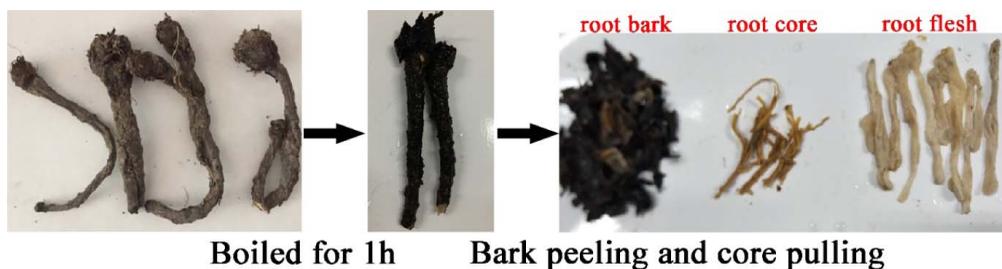

root bark   root core   root flesh

Boiled for 1h   Bark peeling and core pulling
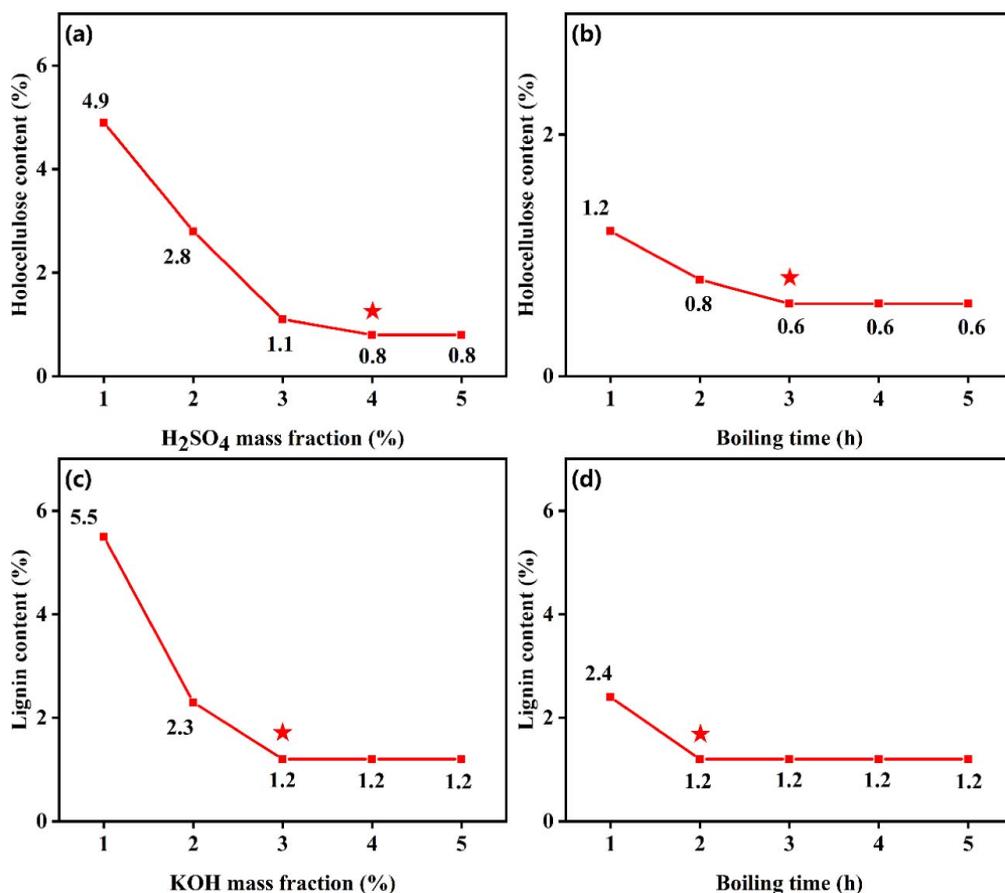
FIG. 13. — Pretreatment process steps.

FIG. 14. — (a) HC VS H_2SO_4 mass fraction curve; (b) HC VS BT curve; (c) LC VS KOH mass fraction curve; (d) LC VS BT curve.

for 2 h, the lignin content in the root bark decreased to the lowest percentage, 1.2%, so 2 h was selected as the optimal KOH boiling time.

