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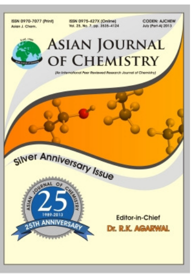

Modification and Application of Waste Rubber Powder†

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The surface of waste rubber powder was modified by maleic anhydride and styrene *via* an ultraviolet treatment. Modified waste rubber powder/natural rubber composites were prepared. Modified waste rubber powder were characterized by scanning electron microscope and thermogravimetric analysis. The effects of content of modified waste rubber powder and mass ratio of styrene-maleic anhydride on tensile strength of composites were investigated. The results show that maleic anhydride and styrene have been successfully grafted onto the surface of waste rubber powder. Better compatibility between modified waste rubber powder and natural rubber is responsible for the enhancement of tensile strength of composites.

Key Words: Waste rubber powder, Natural rubber, UV grafting, Tensile strength.

INTRODUCTION

The generation rate of waste rubber has increased dramatically in the past two decades. The accumulation of large quantities of waste rubber has brought about serious environment problems. The waste rubber was ground into a powder, which was a main method to utilization and recycling. In general, the addition of waste rubber powder to polymer will cause considerable deterioration of the mechanical properties because of low compatibility and poor interfacial adhesion between the waste rubber powder and polymer[1]. The surface of waste rubber powder must be modified in order to enhance the miscibility between waste rubber powder and polymer matrix.

Photografting of monomer onto waste rubber powder using UV was a simple and efficient method[2]. In this study, photografting of maleic anhydride and styrene onto waste rubber powder was carried out to modify the surface characteristics of the waste rubber powder and surface-modified waste rubber powder was blended with natural rubber.

EXPERIMENTAL

Styrene was obtained from Tianjin Damao Chemical Reagent Co. Ltd., was washed with 5 wt % NaOH solution and dried with Na_2SO_4 before use. Maleic anhydride was obtained from Shanghai Pharmaceutical Group Chemical Reagent Co. Ltd., Benzophenone was obtained from Sinopharm Chemical Reagent Co. Ltd. Acetone was obtained from Wuxi Yasheng Chemical Reagent Co. Ltd. All reagents were of analytical grade. Waste rubber powder was provided by Hangzhou Baoli Materials Recycling Co. Ltd. of particle size 100 meshes (150 μm). Waste rubber powder was extracted with acetone, washed with 5 wt % sodium hydroxide solution, 10 wt % hydrochloric acid and distilled water in turn and finally dried under vacuum to constant weight[1]. Nature rubber (SCR5) was produced by Nanjing Meixin Traffic Material Co. Ltd. Other rubber ingredients were of commercial grade.

Waste rubber powder, maleic anhydride (10 wt %), benzophenone (9 wt %) were immersed in 50 mL acetone with stirring for 1 h. After immersion, the waste rubber powder was dried for 3 h at ambient temperature to remove acetone. The dried waste rubber powder was placed in a beaker and UV-irradiated for 10 min under high-speed mixing conditions and a nitrogen atmosphere. Modified waste rubber powder was washed with acetone and distilled water to remove the ungrafted components and dried at 80 ºC for 24 h. A 400-W medium-pressure mercury lamp was used for the photografting reaction. Preparation of modified waste rubber powder/NR composites: The compound recipes were listed: NR (100 phr), zinc oxide (6 phr), stearic acid (1 phr), accelerant CZ (0.7 phr), accelerant TMTD (0.3 phr), antioxidant 4010NA (1.5 phr), plasticizers (2 phr), carbon black (60 phr), sulfur (2.5 phr). The composites were prepared by open mill for 25 min. The compounds were then compression molded into 2 mm thickness sheets by 145 ºC for 7 min.

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Detection methods: SEM analysis was carried on the scanning electron microscopy machine (Hitachi, S-3000 N, Japan) at an accelerating voltage of 15 Kv.TGA studies were performed with the thermogravimetric analyzer (TA instruments, SDT2960, USA). Tensile strength were tested on test machine (KQL instruments, WDW-50, CHINA) at 25 mm/min stretch speed, according to the GB/T528-1998 standard.

RESULTS AND DISCUSSION

SEM analysis: Fig. 1 shows the scanning electron microscope photographs of the unmodified waste rubber powder and modified waste rubber powder. Morphology of modified waste rubber powder changes obviously as compared to unmodified waste rubber powder. In Fig. 1a, unmodified waste rubber powder shows an regular aggregate structure, an smooth surface. In Fig.1b, the surface of modified waste rubber powder becomes unsmooth and has distinct cracks. The results indicate that the encapsulation of waste rubber powder by maleic anhydride and styrene chains is achieved.

