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ORIGINAL PAPER

Graft polymerization of styrene onto waste rubber powder and surface characterization of graft copolymer

Jin Long Zhang · Hong Xiang Chen · Chang Mei Ke ·
Yu Zhou · Hui Zhen Lu · Dao Long Wang

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Abstract The surface of waste rubber powder (WRP) was graft-modified with styrene (St) by bulk polymerization method. The effects of styrene content, initiator mass, time of reaction, and temperature on the graft efficiency were investigated. The results showed that the graft efficiency (%) was highest when 89 wt% styrene and 0.11 g of initiator were added for reaction time of 25 h at 85 °C. The surface of graft-modified rubber powder was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), energy dispersive X-ray (EDXS) analysis, and thermogravimetric (TG/DTG) analysis. The results showed that polystyrene (PS) was grafted onto waste rubber powder, which formed a WRP/PS core–shell structure.

Keywords Waste rubber powder · Graft polymerization · Polystyrene · Surface

Introduction

The generation rate of waste tire rubber has increased dramatically with the rapid development of vehicles in the past two decades [1, 2]. The accumulation of large quantities of waste tire has brought about serious environment problems. The waste tire rubber is ground into a powder, which is a main method to utilization and recycling of waste tire rubber in large scale.

With a view of expanding the applications of WRP, the utilization of WRP by means of blending with polymeric materials has become an important topic [3–5]. The main advantages of polystyrene (PS) are its good transparency, high stiffness, excellent processibility, and good dielectric properties, etc. However, its

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J. L. Zhang · H. X. Chen (✉) · C. M. Ke · Y. Zhou · H. Z. Lu · D. L. Wang
Hubei Key Laboratory of Coal Conversion and New Carbon Material, College of Chemical Engineering and Technology, Wuhan University of Science and Technology, Wuhan 430081, China
e-mail: chenhx_916@hotmail.com

disadvantage is low impact strength at low temperature. WRP-filled polymer partially retains the cost reduction and processability of polymers, with improvement in the impact resistance. The interfacial adhesion between the dispersed rubber particles and the polymer matrix plays an important role in the toughening of polymer [6]. In general, the addition of WRP to polymer will cause considerable deterioration of the mechanical properties because of low compatibility and poor interfacial adhesion between the WRP and polymer [7]. The surface of WRP must be modified in order to enhance the miscibility between WRP and polymer matrix. The surface of WRP can be modified by chemical oxidation, radiation, gas modification, and graft polymerization, etc. Surface functionalization of WRP by oxidation treatment such as potassium permanganate [7], nitric acid [8], sulfuric acid [9], and hydrogen peroxide [10], resulted in an increase of the polar group on the surface and a good adhesion of WRP and the polymer matrix. Feng et al. [11] and Kim et al. [12] reported the surface modification of WRP with ultrasound, Hunt [13], Scuracchio et al. [14], Tyler and Cerny [15], and Novotny et al. [16] applied microwave to modify the surface of WRP, Sonnier et al. [7] and Hassan [5], et al. used γ-ray to modify WRP, and Li et al. [17] developed plasma treatment of WRP. The studies showed the number of polar groups on the surface of WRP increased, physical or chemical properties of WRP were varied after radiation. Tan et al. [18], Naskar et al. [3], Wu et al. [19] reported that WRP was modified by chlorination, and Lee et al. [2] attempted to modify the WRP surface by ozone. The results showed that these treatments improved the compatibility between WRP and polymer matrix, and enhanced the properties of composites. The above-mentioned treatment methods could improve the surface activity of WRP, but the modifications were lack of selection aiming at the structure of polymer substrate. On the contrary, the selective modification can be obtained with graft polymerization.