Strong water shearing posttreatment process. — The strong water shearing process mentioned above was used to continue the rubber extraction of TKS roots after it was pretreated by the acid–base process. The TKS obtained was subjected to purity, lignin, and holocellulose content determination. The results are shown in Table IV; the rubber purity had been greatly improved to about 94%, and the impurity content had also decreased significantly. This showed that the quality of rubber was significantly improved by the acid–base pretreatment process, as compared with the results in Table IV.

Solvent Extraction Process. — To evaluate the effects of the above two processes more intuitively, the traditional solvent process was used to extract rubber. The effect of extraction time (*T*) and the material–liquid ratio [root weight (g): solvent volume (mL)] on the rubber purity would be explored and optimized. Toluene was selected as the solvent used to extract TKS rubber. The initial conditions were: extraction time = 3 h, and material–liquid ratios (M/L) = 1:25, and *T* was set as a variable. The experimental results are shown in Figure 15a. The rubber purity increased with the extraction time. When the extraction time exceeded 3 h, the rubber purity reached the highest percentage, 97.3%. So *T* = 3 h was considered the best extraction time. Changing the M/L ratio, the

TABLE IV
COMPONENT CONTENT OF ACID–BASE RUBBER

	Purity, %	Lignin content, %	Holocellulose content, %	Others, %
Root flesh (acid method)	93.9	1.1	2.1	2.9
Root bark (alkali method)	94.1	2.5	0.8	2.6

obtained rubber purity curve is shown in Figure 15b. The increase of solvent had little effect on the purity of rubber, and its purity increased very slowly. M/L = 1:20 and M/L = 1:25 achieved almost the same purity. Therefore, considering the production cost, the optimal M/L was 1:20. In the end, the optimal solvent extraction process conditions were M/L = 1:20, $T = 3$ h.

Comparison of Appearance of Rubber Extracted in Different Processes. — Figure 16 shows that four products were prepared and analyzed for appearance comparison. Water-based rubber, acid rubber, and solvent rubber had very similar appearance characteristics. The color of solvent rubber was lighter than those of water-based and acid rubber because it had the highest purity and fewer phenolic substances. The color of water-based products was darker and uneven. This was due to the dual effects of browning and impurities. The sporadic lignocellulose residues on the surface were still visible with careful observation . Alkaline rubber had a black appearance, which was thought to be caused by the decomposition of lignin, similar to the black liquor used by the papermaking industry.[24]

