

# Preparation and characterization of environment friendly used rubber powder modified pulp sediments composites

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**Abstract** In recent years, with growing contradiction between energy supply and demand, the more and more high demand of the environmental protection is needed. The work represented an environment friendly method for recycling of waste rubber and pulp sediment that a new composite material was prepared using pulp sediment as the matrix, used rubber powder as the toughening agent, and sawdust as the reinforcement. The effects of used rubber powder content on the mechanical properties of the pulp sediment and sawdust/pulp sediment were studied by measuring Shore A hardness, tensile stress, and elongation-at-break. The morphology of used rubber powder/pulp sediment composites was analyzed by scanning electronic microscopy and transmission electron microscopy. The curing conditions were also discussed. The results showed when the used rubber powder/pulp sediment mass ratio was 8/100, the used rubber powder/pulp sediment sample showed smooth surface, high hardness, compact structure, uniform arrangement, and good compatibility. When the pulp sediment used as the matrix, sawdust as the reinforcement, and used rubber powder as the toughening agent, the proper recipe of the composites was 100 phr pulp sediment, 30 phr sawdust, and 10 phr used rubber powder. The mechanical properties of the used rubber powder/pulp sediment were greater than those of pure pulp sediment and used rubber powder/sawdust/pulp sediment. The best curing conditions for the used rubber powder/pulp sediment composites were at 150 °C under 5 MPa for 15 min. The study on used rubber powder modified pulp sediment, exploits a new way to recycle used rubber powder and pulp

sediment, not only benefit environment purification, but also reduce cost of sheet materials, and develops a new way for the economy and environment protection.

**Keywords** Pulp sediments · Used rubber powder · Preparation · Characterization

## Introduction

In recent years, with growing contradiction between energy supply and demand, the more and more demand of the environmental protection is needed [1]. The industrial and life waste treatments have attracted increasingly people's attention [2]. A variety of industrial production wastes contain different pollutants [3]. The industrial wastes mishandling not only cause serious environment pollution [4] but also lead to waste of resources [5]. In order to get out of the natural resource scarcity [6], the energy crisis problems and waste material pollution to the environment [7], the economic, effective recycling of the industrial wastes have always been the focus of attention in the whole society [8]. The worldwide experts have studied industrial production toward renewable resources [9] and secondary energy utilization [10].

Modern paper industry is one of the major industries. Paper and cardboard production has been used to mark a national modernization and civilization [11]. In China, the paper industry has been an important part of the national economy. According to the material forecast, paper and cardboard demand will reach 75–80 million ton by 2015 [12]. Owing to the process technology of the Chinese papermaking industry has been relatively backward for years, the products are in low level, and environmental pollution is serious. In addition, because the papermaking

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industry is a modern industry with intensive technology and capital, the input of fixed assets is as 3 times as those of food and textile industry. The production for 1 t pulp needs 4–5 m<sup>3</sup> raw woods. From the above, the fast growth paper industry is restricted more and more by raw material, environmental protection, capital, and other factors. Therefore, recycling waste paper pulp is particularly important.

Pulp sediment, which mainly comes from the waste paper pulp sediment, is considered in some of the plants as raw material, and is the basic material of paper industry. The constituents of pulp sediment mainly are cellulose [13], also includes something such as hemicellulose, lignin, resin, pigment, pectin, ash, etc. Pure pulp sediment is high hardness and easy fragile. At present, it is important to produce packing box [14], the environmental protection bags [15], paper handicraft [16], low-level paper [17], and pulp molding industry [18]. As poor toughness and strength of pulp sediment products [19], the used rubber powder toughened pulp sediment and sawdust reinforced pulp sediment were studied in this work to make full use of pulp sediment.

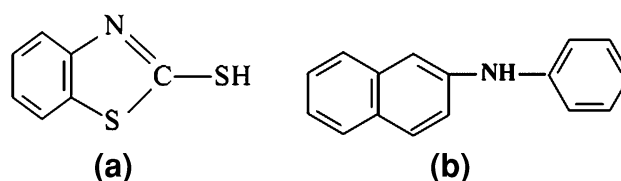
At present, the studies on pulp sediment [20] or used rubber powder [21] are very common at home and abroad [22], but the study on their mixture has not reported. Thus, the used rubber powder and pulp sediment are mixed to make a kind of high performance-to-price ratio composites in this work.