To improve the miscibility and interfacial adhesion between PS matrix and WRP, WRP will be graft modified with styrene, grafting of PS onto WRP will form a package structure, and hence can toughen polystyrene. Tuchman and Rosen [20] reported that the impact strength of polystyrene was improved by grafting a small amount of styrene onto waste rubber powder, but the polymerization reaction was not investigated in details. A method was patented by Freeguard [21] to prepare styrene/rubber powder graft copolymer, but only a few details about graft polymerization was discussed and it was not sufficient in characterization of graft copolymer. Pittolo and Burford [22] reported the polymerization reaction of rubber powder and styrene by different initiators and mechanical properties of composite, but there was not surface characterization about graft product. Coiai et al. [23, 24] investigated the grafting PS onto the surface of rubber powder, but the reaction time and temperature were not discussed.

In this work, WRP was graft modified by polystyrene chain covalently bound to the surface of WRP. Graft copolymerization via a free radical polymerization was investigated using dibenzoyl peroxide (BPO) initiator. The effects of styrene content, initiator (BPO) mass, time of reaction, and temperature on the graft efficiency were discussed, respectively. The surface structure of grafted WRP was characterized by FTIR, SEM, EDXS, and TG/DTG.

Experimental

Materials

Styrene (Tianjin Guang Cheng Chemical Co., Ltd, China) was washed with 5 wt% NaOH solution and dried with Na_2SO_4 before use. Dibenzoyl peroxide (Shanghai Shan Pu Chemical Co., Ltd, China) was recrystallized from methanol. The average particle size of WRP (Jilin Huadian, China) was determined to be 134.8 μm by the particle size analyzer. The recipes of WRP were listed in Table 1. WRP was extracted with acetone, washed with 5 wt% sodium hydroxide solution and 10 wt% hydrochloric acid in turn, and finally immersed in styrene for several days. Methanol was obtained from Shanghai Zhenxing No.1 chemical paint. Chloroform was obtained from Tianjin Bodi Chemical Co. Ltd. Acetone was obtained from Tianjin Tianda Chemical Co., Ltd. Butanone was provided by Shanghai Hengli Fine Chemical Co., Ltd.

Measurement of double bonds by Wijs method

Wijs agents were prepared by dissolution of 2.25 g of I_2 and 2 g of ICl_3 in 250 mL of glacial acetic acid, filtered and stored in a brown bottle in a dark place.

A sample of WRP (0.5 g) was added to 30 mL of $CHCl_3$ in a 250-mL Erlenmeyer flask. Wijs agent (25 mL) was added and the mixture was placed in a dark closet for 30 min. Then, 10 mL of 20 wt% KI solution and 100 mL of distilled water were added to the Erlenmeyer flask. The standard solution was sodium thiosulfate solution which had been titrated by titrating solution of potassium dichromate before use. The mixture was titrated with 0.09 mol L^{-1} of sodium thiosulfate solution. At the same time, the blank was titrated under the same conditions. The content of double bonds is easily obtained as follows:

$$\text{The content of double bonds} = (V_0 - V) \times 10^{-3} \times C/m \tag{1}$$

where V is the volume of standard solution for the sample, V_0 is the volume of standard solution for the blank, C is the concentration of standard solution, m is the weight of the sample.

The titration results revealed that the content of C=C double bonds on the surface of WRP was 5.0×10^{-3} mol g^{-1}. The WRP rich in double bonds was suitable for graft polymerization.

Table 1 The recipes for surface grafting of WRP

Ingredients	Content/wt%
Natural rubber	36.4
Styrene–butadiene rubber	15.1
Polybutadiene	3.1
Oil	6.6
Carbon black	32.8
Ash	6.0