Optimized Route of TKS Rubber Extraction Process. — This paper proposed two new aqueous-based extraction processes of TKS solid rubber: the water-based rubber extraction process and the acid–base rubber extraction process. Because the two processes were different in pretreatment methods, the purity and quality of the rubber products obtained were also different. The water-based process was divided into four procedures: mechanical pretreatment, strong shear shearing, ball milling, and centrifugal separation. The traditional Chinese medicine grinding pretreatment process was preferred in the water-based process. The best conditions for this processes were: M/L = 1:15 (g/mL), $T = 60\,°C$, RS = 6000 rpm, St = 20 min, MF = 30 Hz, MT = 180 s. Satisfying the above conditions could increase the rubber purity to more than 91%. Similarly, the acid–base process was also divided into three procedures: peeling pretreatment, acid–base extraction process, and strong water shearing posttreatment process. During the acid–base
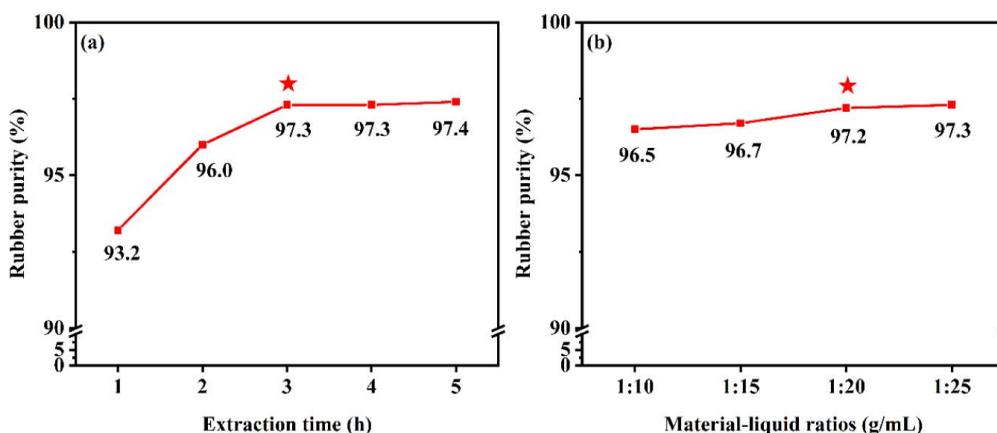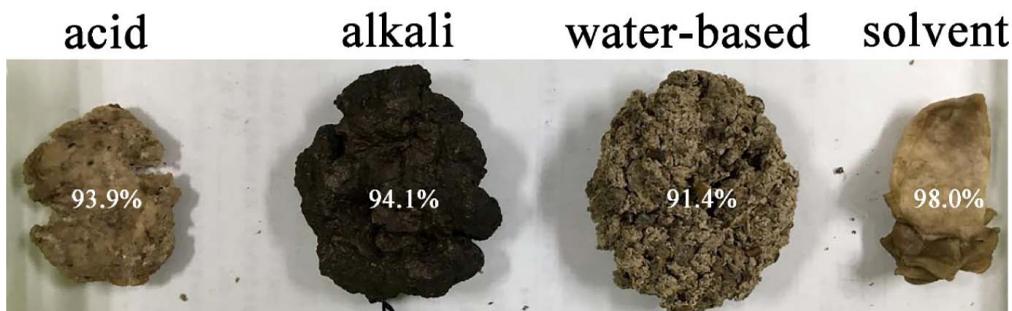

FIG. 15. — (a) RP VS M/L curve; (b) RP VS T curve.

FIG. 16. — Rubber products prepared and their purities by four methods.

extraction process, the self-made peeling machine was used in the pretreatment process to separate the root flesh and root bark, which were treated in 4% and 3% dilute acid and dilute alkali for 3 h and 2 h, respectively. After being processed according to the above-mentioned optimal parameters of the water-based method, the purity of the rubber would reach about 94%. Considering that the water-based treatment of these two processes was the same, the process flow diagrams of the two processes were merged, as shown in Figure 17. In recent years, there have been many studies on the TKS rubber extraction process, but there were few introductions to the factors affecting the process parameters and their optimization. Therefore, many factors that affected the purity of rubber have been analyzed and optimized in this process, which may provide new ideas for the industrial preparation of TKS rubber and promote its development.

CHARACTERIZATION AND COMPARISON OF RAW TKS RUBBER

Comparative Analysis of the Molecular Structure of TKS Rubber. — Figure 18 shows that the Fourier transform infrared (FTIR) spectra of the four rubber products and *Hevea* NR product all showed a similar characteristic band. Among them, 833 cm^{-1} was the characteristic vibration peak of natural rubber skeleton stretching; 1377 cm^{-1} was the deformation vibration peak of the –CH$_3$ group; 1443 cm^{-1} was the bending vibration peak of –CH$_2$; 1642 cm^{-1} was the stretching vibration peak of the C=C double bond, all of which showed the characteristics of *cis*-1,4-polyisoprene (CPI). Analyzing the groups represented by the above characteristic peaks shows that the structures of the four rubber products were basically the same, and the extracted product was indeed TKS rubber.

Natural rubber contains nonrubber components (NRCs) such as proteins and lipids. The main absorption peaks of the infrared spectrum of protein in natural rubber were at 3280 cm^{-1}, which were the vibrational absorption of N–H bonds, amides I and II, respectively.[25,26] The amide I peak in the three rubber products shifted to around 1642 cm^{-1}, which is close to the C=C stretching vibration absorption peak. The movement of the amine absorption band and the amide I absorption band of the acid process product, the alkali process product and the NR product were observed around 3442 cm^{-1} and 1642 cm^{-1}. However, this characteristic peak was not observed in the spectra of water-based and solvent products. The amide II band at 1523 cm^{-1} was seen in five rubbers. In the lipid absorption region of natural rubber, the carbonyl stretching band between 1748 cm^{-1} and 1738 cm^{-1} was related to ester groups.[27] In the solvent product, the carbonyl stretches band was not detected. This was because the lipids in the rubber were dissolved by a mixed solution of toluene and ethanol. In short, the water-based extraction process and the solvent extraction process had changed the composition of NRCs in rubber to a different extent.