This composite material can be used in packing boxes and plank material alternatives such as medium density board, etc. Therefore, it can save a lot of wood. The study on used rubber powder modified pulp sediment, exploits a new way to recycle used rubber powder and pulp sediment, not only benefits environment decontamination, but also reduces the cost of sheet materials production, and develops a new way for the economy and environment protection.

## Experimental

### Materials

Pulp sediment (PS) was manufactured by Qiqihaer Fuyuan Paper Ltd., China, in block shaped with diameter of 5–10 mm and water content of 48–51 wt %. Used rubber powder (URP) which principally is made of waste tire, was supplied by Heilongjiang Jiarui Rubber Ltd., China, with diameter of 0.10–0.32 mm, which its main composition is butadiene rubber and styrene butadiene rubber. Sawdust was provided by Qiqihaer Fuqiang Wood Process Factory, China, with diameter of 0.40–0.10 mm. Sulfur, mercapto benzothiazole (accelerator M, Scheme 1a), and *N*-phenyl- $\beta$ -naphthylamine (antioxidant D, Scheme 1b) were respectively supplied by Shandong Zibo Shuanggou Dongfeng Chemical Plant, Henan Kailun Chemical Ltd., and



**Scheme 1** Chemical formulas of (a) accelerator M and (b) antioxidant D

Jiatong Chemical Ltd. as industrial grade, in which sulfur is curing agent.

### Sample preparation

In the work, the principal formulation is 100 phr (part by mass, g) pulp sediments, 30 phr sawdust, and 8 phr used rubber powder, in which the contents of sulfur, accelerator M and antioxidant D are all 2 wt % of used rubber powder.

Initially, pulp sediments and sawdust were masticated on XK-160 two-roll mill for 3 min at 45–55 °C, while the distance between two rolls was about 0.8 mm. Then, the distance between two rolls was adjusted 4 mm, and added used rubber powder at 50–60 °C. After that, various ingredients were mixed in turn on the two-roll mill for 10 min according to principal formulation. At the end, cured on plate vulcanize machine (model XLB-D350×350, The first rubber factory of Shanghai, Shanghai, China) at 150 °C under 4 MPa for 10 min.