Table 2 The variables and ingredients of graft reaction

Time/h	Temperature/°C	Initiator/g	WRP/g	Styrene/mL
25	85	0.11	2.95	21.60
25	85	0.11	2.63	21.60
25	85	0.11	2.10	21.60
25	85	0.11	1.69	21.60
25	70	0.11	2.10	21.60
25	75	0.11	2.10	21.60
25	80	0.11	2.10	21.60
25	83	0.11	2.10	21.60
25	85	0.11	2.10	21.60
25	90	0.11	2.10	21.60
15	85	0.11	2.10	21.60
18	85	0.11	2.10	21.60
25	85	0.11	2.10	21.60
30	85	0.11	2.10	21.60
35	85	0.11	2.10	21.60
25	85	0.064	2.10	21.60
25	85	0.087	2.10	21.60
25	85	0.110	2.10	21.60
25	85	0.150	2.10	21.60
25	85	0.170	2.10	21.60

Surface grafting of WRP

A solution of initiator dissolved in amount of styrene was added to the reactor under nitrogen, and later WRP was added with stirring for 2–3 h to get an adequate mixing. The reaction mixture was stirred at 70–90 °C for 15–36 h. The product was suspended in chloroform, precipitated in methanol, and dried under vacuum until constant weight. The gross graft copolymer was extracted using a Soxhlet apparatus with butanone/acetone 1:1 mixture for 36 h. The insoluble residue was dried under vacuum to constant weight. The variables and ingredients of graft reaction were shown in Table 2.

Characterization of graft product

Graft efficiency (GE)

The definition of grafting efficiency is the ratio of the weight of grafted polystyrene to the total weight of polystyrene formed during graft copolymerization. The graft efficiency is calculated as follows:

$$\mathrm{GE} = m_1/m_0 \tag{2}$$

where m_1 is weight of extracted graft copolymer, m_0 is the total weight of polystyrene.

Fourier transform infrared spectroscopy

FTIR spectra of the modified and unmodified rubber powders were collected using a Nicolet-5700 spectrometer (Thermo Fisher Scientific) in the range of 4,000–400 cm^{-1}.

Scanning electron microscope

The surface morphology of the modified and unmodified rubber powders was characterized with a Nova400Nano SEM (Philips Electron Optics). The samples were sputtered with gold before observing.

Elemental analysis

Surface element elemental analysis of modified and unmodified rubber powder was performed with an Ie350 Penta FET x-3 energy dispersive X-ray spectrometer (Britain Oxford Corporation).

Thermogravimetric analysis

TG curves of the samples were recorded by a DTG-60 thermogravimetric analyzer (Shimadzu). The modified and unmodified rubber powders were heated up to 750 °C at the heating rate of 15 °C min^{-1} using a nitrogen atmosphere.

Results and discussion

Effect of reaction variables on grafting of polystyrene onto WRP

Monomer content

Figure 1 demonstrates the effect of monomer content on the graft efficiency. It can be seen that the graft efficiency increases at first and decreases later with increasing styrene content, and attains maximum value at 89 wt%.

The concentration of rubber powder–monomer radical increases with the increase of monomer content, the graft polymerization rate of WRP also increases. On the other hand, the swelling degree of rubber powder in styrene increases with increasing content of monomer, which will promote the diffusion of monomer into reactive sites on the WRP and improve the probability of collision between monomer radical or macromolecule radical and graft reactive center on WRP, as a result, the graft efficiency increases obviously. However, the homopolymerization accelerates with a further increase in monomer content, and reactive radicals will be shielded as a result of graft copolymer swelling, and hence the graft efficiency decreases.

Fig. 1 Effect of styrene content on GE (reaction time 25 h, initiator 0.11 g, temperature 85 °C)

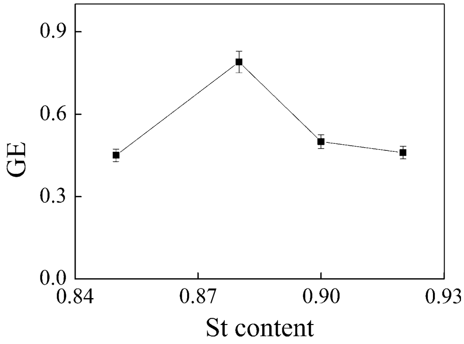
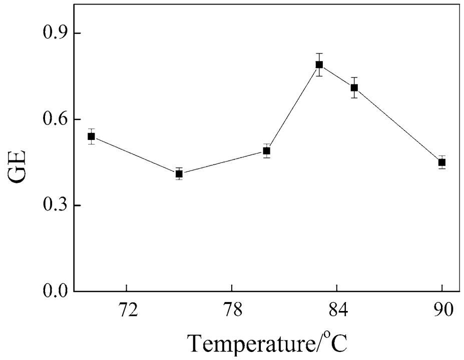