H^1-NMR spectra of five raw rubber products are shown in Figure 19. Just as in *Hevea* NR, the *cis* –CH$_3$ peak, –CH$_2$ peak, and –CH peaks in the four TKS rubbers successively appeared at the
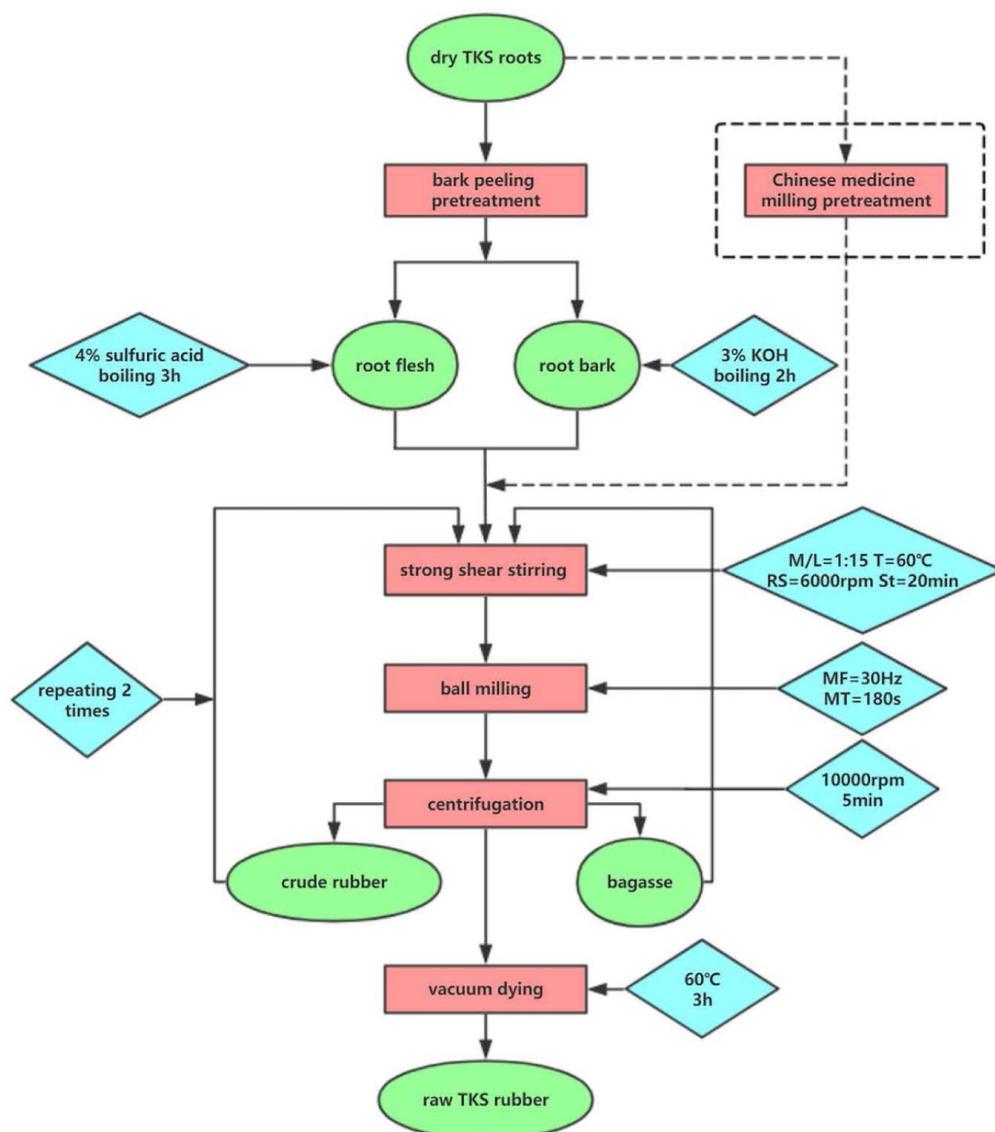
FIG. 17. — Optimized water-based process route.

