
Effects of Plant Polyphenols on the Interface and Mechanical Properties of Rubber/Silica Composites

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SUMMARY

Based on the abundant surface hydroxyl groups of plant polyphenols and their tendency for complexation with metal ions, a facile and green approach to improve the interfacial interactions between silica and a rubber matrix is proposed. The interface interactions of plant phenols with silica and Zn ions are characterized by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The results suggest that, with the introduction of plant phenols, strong interface interaction between rubber matrix and silica can be formed through hydrogen bonding and chelating effects. The investigation of mechanical performance of the composites indicates that the proposed approach produces remarkable reinforcing effects on the rubber matrix.

Keywords: Polyphenols, Interface, Hydrogen bonding, Chelating, Rubber, Reinforce

1. INTRODUCTION

It is well recognized that for rubber/filler composites the interface between the rubber and fillers plays a crucial role for the properties of the rubber composites¹⁻². However, due to the great difference of polarity, the compatibility of rubber and filler is usually very poor and, therefore, weakens the reinforcing effects of the filler³⁻⁴. As a consequence, many methods and processes, such as filler surface treatment by coupling agent, rubber modification, etc., have been utilized to improve the interface and mechanical performance of rubber composites^{4,5-10}.

Plant polyphenols, known as vegetable tannins, are complex phenolic secondary metabolites of plants¹¹. According to their different chemical structure, plant polyphenols can be divided into two basic types,

hydrolysable tannin (and esters of polyphenols) and condensed tannins (polyphenols poly flavanols). Although they have a different skeleton of unit constitution, both of the molecular structures have some general characters, such as abundant adjacent phenolic groups, high molecular weight and wide distribution, which endow them with versatile properties, including anti-oxidant ability¹²⁻¹⁴, reaction with protein and alkaloid¹⁵⁻¹⁸, complex reaction with metal ions¹⁸⁻¹⁹ and so on. Recently, more and more researches related to plant polyphenols have been reported²⁰⁻²¹. However, applications of plant polyphenols for the reinforcement of interfacial interactions between rubbers and fillers have not been found.

In this paper, due to the high surface activity of plant polyphenols (abundant surface hydroxyls and tendency

for complexation with metal ions), we utilized plant polyphenols to reinforce the compatibility of rubbers and silica to improve the mechanical performance of rubber composites. The interfacial interactions in rubber/silica composites and their effects on the mechanical performance of the rubber matrix were investigated.

2. EXPERIMENTAL

2.1 Materials

Styrene butadiene rubber (SBR), with brand of 1502, was purchased from Jilin Petrochemical Company of China Petroleum.

Natural rubber (NR) (STR 5L) was manufactured by Thailand.

Precipitated silica was provided by Zhuzhou Xinglong Chemical Industry Co., Ltd.

Tea polyphenols (TP) product was provided by Xuancheng Baicao Plants Industry and Trade Co., Ltd.

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Tannic acid (TA) was purchased from Zunyi Linyuan Pharmaceutical Chemical Co., Ltd.

Dibenzothiazole disulfide (DM), tetramethyl thiuram disulfide (TT), N-isopropyl-N'-phenyl-p-phenylenediamine (4010NA), sulfur (S), zinc oxide (ZnO), stearic acid (SA) and other additives were commercial products, and were used as received.

2.2 Preparation of the Rubber/Silica Composites

Rubber composites were prepared through traditional mixing and curing process. The rubber matrix, silica, plant polyphenols and other additives were compounded with a two-roll mill. Then the optimum cure time (T_{90}) was determined by a disc rheometer and compression moulded at 143 °C (NR) and 160 °C (SBR), respectively. The basic formula of the study was as follows: Rubber, 100 phr, Silica, 30 phr; DM, 2.5 phr; TT, 0.5 phr; 4010NA, 1.5 phr; S, 2.5 phr; ZnO, 5.0 phr; SA, 1.0 phr.