Fig. 2 Effect of reaction temperature on GE (time 25 h, initiator 0.11 g, monomer content 90%)



Reaction temperature

The effect of reaction temperature on the graft efficiency is presented in Fig. 2. It is observed that the graft efficiency changes little for temperature upto 80 °C, the graft efficiency first increases, then decreases with a further increase in temperature, and attains maximum value at 83 °C.

The initiation rate by BPO is relatively low and the diffusion of monomer into WRP is difficult due to low temperature of the reaction mixture during the graft polymerization, so the graft efficiency changes little at temperature below 80 °C. The decomposition of initiator hastens with increase in temperature, which improves initiation rate and produces much more free radicals, meanwhile, the increase of temperature quickens the movement of molecules and promotes the diffusion of free radicals into WRP, therefore, the graft efficiency increases. With a further increase in temperature, radical termination also increases and, as a result, the graft efficiency has a tendency to decrease.

Reaction time

The effect of reaction time on the graft copolymerization is shown in Fig. 3. The graft efficiency first increases with reaction time up to 25 h, and then decreases. It can be understood that the decomposition of initiator produces more free radicals,

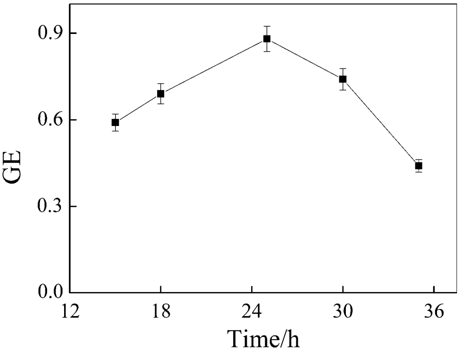


Fig. 3 Effect of reaction time on GE (monomer content 90%, temperature 85 °C, initiator 0.11 g)

which brings about more reactive sites on the WRP, and enhance the graft polymerization at the high temperature. Moreover, there is enough time for the diffusion of monomer, initiator, and primary radical into WRP with increase in reaction time, which will promote the graft polymerization. Because of lots of space on the grafted WRP, molecular backbone is occupied by grafted chains with their rigid structure and tremendous volume in excess of 25 h, it is difficult to bring on new graft reactive sites, and thus the reaction equilibrium is achieved (i.e. the rate of free radical production and the rate of consumption rate are equal). In addition, the concentration of monomer and initiator decreases, the viscosity of the reaction system increases with increase in reaction time, thereby graft polymerization becomes difficult. But styrene homopolymerization still takes place continuously, resulting in increase of the total weight of polymer, so the graft efficiency decreases.

Initiator content

Figure 4 shows the effect of initiator mass on the graft copolymerization. It can be seen that the graft efficiency increases with the increase of the mass of initiator, and attains maximum value at 0.12 g, and then decreases. It can be understood that the initiator at high temperature generates free radicals, which can initiate the graft copolymerizeation of styrene on WRP. Initially, with the increase in initiator mass, radicals on the surface of rubber powders increase, and graft efficiency also increases. Although there are more grafting active sites on the WRP with excessive initiator