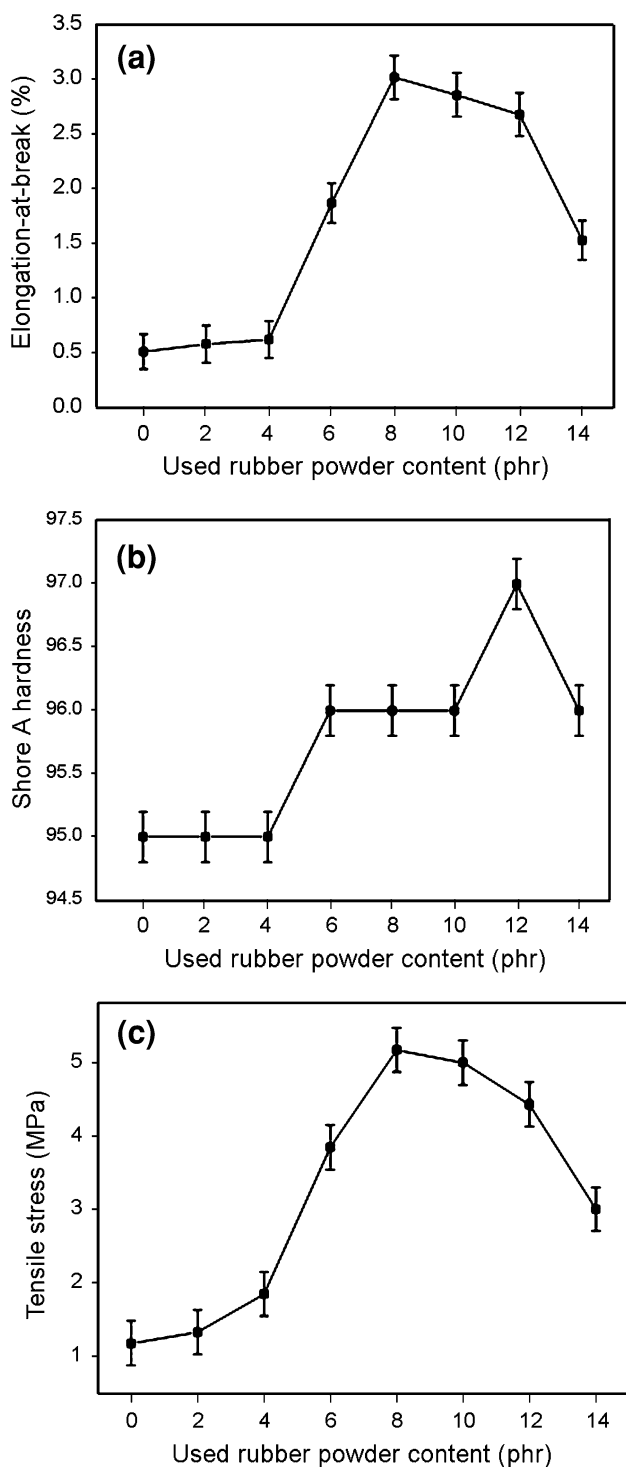
### Measurements

The dumb-bell shaped rubber specimens were prepared from a sheet of the vulcanizates by cutting. The mechanical properties were tested by an electronic universal testing machine (model CSS-2200, Zhongji Application Technical Institute, Changchun, China) according to ISO 37-1994. For each of the measurements, an average of at least five readings was taken. Errors in the measurement of mechanical properties were within 10 %. Scanning electron microscopy (SEM) (model S-4300, Hitachi Co., Japan) was used to characterize microstructure of the composites. Transmission electron microscopy (TEM) measurements were performed using a JEOL Hitachi H-7650 (Japan) electron microscope operating at an acceleration voltage of 80 kV.

## Results and discussion

### Effects of used rubber powder on the pulp sediment

Effects of used rubber powder content on the properties of pulp sediment are shown in Fig. 1. It is found that the



**Fig. 1** Effect of used rubber powder content on the mechanical properties of pulp sediments: **a** elongation-at-break, **b** Shore A hardness, and **c** tensile stress (no sawdust)

hardness changes insignificantly when the used rubber powder's content is less than 4 phr, but tensile strength is low. The properties are improved when the used rubber powder's content increased. When used rubber powder's