2.3 Preparation of Silica/Plant Polyphenols Model Compounds

30 g silica and 2.5 g plant polyphenols were mixed in the high-speed multi mill (the speed is 29000 rpm) for 1 minute, then put in the oven for 10 minutes at the curing temperature.

2.4 Preparation of ZnO/TP Model Compounds

5 g ZnO and 2.5 g TP were mixed with the high-speed multi mill (the speed is 29000 rpm) for 1 minute, followed by a heat of curing temperature for 10 minutes.

2.5 Characterization

2.5.1 Strain-stress Performance Determinations

Instron 3367 universal testing machine was used to perform the tensile strength of rubber/silica composites according to ISO 37: 1994.

2.5.2 Attenuated Total Refraction Fourier Transform Infrared Spectroscopy (ATR-FTIR)

All the samples were sheet moulded to small discs with diameter of 10 mm and thickness of 2 mm, then the little discs were analyzed by a 5700 Fourier transform infrared spectrometer (Nicolet). Thirty-two consecutive scans were taken at each sampling time, and their average was stored. Spectra were taken from 4000 to 400 wavenumbers (cm^{-1}).

2.5.3 X-ray Photoelectron Spectroscopy (XPS)

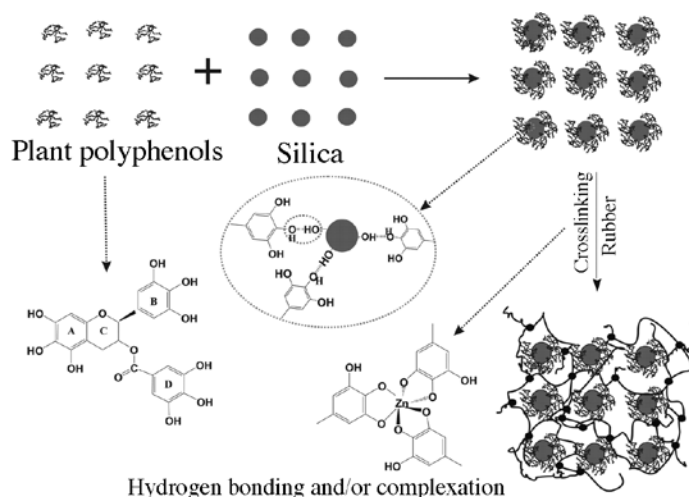
X-ray photoelectron spectra of silica, plant polyphenols and their model compounds were recorded by using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an aluminium (mono) $K\alpha$ source (1486.6 eV). The aluminium $K\alpha$ source was operated at 15 kV and 10 mA. For all the samples, a low-resolution survey run (0-1100 eV, pass energy = 160 eV) was performed. In order to obtain more information about the formation of hydrogen bonding and/or complexation, a high-resolution survey (pass energy = 48 eV) was performed in spectral regions relating to oxygen.

3. RESULTS AND DISCUSSION

3.1. Construction and Characterization of the Interface Between Silica and Rubber Matrix

Most inorganics are hydrophilic and possess hydroxyl groups on their surfaces²²⁻²³ and the hydroxyls could be used for the formation of hydrogen bonding¹⁹. The facile and green approach proposed in this paper to improve the interfacial interactions between silica and rubber matrix, is schematically illustrated in **Figure 1**. In this approach, due to the hydrogen bonding between the multiple phenolic hydroxyls and the hydroxyl groups on the surface of silica, plant phenols with much more activity are "coated" onto the surface of silica. Then in the vulcanization process, chelating interactions will occur between the phenolic hydroxyls and zinc ions in the vulcanization compositions. Therefore, through the hydrogen bonding interaction and chelating effects, stronger interface interaction between rubber matrix and silica can be formed to enhance the mechanical properties of the final composite.