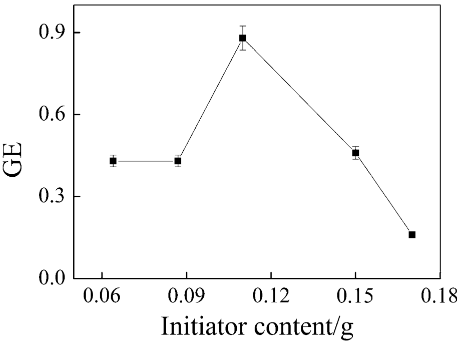


Fig. 4 Effect of initiator content on GE (monomer content 90%, temperature 85 °C, reaction time 25 h)

mass, but grafted side chains shorten, the relative molecular weight of side chain decreases according to the theory that kinetic chain length is inversely proportional to the square root of initiator concentration. In addition, redundant radicals stimulate the couple termination of graft polymerization. Meanwhile, due to generate more free radicals resulting from initiator concentration the homopolymerization is more facile than graft copolymerization. The above results to decrease of graft efficiency.

Characterization of rubber-g-polystyrene

FTIR

The attenuated total reflectance FTIR spectra of the unmodified and modified rubber powder (i.e. extracted graft copolymer) are shown in Fig. 5. The peaks at 2915, 2856 cm^{-1} correspond to the C–H unsymmetric and symmetric stretching vibration of CH_2, respectively. The peaks at 1735, 1726 cm^{-1} are attributed to C=O stretching due to partial oxidation during the grinding of waste rubber. The peaks at 1,610 and 1,582 cm^{-1} may be due to the benzene ring skeleton vibration. The peaks at 1551, 1544 cm^{-1} represent COO^- and the peak at 1,448 cm^{-1} corresponds to deformation vibration of saturated C–H bond. The peak at 990 cm^{-1} corresponds to C–H out-plane deformation vibration of trans-double bond.

As compared to the unmodified WRP, the characteristic peaks of polystyrene can be found in the spectrum of modified-WRP, such as the low peak at 3,028 cm^{-1} assigned to C–H stretching vibration of benzene ring, the peaks in the range of 1,950–1,700 cm^{-1} assigned to frequency multiplication and sum frequency of C–H out-plane deformation vibration in benzene ring, the peaks at 758, 684 cm^{-1}

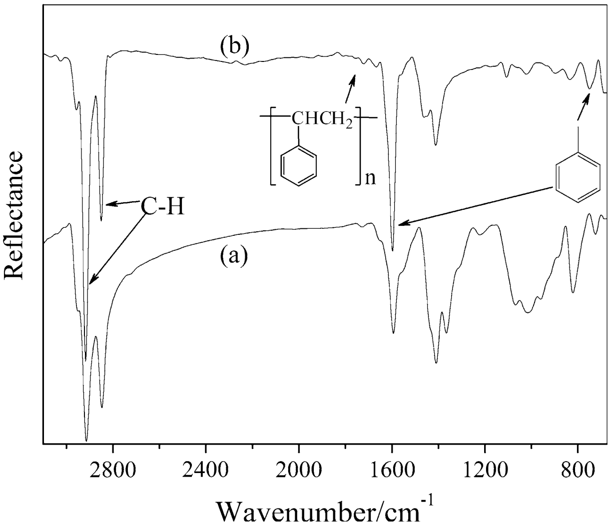


Fig. 5 FTIR spectra of: **a** unmodified rubber powder and **b** modified rubber powder (i.e. extracted graft copolymer)