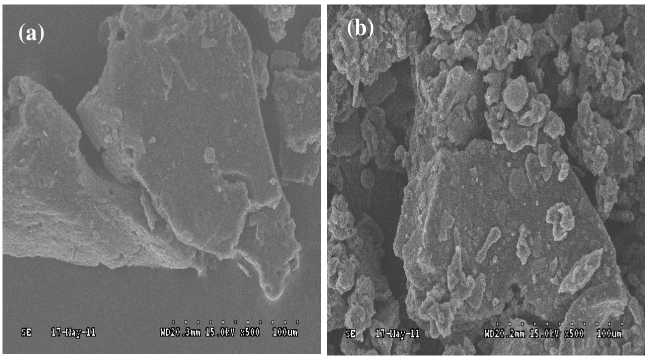

Fig. 1. SEM photographs of: (a) unmodified waste rubber powder and (b) modified waste rubber powder (MAH monomer content 10 wt %, mass ratio of St-MAH 0.8)

Fig. 2 shows the fractured surface of composites. It is observed that many waste rubber powders still remain on the fractured surface of the modified waste rubber powder-filled composites, while few waste rubber powders are found in the unmodified waste rubber powder-filled composites. The fractured surface morphology difference of the two samples is dependent on the existence of an interfacial reaction between the modified waste rubber powder and NR[2].

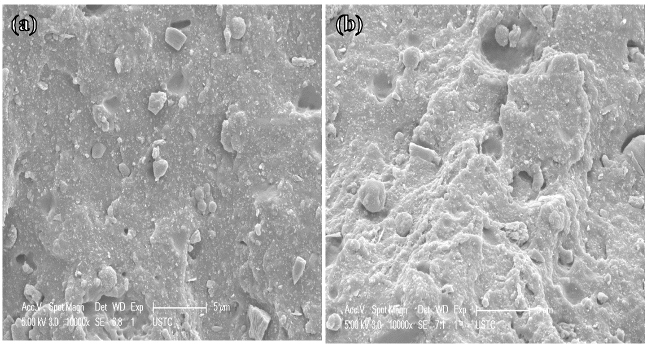

Fig. 2. SEM photographs of fractured surface of: (a) 10 wt % unmodified waste rubber powder/natural rubber and (b) 10 wt % modified waste rubber powder/natural rubber composites (MAH monomer content 10 wt %, mass ratio of St-MAH 0.8)

Thermogravimetric analysis: Fig. 3 shows the TGA for unmodified and modified waste rubber powder. The tests were performed in the temperature range between room temperature and 700 ºC at a heating rate of 10 ºC/min in an atmosphere of nitrogen, flowing at 10 mL/min. A sample of 5-10 mg of the materials was heated in the sample pan. The initial degradation start at 200 ºC, 196 ºC for unmodified and modified waste rubber powder, which may be due to the degradation of low molecular weight molecules like plasticizers. The thermal degradation of low molecular weight substances occurs at low temperature due to its migration onto the surface[3,4]. The results show that the thermal stability of waste rubber powder is almost no change by grafting modification. In addition, the residual weight (%) of unmodified and modified waste rubber powder from the TGA curves tends toward stability at 600 ºC and their weight (%) are 10.6 %, 10.4 %, respectively.

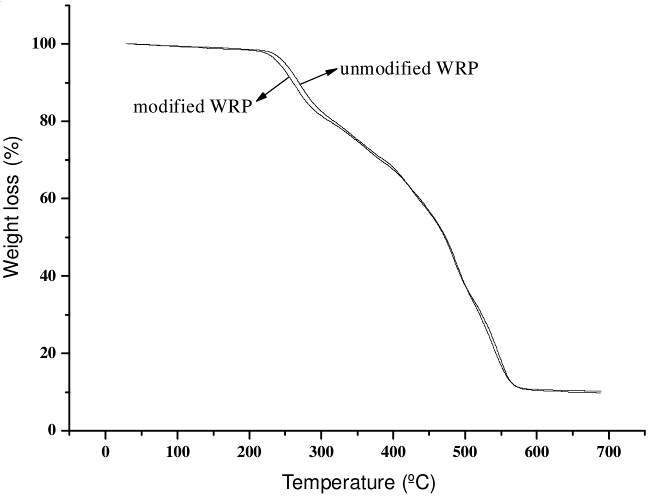

Fig. 3. TGA curves of unmodified waste rubber powder and modifified waste rubber powder (MAH monomer content 10 wt %, mass ratio of St-MAH 0.8)

Effect of mass ratio of styrene-maleic anhydride on tensile strength: When other conditions remain unchanged (modified waste rubber powder content 10 wt %) from Fig. 4, it is revealed that the tensile strength first increases and then decreases with the increase of the mass ratio of styrene/maleic anhydride and reaches a maximum when the mass raito of styrene/maleic anhydride is 0.8. The larger difference as the polarity of the two monomers of styrene and maleic anhydride and $r_1 = 0.04$, $r_2 = 0.015$, $r_1 \times r_2 \rightarrow 0$ prone alternating copolymerization reaction. Modified waste rubber powder and natural rubber have a good compatibility, interaction is enhanced, thereby tensile strength of composites increases. When the mass ratio styrene/maleic anhydride is greater than 0.8, consumption of small content monomer is completed, homopolymerization of excess monomer may become a stress concentration in the composites, tensile strength of composites decreases.