Figure 1. Schematic diagram of the interface construction between silica and rubber matrix



As the rubber matrix will interfere with the ATR-FTIR and XPS of silica and plant polyphenols, direct characterization of interfacial reactions in rubber/silica vulcanizates is rather difficult. As a consequence, silica/plant polyphenols model compounds are prepared to characterize the hydrogen bonding between silica and tea polyphenols. The ATR-FTIR of TP, silica and silica/TP model compounds is shown in **Figure 2**. As shown, the strong absorption peak around 1111 cm^{-1} observed in the spectrum of silica is assigned to the Si-O stretching vibration peak²⁴. However, for the FTIR spectra of silica/TP polyphenols model compounds, a blue shift of about 31 cm^{-1} for the absorption of Si-O stretching vibrations is observed, which is ascribed to the strong interface interaction resulting from the hydrogen bonding between silica and TP. **Figure 3** shows the ATR-FTIR spectra of TA, silica and silica/TA model compounds. Similarly, the absorption around 1110 cm^{-1} in silica is assigned to the Si-O stretching vibration peaks and the absorption peak blue shifted in model compounds due to the strong interface interaction resulting from the hydrogen bonding between silica and TP. In addition, a bigger blue shift of 17 cm^{-1} is seen in silica/TA model compounds at $160\text{ }^{\circ}\text{C}$ than that in silica/TA model compounds at $143\text{ }^{\circ}\text{C}$, indicating that the higher the temperature, the bigger the strong absorption peak of Si-O shifts, and the stronger hydrogen bonding interactions between silica and plant polyphenols.

In the chemical analysis of surface and interface, XPS is one of the most effective methods, through which we can get the information about material surface construction elements and the state of chemical combination by measuring the surface layer of material (about 10 nm)²⁵. In order to further substantiate the formation of hydrogen bonding between silica and plant polyphenols in the rubber/silica composites, XPS experiments on the model compound, the TP and silica

were performed. As shown in **Figure 4**, compared with the binding energy of Si atoms and O atoms in silica and in TP, respectively, there is a significant shifting of 0.3 eV and 0.2 eV in model compounds, respectively, indicating the change of chemical environment of Si atoms and O atoms in the silica/TP model compounds. We believe that this change results from hydrogen bonding, where Si atoms and O atoms are involved. **Figure 5** shows the high resolution XPS spectra of Si atoms in silica and silica/TP model mixture. As shown, the binding energy of Si

atoms in silica is 103.4 eV . However, their binding energy shifts to 103.7 eV in silica/TP model mixture, which also suggests that the Si atoms really participate in the hydrogen bonding in silica/plant polyphenol model compounds.

In order to better reveal the change of binding energy of O atoms in silica/tea polyphenol model compounds, the spectrum of O atoms in the silica/TP model compounds was deconvoluted using ORIGIN 7.5 software into two peaks, locating at 532.7 eV and