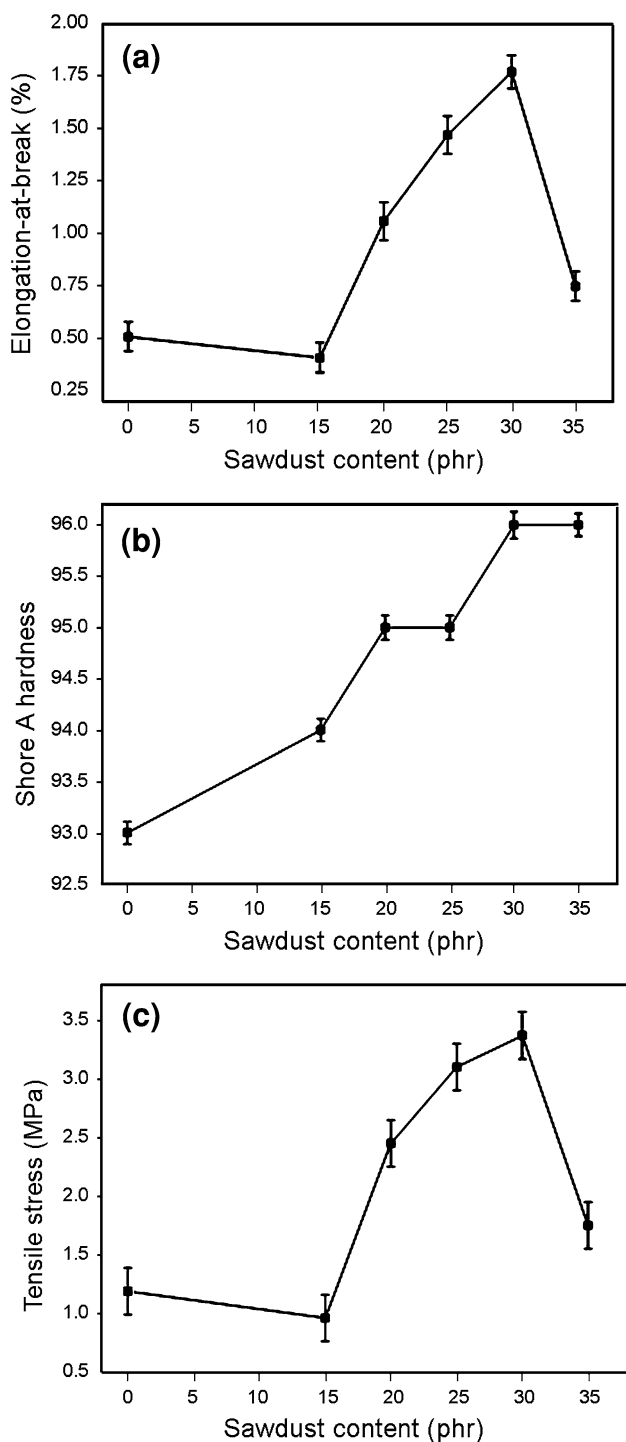
content is more than 8 phr, tensile stress and elongation-at-break of the specimens decrease gradually. Tensile stress and elongation-at-break values were highest at 8 phr used rubber powder, but hardness changes unclearly. It suggests that the properties of the used rubber powder/pulp sediment sample are good at 8 phr used rubber powder. This is due to the used rubber powder which is made of worn out rubber products (tires, rubber shoes, etc.) its main compositions are rubber and filler. Used rubber powder increases toughness of pulp sediment, and fills the gaps of pulp sediment fibers. When the contents of used rubber powder is more than 8 phr, the excess used rubber powder is able to increase the gap between pulp sediment fibers, and results in mechanical properties decline. Therefore, 8 phr used rubber powder is suitable for URP/PS composites.

#### Effects of sawdust on the pulp sediments

It was tried to use sawdust as reinforcement, the effects of sawdust on the mechanical properties of pulp sediment are shown in Fig. 2. With increasing of sawdust content, the tensile stress, elongation-at-break and Shore A hardness values of the specimens show trends in rise after restrain. When sawdust content is 30 phr, the curves present turning point. It should be considered that sawdust is powder, from which is scattered down in wood processing [23], and is similar to pulp sediment quality, therefore, its hardness does not obviously change. Because the particle diameter of sawdust is far less than that of pulp sediment, the sawdust can be filled into pulp sediment to play a role of reinforcement. When the content of the sawdust goes over 30 phr, the excess sawdust can bring about gap and decrease the interaction between wood fibers and therefore, decrease the mechanical properties of sawdust/PS samples. Thus, 30 phr sawdust was suitable for the sawdust reinforced pulp sediment.