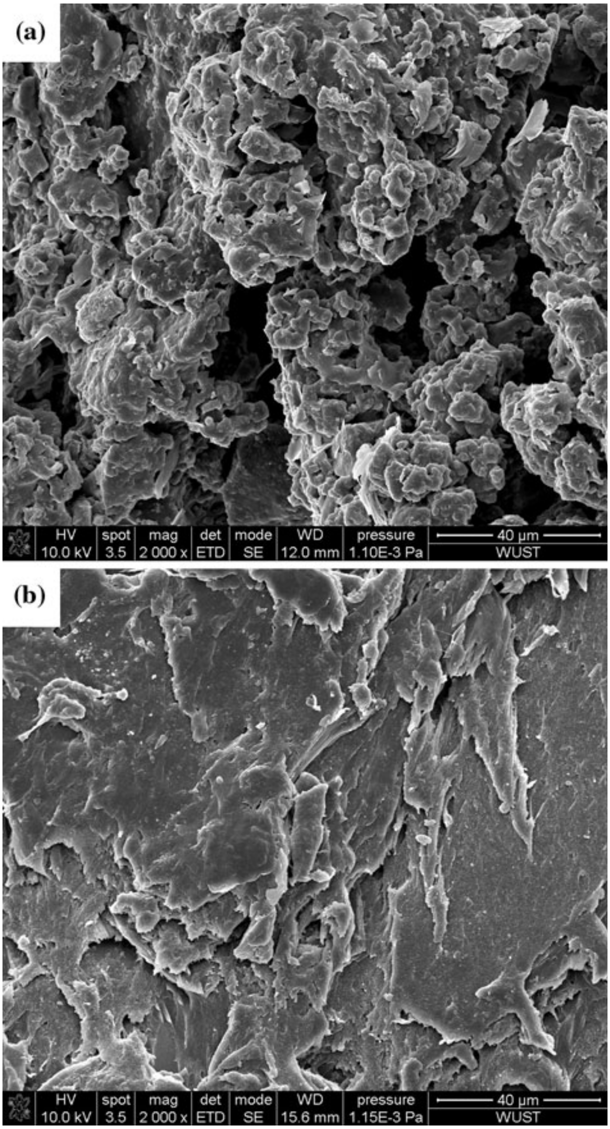


Fig. 6 SEM photographs of: **a** unmodified rubber powder and **b** modified rubber powder (temperature 85 °C, reaction time 25 h, monomer content 90%, and BPO mass of 0.11 g)

attributed to C–H vibration of monosubstituted benzene. The above analyses demonstrate that the polystyrene has grafted onto the surface of the rubber powder.

SEM

Figure 6 shows the scanning electron microscope photographs of the WRP and modified-WRP. Morphology and particle size of modified-WRP changes obviously

Table 3 Surface element content of unmodified and modified rubber powder

Element	Unmodified rubber (at.%)	Modified rubber (at.%)
C	76.08	90.53
O	17.83	9.47
Al	1.25	–
Si	2.06	–
Ca	2.01	–
Zn	0.76	–

as compared to WRP. In Fig. 6a, unmodified rubber powder shows an irregular aggregate structure, an unsmooth surface and has some pores. In Fig. 6b, the particle size of modified rubber powder becomes larger than that of unmodified rubber powder, as well as the space between particles becomes smaller. The surface of modified rubber powder becomes smooth, and has no distinct cracks. The results indicate that the encapsulation of the waste rubber powder by polystyrene chains is achieved.

It is inferred from the above FTIR and SEM data that there is a chemical reaction between polystyrene and surface of rubber powder, namely polystyrene has grafted onto waste rubber powder.

Elemental analysis

Besides hydrogen atom, the other element content of unmodified and modified rubber powder is listed in Table 3. The variation of the element content can reflect surface properties of unmodified and modified rubber powders. The unmodified rubber powder contains several elements (C, O, Si, Ca, and Zn, etc.). The modified rubber powder contains two elements (C and O) and Si, Ca, and Zn elements disappear. WRP contains some inorganic elements because the WRP used for this study is composed of rubber, carbon black, antioxidant, reinforcing filler, and so on. The content of inorganic elements in modified rubber powder will reduce and disappear when the part of WRP surface is covered with polystyrene. The results of elemental analysis show the composites have formed the core–shell structure after graft polymerization, as seem as the results of SEM.