Figure 2. ATR-FTIR spectra of silica, TP and silica/TP model mixture

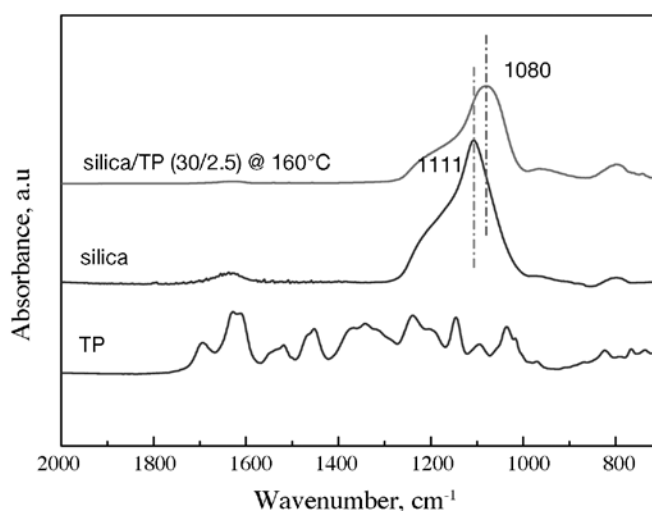


Figure 3. ATR-FTIR spectra of silica, TA and silica/TA model mixture

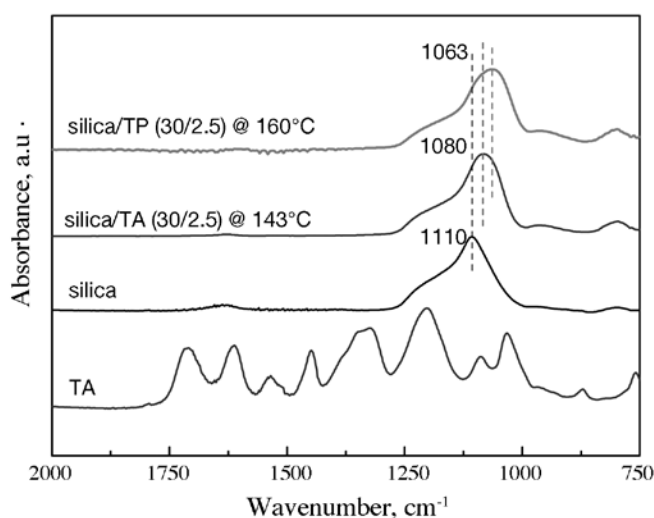


Figure 4. The low-resolution XPS scanning spectra of silica (a) TP (b) and silica/TP model compounds (c)

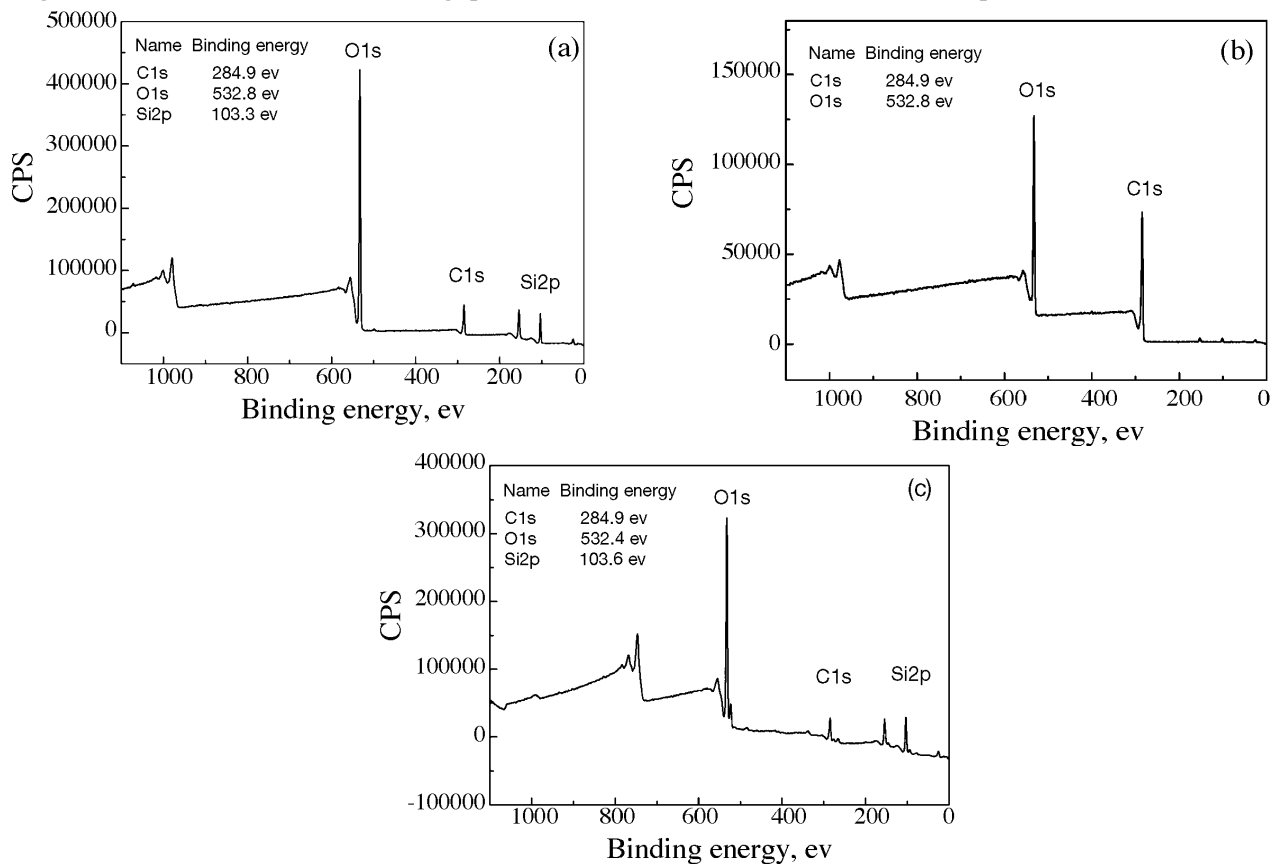
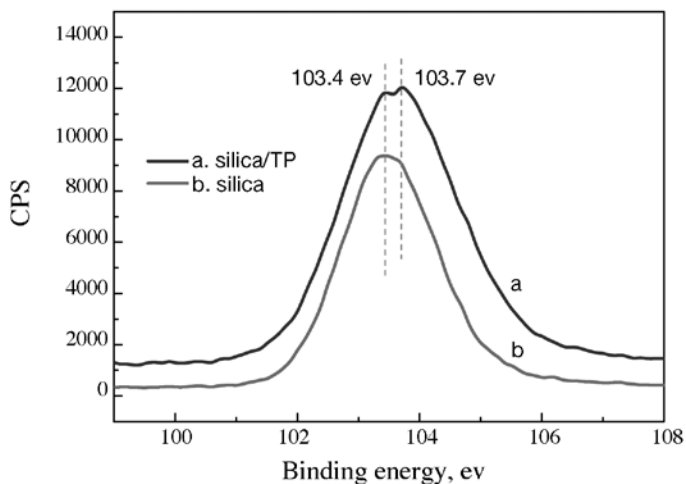