chemical shifts of 1.75, 2.05, and 5.15 ppm, which indicated that the basic structure of TKS rubber was consistent with NR, and its molecular chain contains CPI structural units. The peak shapes of the five rubber products were very close. Compared with *Hevea* NR, many noise peaks caused by NRCs existed in the peak shape of the remaining four rubbers, which was consistent with the peak shape of their infrared spectrum. The water-based product had the most impurity peaks because the rubber purity was the lowest among the five products; the solvent product had the least impurity peaks because the highest purity was the closest to *Hevea* NR. In addition, the FTIR and NMR analysis showed that different extraction processes would basically not damage the molecular structure of the rubber and negatively affect the performance of the TKS rubber.
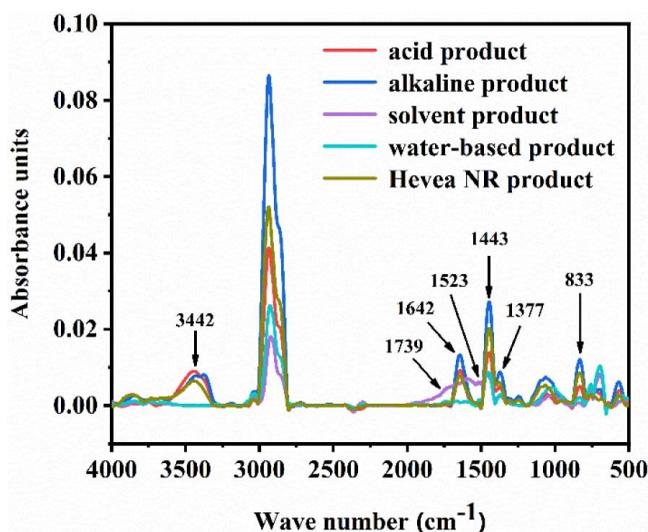
FIG. 18. — Infrared spectrum of five raw rubber products.

The XPS curves of the four TKS rubbers are shown in Figure 20. These four curves were fitted and divided according to the binding energy of the three peaks C–C, C–OH, and C–O–C. Element C had three different chemical states, in which the rubber component contained C–C groups, lignin contains C–OH groups, and holocellulose contained C–OH and C–O–C groups. Comparing these four curves, the C–OH and C–O–C curve strengths of the water-based method products were the highest, because neither lignin nor hemicellulose was specifically removed. Compared with water-based products, the strength of C–OH and C–O–C groups in acid and alkali products was weakened due to a certain degree of removal of lignin and holocellulose. The solvent method product had the weakest curve of these two groups because of its minimum impurity content.
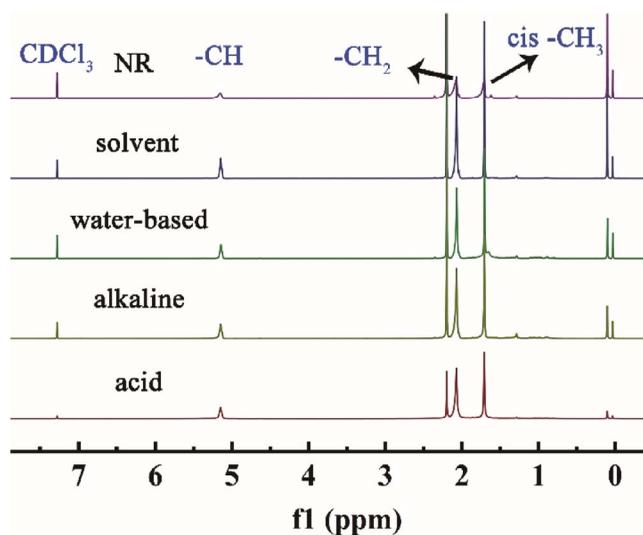