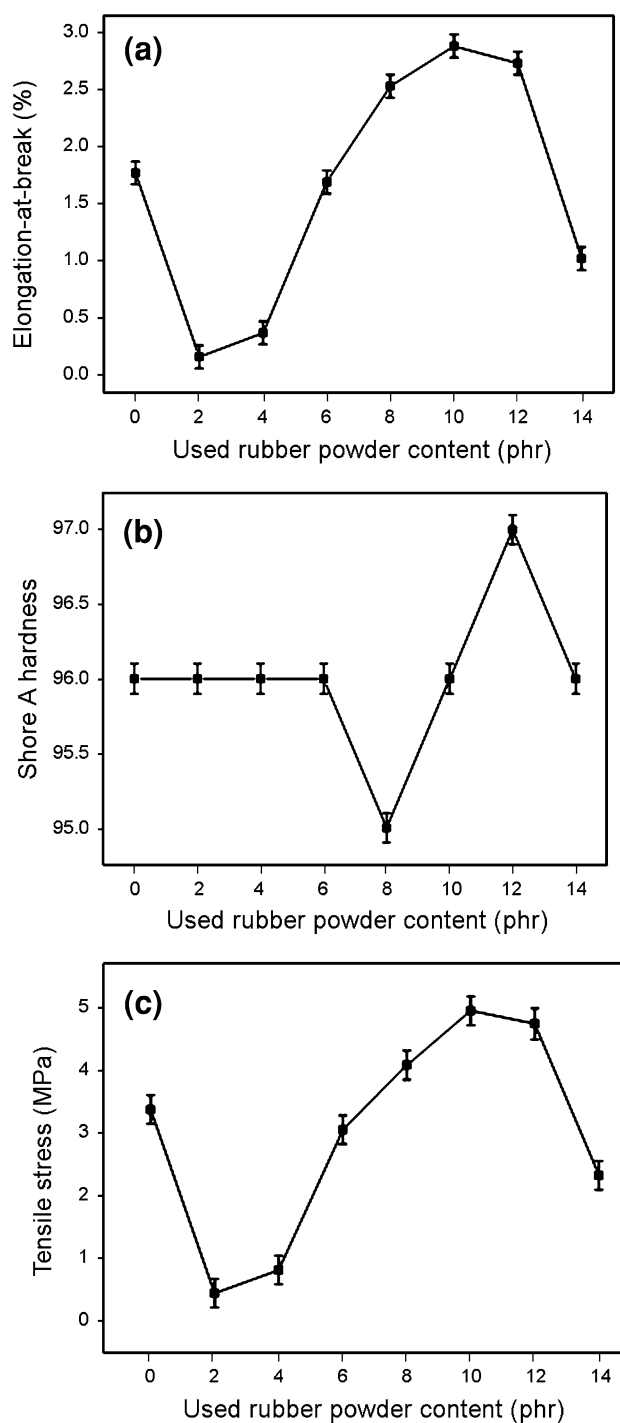
#### Effects of used rubber powder on the sawdust/pulp sediment

The used rubber powder/sawdust/pulp sediment composites were studied, in which sawdust was used as reinforcement and rubber powder as toughening phase. The results are presented in Fig. 3. It can be seen that tensile stress and elongation-at-break values of the samples show the trend in rise after restrain, and then decrease with increasing the used rubber powder content. As the amount of used rubber powder was 10 phr, both mechanical properties show maximum value on the curves, but the hardness changed very little. The reason is that sawdust and pulp sediment belong to the same kind of materials, adding sawdust equals adding pulp sediment. Compared with the URP/PS curve, the peak value for the URP/sawdust/PS



**Fig. 2** Effect of sawdust content on the mechanical properties of pulp sediments: **a** elongation-at-break, **b** Shore A hardness, and **c** tensile stress (no rubber powder)

curve was only delayed. It is the case, when 10 phr (0.08 × 130 = 10.4) of used rubber powder was added. Therefore, when the PS, sawdust, and URP are separately 100, 30, and 10 phr, respectively, the mechanical properties of sample is acceptable.



**Fig. 3** Effect of used rubber powder content on the mechanical properties of the sawdust/pulp sediments (30/100): **a** elongation-at-break, **b** Shore A hardness, and **c** tensile stress

In Figs. 1, 2, 3, it is found that mechanical properties of pure pulp sediment are poor in contrast with URP/PS and URP/sawdust/PS, but the mechanical properties of URP/PS are better than those of URP/sawdust/PS or sawdust/PS sawdust. Therefore, the best formulation is 100 phr pulp sediments and 8 phr used rubber pulp.

## Effects of curing conditions on the used rubber powder/pulp sediment

The vulcanization is indispensable in composites process, and has the important effects on the performances of the composites. The effects of curing conditions (temperature, time, and pressure) on the mechanical properties are shown in Table 1. As the melting point of curing agent is at 140 °C, the paper's flash point is 155 °C, so take curing temperature at 130–155 °C, but high temperature makes paper burn and low temperature cannot cure the sample. It can be seen that the sample properties are best at 150 °C.

When curing temperature is below 150 °C, the curing agent is not able to fully decompose, and so a little of used rubber powder cannot be cured. When curing temperature is over 150 °C, due to reaching to the burning point of the paper, the sample properties declined. Thus, the best curing temperature of URP/PS lies at 150 °C.