Figure 5. High resolution XPS spectra of Si atoms in silica and silica/TP model compounds



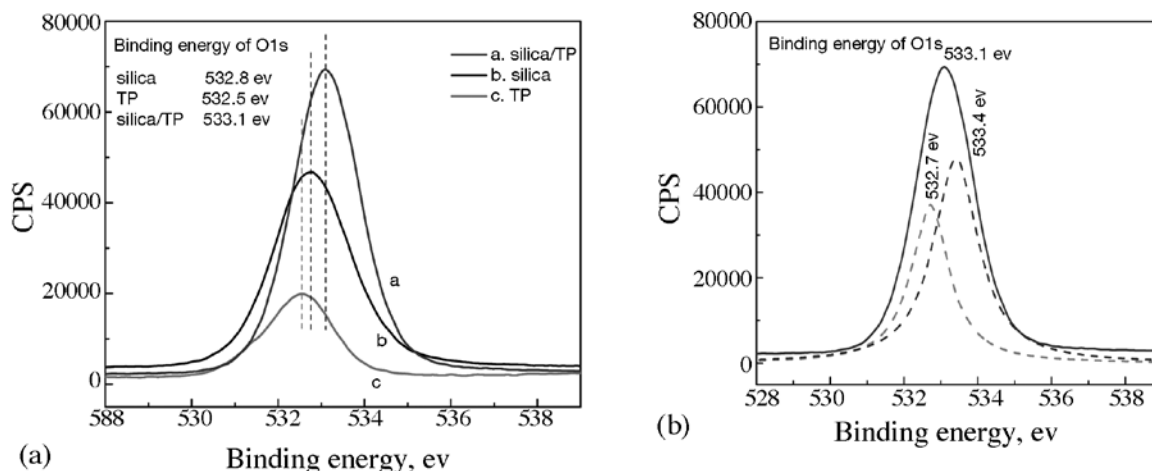
533.4 eV, according to the two kinds of chemical environment in the model compounds, which is attributed to the O1s in TP and silica respectively. Compared with the binding energy of O1s in TP and silica, a shift of 0.2 eV and 0.3 eV occurred for that of O1s

in the silica/TP model compounds, indicating the hydrogen bonding between silica and TP.