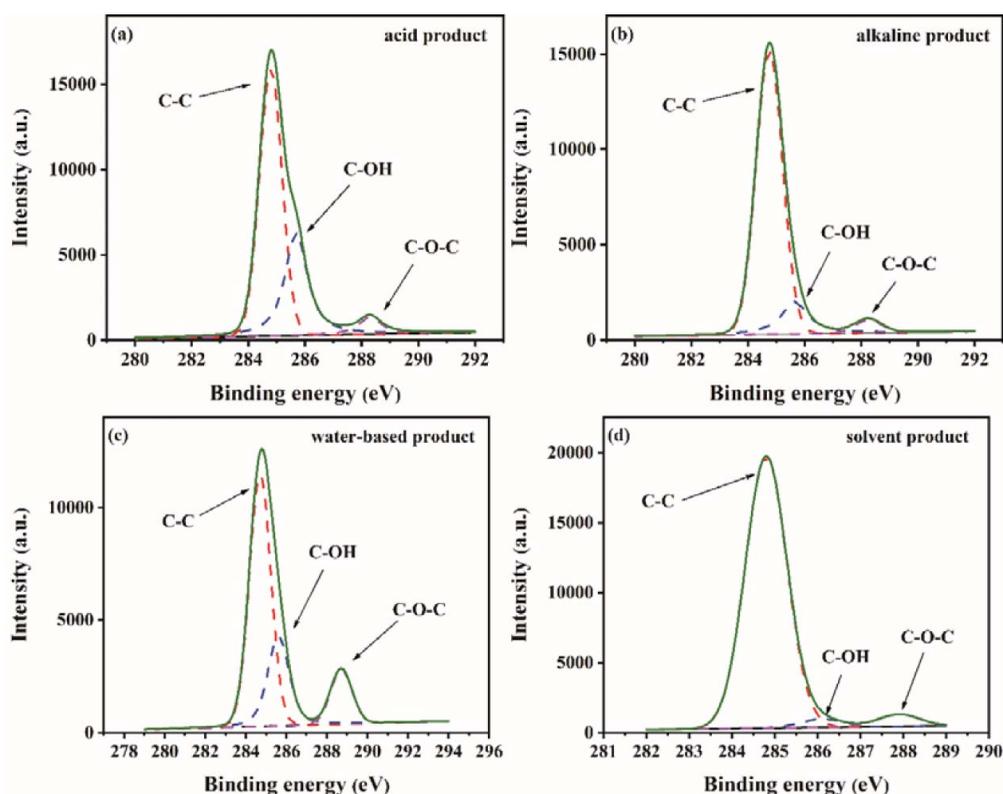FIG. 19. — ^{1}H spectra of five raw rubber products tested by NMR.

FIG. 20. — XPS spectra of four raw rubber products.

Comparative Analysis of Molecular Weight and Molecular Weight Distribution. — Table V showed the molecular weight and distribution of the four TKS rubbers. The molecular weight of acid–rubber was the smallest, and the molecular weight distribution was the largest, which indicated that the acid treatment had greater damage to the rubber molecules. The molecular weight of alkali–rubber was the largest, which showed that the rubber quality was the least damaged by the alkali process. Interestingly, the water-based rubber and the solvent rubber had very similar molecular weights and distributions. This was because mechanical and solvent treatments had very similar effects on rubber. However, the molecular weights of these two rubbers were much smaller

TABLE V
MOLECULAR WEIGHT OF FIVE RAW RUBBER PRODUCTS

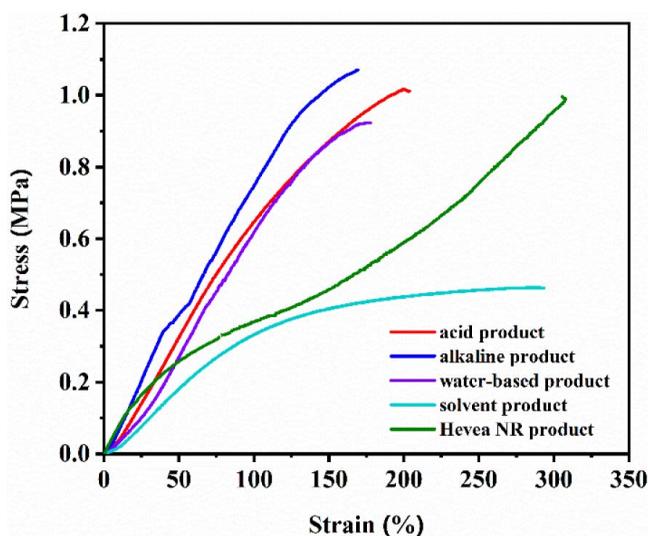|	Number-average molecular weight	Weight-average molecular weight	Molecular weight polydispersity (Mw/Mn)
	Mn ($\times 10^3$), g/mo	Mw ($\times 10^3$), g/mol	
Acid product	114	352	3.1
Alkaline product	144	384	2.7
Water-based product	128	357	2.8
Solvent product	131	369	2.8
Hevea NR product	271	728	2.7