Similarly, when curing time is less than 15 min, PS needs long time to dry, in this period of time, URP and curing agent cure incompletely, therefore, the specimen properties are poor. When curing temperature was more than 15 min, partial dry pulp sediment was carbonized, lead to mechanical properties decline. Therefore, the best curing time is 15 min.

**Table 1** Effect of curing conditions on the properties of used rubber powder/pulp sediment

Curing condition	Shore A hardness	Tensile stress (MPa)	Elongation-at-break (%)
Temperature (°C, 4 MPa, 15 min)			
130	96	2.5	1.2
135	94	2.9	1.4
140	93	3.4	1.8
145	96	2.3	1.0
150	97	5.2	3.0
155	94	2.6	1.1
Time (min, 150 °C, 4 MPa)			
5	95	3.3	1.7
10	94	1.0	0.4
15	97	5.2	3.0
20	94	3.5	1.8
25	96	2.5	1.1
Pressure (MPa, 150 °C, 15 min)			
2	96	4.4	2.6
3	96	4.9	2.8
4	97	5.2	3.0
5	97	5.8	3.5
6	95	3.6	2.0

Pulp sediment = 100 phr, used rubber powder = 8 phr

In addition, when curing pressure was less than 5 MPa, URP and PS cannot be compacted closely and lead to the sample existing gap and structure loosening. When curing pressure is more than 5 MPa, on the one hand, it put the URP and PS together tightly, not easy heat diffusion and result in overheating char. On the other hand, the pulp fibers were ruptured under high pressure. Both would lead to decrease in properties of the sample. Thus, the best curing conditions are 150 °C, 5 MPa, and 15 min.