Many researchers have found that TP are able to form complexes by chelating with metal ions (Cu²⁺, Pt⁴⁺ and

Pd²⁺, etc.)^{18,19,26}, so it is supposed that stable multi-ring complexes will be formed by the chelating effects between TP and zinc ions. As the chelating reaction will occur between the O atoms and Zn atoms and induce the change of the bonding energy of the two type atoms, the XPS survey was performed to verify the chelating reaction between TP and zinc ions. As shown in Figure 7, the binding energy of O atoms in TP and ZnO is 530.9 eV and 530.0 eV, respectively. However, the binding energy of O atoms in the model compounds shifts to 530.3 eV. According to the two different kinds of chemical environment in model compounds, the spectrum of O atom in the model compounds was processed using ORIGIN 7.5 and XPS Peak Fit software. The peaks at 531.2 eV and 530.3 eV are assigned to the O atoms in TP and ZnO, respectively. Compared with that in TP and ZnO, it can be seen that both the binding energy of O atoms in the model compounds changed evidently, indicating the

Figure 6. High resolution XPS spectra of O atoms in silica, TP and silica/TP model compounds (a) and in the silica/TP model compounds after deconvolution (b)



chelating reaction between TP and ZnO. The binding energies of Zn in ZnO and the model compounds are shown in **Figure 8**. Similarly, the binding energy of Zn in the model compounds is deconvoluted into two peaks, locating at 1021.1 eV and 1021.5 eV, respectively. The chemical shift of 0.4 eV suggested that part of the Zn atoms are involved in the chelating reaction with TP. As a consequence, we believe that the chelating reaction between TP and ZnO will enhance the interface interaction between ZnO and rubber matrix.

3.2 Effects of Plant Polyphenols on the Mechanical Properties of Rubber/Silica Composites

To further verify the effect of the plant polyphenols on the interfacial regions of the rubber/silica composites, the mechanical properties of rubber/silica composites are researched. The influence of TP on the mechanical performance of SBR/silica composites is shown in **Figure 9**. As shown, with the incorporation of TP, the tensile strength of SBR/silica composites is continuous growing. When TP content is 10 phr, the tensile strength reaches the maximum value of 15.19 MPa. Similarly, **Figure 10** shows the effect of TA on the mechanical performance of SBR/silica composites. As shown, with