FIG. 21. — Stress–strain curves of five raw rubber products.

than that of *Hevea* NR. This was because these methods were affected by mechanical or shearing forces, which reduced the molecular weight and broadens the distribution. Namely, mechanical treatment would break the network molecular structure, and solvent would only dissolve the linear molecules.

Mechanical Properties of TKS Rubber. — Figure 21 presents the stress–strain curves of five rubbers. Among the four TKS rubbers, the acid rubber, alkali rubber and water-based rubber had significantly higher stress under the same strain than that of the solvent rubber, which indicated that the solvent rubber only dissolved linear rubber hydrocarbon molecules, and the insolubility of the network molecular structure led to its tensile strength being much lower than that of nonsolvent rubbers. There were two possible reasons for the higher tensile strength of nonsolvent rubbers. First, nonsolvent rubber contained complex network molecular structures. The second reason was that more impurities like rigid fillers would lead to an increase in tensile strength. But at the same time, the elongation at break of the stress concentration point of nonsolvent rubber was significantly lower than that of solvent rubber and NR. Figure 21 shows that NR showed the obvious inverse S-curve of strain-induced crystallization. However, in contrast with the report that TKS rubber had the strain-induced crystallization phenomena,[11] the TKS rubber extracted in the present paper did not show the strain-induced crystallization phenomena. The solvent TKS rubber only dissolves the linear molecules whose stress–strain curve was similar to IR. The other three TKS rubbers had higher modulus and short elongation at break, which indicated that lignocellulose granules remained in the rubber and played the role of fillers. Maybe the samples had broken before the strain-induced crystallization phenomenon occurred.