Effect of content of modified waste rubber powder on tensile strength: The effect of content of modified waste rubber powder on tensile strength are shown in Fig. 5. Tensile strength increases first and then decreases with the content of modified waste rubber powder. Tensile strength of the composites

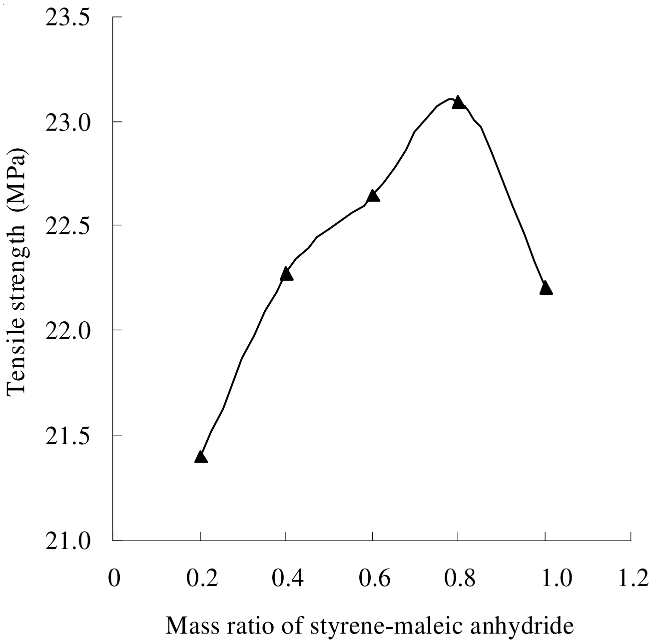

Fig. 4. Effect of mass ratio of St-MAH on tensile strength of composites (MAH monomer content 10 wt %,modified WRP 10 wt %)

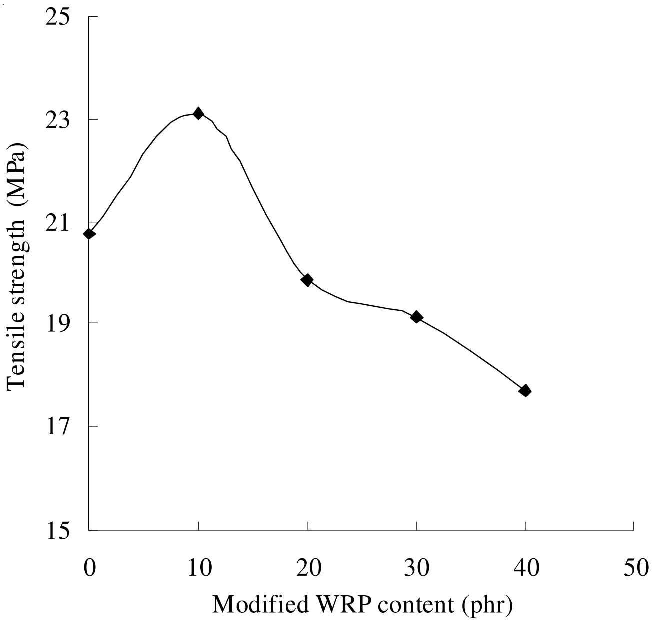

Fig. 5. Effect of content of modified WRP on tensile strength of composites (MAH monomer content 10 wt %, mass ratio of St-MAH 0.8)

is increased at the 10 wt % modified waste rubber powder loading to a maximum value of 23.09 MPa. It can give a good indication to the interfacial bonding between modified waste rubber powder and NR[5].

Conclusion

Maleic anhydride and styrene can be grafted onto the surface of waste rubber powder. UV was used for photografting and photoinitiator used was benzophenone. The surface properties of the unmodified and modified waste rubber powder were investigated by SEM and TGA. SEM results indicate that the surface of modified waste rubber powder becomes unsmooth and has distinct cracks, whereas unmodified waste rubber powder shows smooth surface. TGA analyses indicate that the thermal stability of modified waste rubber powder is almost no change. Tensile strength of composites is best for 10 wt % modified waste rubber powder loading, mass ratio of styrene-maleic anhydride is ~ 0.8.

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