Figure 7. High resolution XPS spectra of O atoms in ZnO and model compound

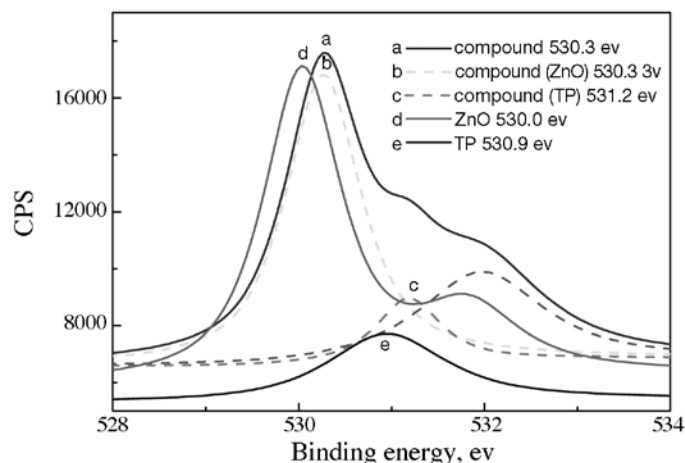


Figure 8. High resolution XPS spectra of Zn atoms in ZnO and model compound

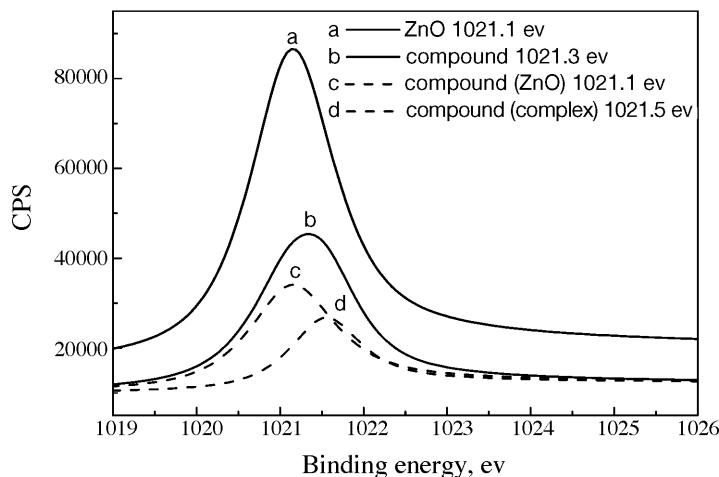


Figure 9. Effects of TP on the mechanical performance of SBR/silica composites

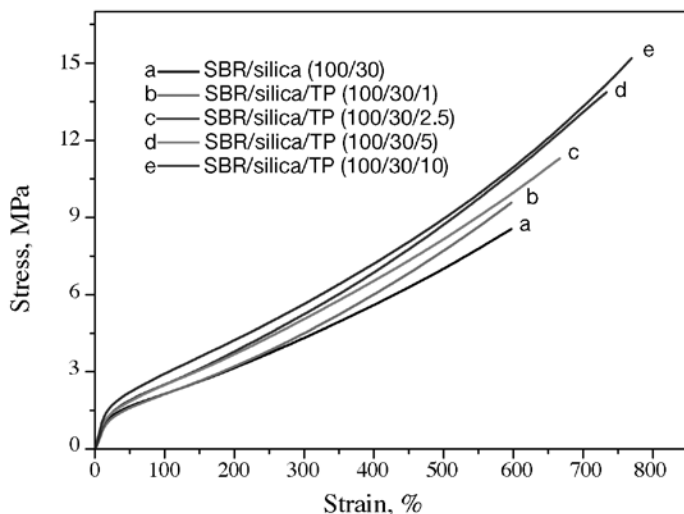


Figure 10. Effects of TA on the mechanical performance of SBR/silica composites

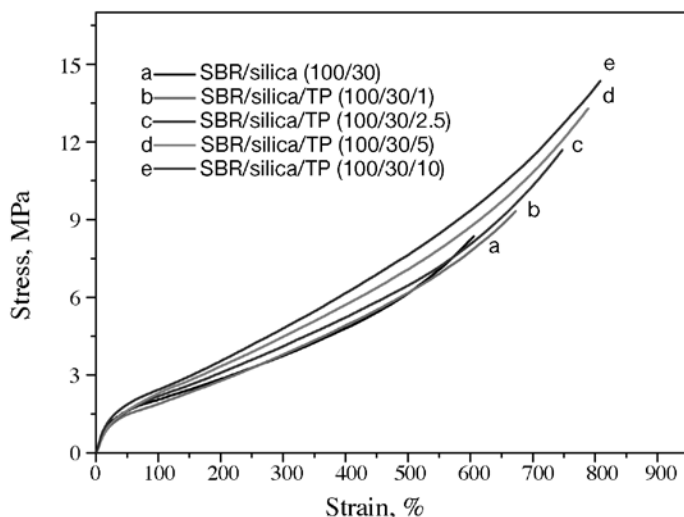
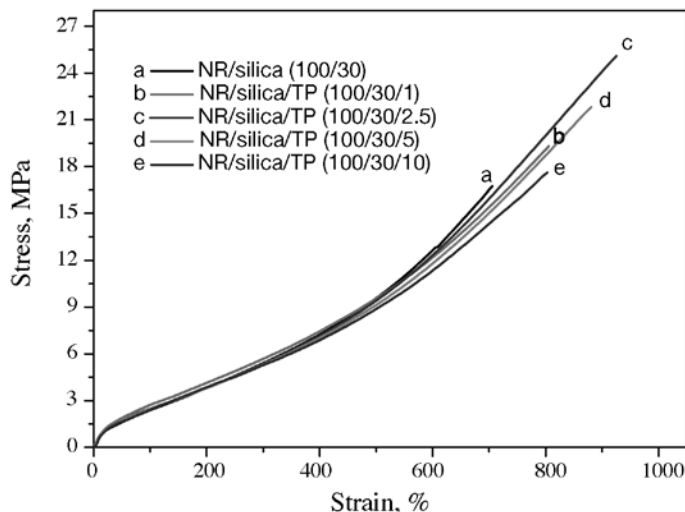