CHARACTERIZATION OF WINTER TIRE COMPOUND RUBBER PERFORMANCE

Figure 22a shows the vulcanization curve of Formulas 1–4 winter tire tread compounds of Table I. From the scorch time to torque, it could be seen that the four rubbers were not significantly different. Therefore, these four rubber had a similar vulcanization performance. Figure 22b shows the four rubbers had a similar Payne effect, except the Formula 3 tread compound had higher G' caused by EUG. Figure 22c shows the Mooney viscosity of four tread compounds, there was no big
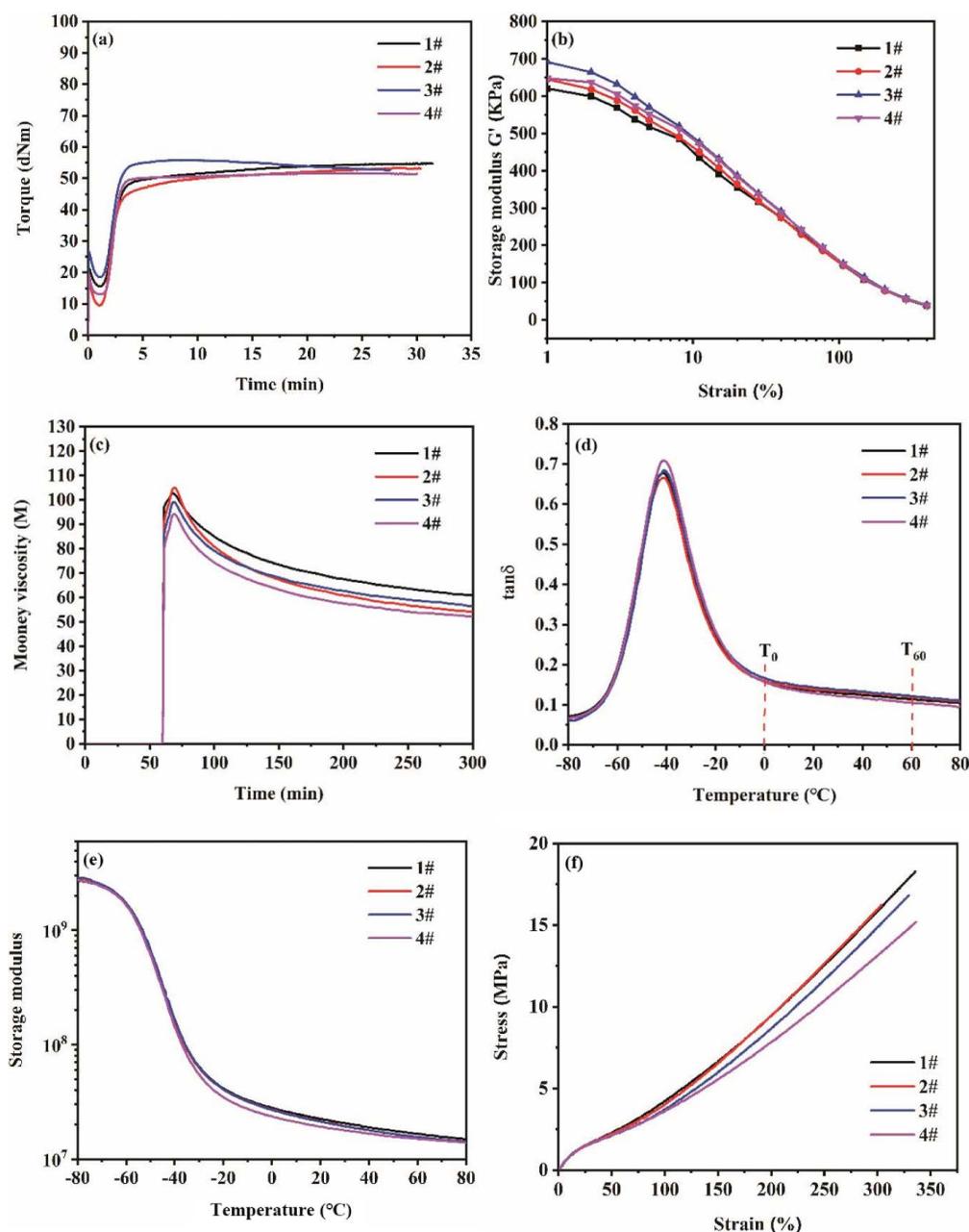
FIG. 22. — Comparison of the performance of four winter tire tread compounds.

difference in the ML100 °C (1+4) value of the four groups of samples, except the *Hevea* NR system was the highest because of the higher molecular weight. This indicated that the processing performance of the four systems of mixing rubber was very similar. Figure 22d,e shows the loss factor tan δ–T curves of Formulas 1–4. Among them, T_{60} reflected the rolling resistance of the tire sample, and T_0 reflected the wet resistance of the tire sample. The IR system was more resistant to wet slip than other samples, but the rolling resistance was slightly larger. In short, the four groups of

samples exhibited almost the same dynamic mechanical properties. Figure 22f shows the tensile curves of Formulas 1–4. The tensile strength and elongation at break of *Hevea* NR system and IR system were the maximum and minimum, respectively. The tensile strength of the TKS and EUG blend system and TKS rubber system were similar. Owing to its normal temperature crystallization characteristics, the EUG system had increased elongation at break compared to the TKS system. However, the differences in these properties were very small, which showed that the mechanical properties of the four systems were basically the same.

CONCLUSION

In view of the NR facing a series of problems, including limited tropical planting areas, shortage of labor, long times to tap the latex, and the threat of South American leaf blight (SALB) caused by *Microcyclus ulei*, etc. Developing the TKS rubber grown in temperate regions provides an effective alternative. The present paper systematically studied and analyzed the TKS root chemical composition, establishment, and optimization of the extraction process, characterization, and processing. Two new TKS rubber extraction processes (water-based method process and acid–base method process) were proposed to maximize the purity of the TKS rubber to 91% and 94% approximately, which enriched the extraction method of TKS rubber and provided a new route for the industrial production of TKS rubber. The research on the processing performances and mechanical properties showed that TKS rubber was very close to NR and was a more suitable alternative rubber material to apply to the existing rubber industries.

ACKNOWLEDGEMENTS

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