TG/DTG analysis

The TG/DTG curves of unmodified and modified rubber powder are shown in Fig. 7. It can be seen that the onset of degradation of unmodified rubber powder starts at 377 °C from the first peak in DTG curve. The degradation temperature of modified rubber powder is raised to 455 °C from the peak maximum in DTG curve. The results show that the thermal stability of WRP is improved by grafting modification. In addition, the residual weight (%) of unmodified and modified rubber powders from the TG curves tend toward stability at 550 °C, and their weight (%) are 40.1, 5.6%, respectively.

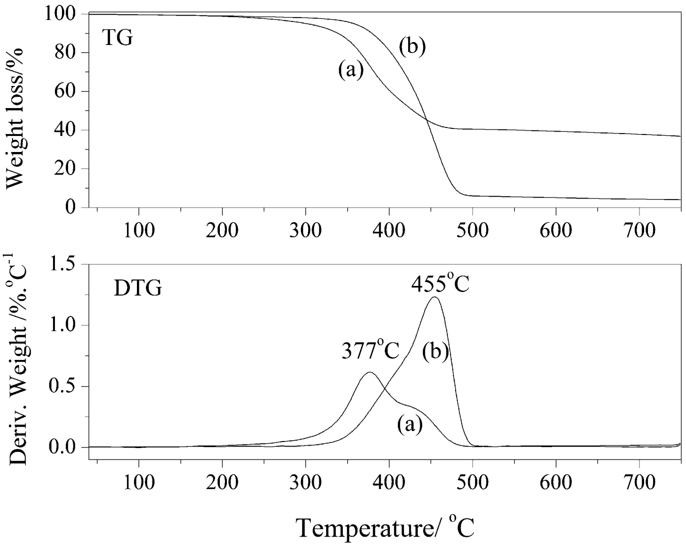


Fig. 7 TG/DTG curves of: **a** unmodified rubber powder and **b** modified rubber powder (temperature 85 °C, reaction time 25 h, monomer content 90% and BPO mass of 0.11 g)

The rubber powder used for this work is made up of nature rubber, styrene butadiene rubber, carbon black, and inorganic fillers. The decomposition of WRP results from the degradation of nature rubber and styrene butadiene rubber under N_2 atmosphere, and therefore, its decomposition temperature is low. However, the degradation behavior of modified-WRP is different from that of WRP. Since the grafted polystyrene molecule chain can form the wrapping layer on the surface of WRP, the degradation of PS on the surface of WRP will occur at first during heating. It can be seen that the decomposition temperature of PS is 410–430 °C from the peak maximum in DTG curves [23, 25, 26]. The thermostability of PS is higher than NR and SBR, and thereby the thermal stability of WRP is improved by grafting modification.

Since the decomposition reaction of carbon black and inorganic fillers does not take place at 550 °C, WRP has a high residual weight. In addition, the content of inorganic fillers in modified-WRP is lower than that in WRP, and thereby residual content of modified-WRP is lower than that of WRP.

From the above analysis, polystyrene has been grafted onto the waste rubber powder.

Conclusions

Polystyrene can be grafted onto the surface of waste rubber powder via free radical polymerization by using dibenzoyl peroxide (BPO) as initiator. There is good graft efficiency when the mass fraction of monomer is 89% and mass of initiator is 0.11 g at 85 °C for 25 h.

The surface properties of the unmodified and modified rubber powder are investigated by FTIR, SEM, EDXS, and TG/DTG analysis. The characteristic peaks of polystyrene can be found from the spectrum of modified-WRP, such as 3028, 1950–1700, 758, and 684 cm^{-1}. SEM results indicate that the surface of WRP modified by polystyrene becomes smooth, and has no distinct cracks, whereas WRP shows an irregular aggregate structure and unsmooth surface. EDXS results show that the content of inorganic elements in modified rubber powder reduces or disappears when the part surface of WRP is covered with polystyrene. TG/DTG analyses indicate that the thermal stability of WRP is improved by grafting modification with styrene compared with waste rubber powder. The above results demonstrate that polystyrene has been grafted onto the waste rubber powder, namely PS chains are covalently bound to the surface of WRP.

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