Figure 11. Effects of TP on the mechanical performance of NR/silica composites



the addition of TA, the tensile strength of SBR/silica composites is enhanced from 7.36 MPa to 14.35 MPa. In addition, both **Figure 9** and **Figure 10** show that with the inclusion of plant polyphenols, the elongation at break of the composites increases obviously.

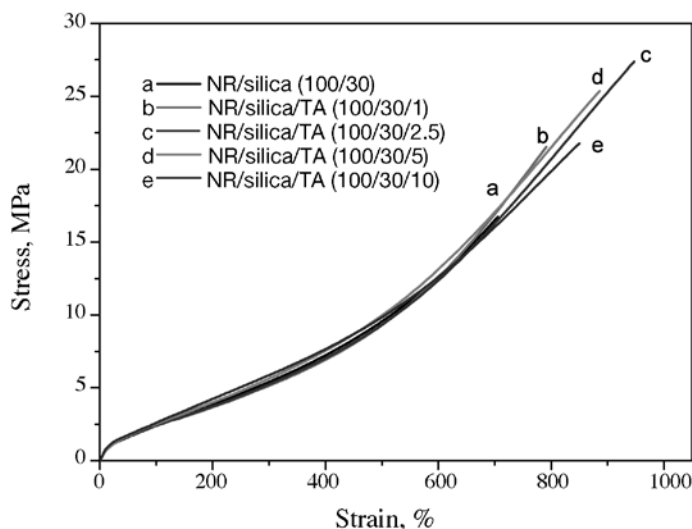
Effects of TP and TA on the mechanical performance of NR/silica composites are shown in **Figure 11** and **Figure 12** respectively. As shown in the figure, similarly to the results of SBR composites, TP and TA exhibit obviously reinforcing effects to NR. Both the tensile strength and elongation at break of NR/silica composites remarkably increases to the maximum value and then decreases slowly with the incorporation of TP or tannic acid.

In summary, both the tensile strength and the elongation at break of the rubber composites are enhanced obviously after TP or TA is added. It is believed, as described above, strong interface interaction between rubber matrix and silica can be formed with incorporation of the TP or TA through hydrogen bonding and chelating effects, resulting in the obviously increased mechanical properties.

4. CONCLUSIONS

A facile and green approach was proposed to improve the interfacial interactions between silica and rubber matrix based on the abundant surface hydroxyls and tendency of complexation with metal ions of plant polyphenols. The interface interactions of plant phenols with silica and Zn ions were characterized by ATR-FTIR and XPS and discussed. The results suggested that, with the introduction of plant phenols, strong interfacial interaction between rubber matrix and silica could be formed through hydrogen bonding and chelating effects. The investigation of mechanical performance of the composites indicated that the proposed approach exhibited remarkable reinforcing effects on the rubber matrix.

Figure 12. Effects of TA on the mechanical performance of NR/silica composites



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