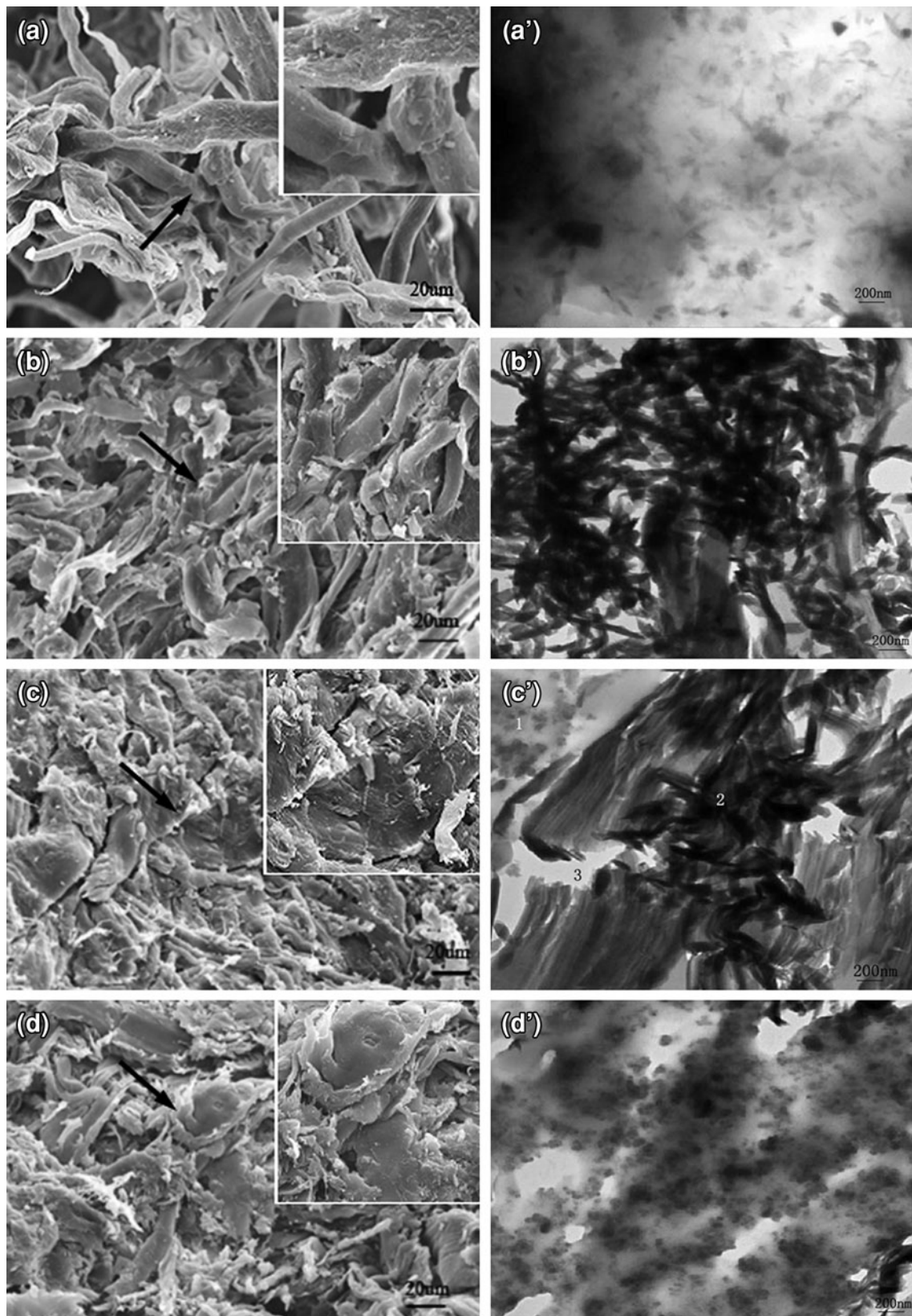
## SEM and TEM analyses

Figure 4a–d shows the SEMs of pure PS, sawdust/PS, sawdust/URP/PS, and URP/PS samples, while Fig. 4a'–d' shows TEM images of these samples, respectively. From the results of SEM and TEM images, it can be seen that the fibers in pure pulp sediment arrange disorderly in Fig. 4a, a', and there exist larger gaps and looser arrangement. Figure 4b, b' exist irregular sawdust block, small clearance, looser arrangement, and unsmooth surface on the sawdust/PS sample. Fibers in the sawdust/URP/PS arrange closely, and the sample has small gap as shown in Fig. 4c, while there exist three independent phase area such as 1 (URP phase), 2 (sawdust phase), and 3 (PS phase) in Fig. 4c'.

In Fig. 4d, there are compact structure and uniform arrangement in the sample, and better entanglement between wood fibers, while URP is evenly dispersed in the wood fiber in Fig. 4d', it may demonstrate excellent compatibility between the URP and PS. It can be explained that the fiber in the PS is longer, lead to entangling disorderly, and more and larger gaps. But the particle diameter of used rubber powder is smaller, it is easy to fill into the gap of fibers to have filler and compatibilizer function, makes sample structure compact, arrange uniform, and improve mechanical properties of URP/PS. Considering of the particle diameter of sawdust is greater than that of the URP, at the same time, sawdust and PS belong to the same kind of materials. Therefore, the compatibility of sawdust/URP/PS is worse than that of URP/PS.

## Conclusion

Used rubber powder modified PS composites were prepared and their curing conditions, mechanical properties, and morphology were investigated. It was found that when the used rubber powder/pulp sediment mass ratio was 8/100, the used rubber powder/pulp sediment sample has smooth surface, high hardness, compact structure, uniform arrangement, and good compatibility. When the pulp sediment used as the matrix, sawdust as the reinforcement and used rubber powder as the toughening agent, the proper recipe of the composites was 100 phr pulp sediment,



**Fig. 4** SEM micrographs of: **a** Pure pulp sediments; **b** 100 phr pulp sediments and 30 phr sawdust; **c** 100 phr sediments, 30 phr sawdust, and 10 phr used rubber powder; and **d** 100 phr pulp sediments and

8 phr used rubber powder, and TEM micrographs (**a'**, **b'**, **c'**, and **d'**) of the same specimens

30 phr sawdust, and 10 phr used rubber powder. Mechanical properties of the used rubber powder/pulp sediment were greater than those of pure pulp sediment and used rubber powder/sawdust/pulp sediment. The best curing conditions for the used rubber powder/pulp sediment composites are at 150 °C under 5 MPa for 15 min. The study on used rubber powder modified pulp sediment exploits a new way to recycle used rubber powder and pulp sediment, not only benefits environment refinement, but also reduces cost of sheet materials, and develops a new way for the economy and environment protection.

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