

# Surface Graft Copolymerization of Poly(methyl methacrylate) onto Waste Tire Rubber Powder Through Ozonization

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**ABSTRACT:** Grinding of tires offers a promising opportunity for recycling waste rubber because fine waste tire rubber particle may be used as fillers and property modifiers in thermoplastic, elastomer, and thermoset blends. However, due to the lack of reactive sites on the WTR surface, the adhesion between WTR powder and matrix is poor. In this article, ozonization of waste tire rubber (WTR) powder was performed to produce some “immobile” reactive points (hydroperoxide groups) on the WTR surface. The free radical generated by the decomposition of hydroperoxide groups on WTR surface, was used to initiate graft polymerization of methyl methacrylate (MMA)

onto the surface of WTR powder. The experimental results showed that MMA was successfully grafted onto the surface of WTR. The hydrophilicity of the MMA grafted WTR (MMA-g-WTR) was improved. The concentration of hydroperoxide groups and the graft degree were both increased with ozonization time. With increasing of polymerization time and polymerization temperature, the grafting degree increased. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2262–2270, 2011

**Key words:** waste tire rubber; ozone; graft copolymerization; hydrophilicity; XPS

## INTRODUCTION

With an ever increasing number of automobiles in the world, the disposal of used rubber tires has been a significant problem in recent year, which has impelled the efforts of the scientific community to provide with solutions to their recovery and reuse.

Preparing fine waste tire rubber (WTR) offers a promising opportunity for recycling waste rubber. WTR powders may be used as fillers and property modifiers in thermoplastic, elastomer, and thermoset blends.<sup>1–4</sup> Unfortunately, due to the crosslinked feature of WTR powder, which inhibits the adhesion between WTR powder and other polymer materials, the incorporation of WTR powders into a number of polymer matrices always significantly impairs the mechanical and viscoelastic properties of the resulting material, even at low rubber content. Furthermore, when WTR blend with polar polymers, the nonpolar nature and relatively low surface energy of WTR restricts the wetting of WTR powder by polar matrices.

Surface and interface modification opens up new opportunities for recycling rubber from WTR into high value applications. In comparison with untreated WTR, the surface-treated WTR is expected to provide better compatibility and stronger interfacial interactions with the host materials. Consequently, it is possible to add a larger percentage of surface-treated WTR into the matrix material while minimizing the detrimental effects commonly experienced with the addition of untreated WTR particles.

Several WTR surface-modification technologies were proposed in literature. McInnis et al. modified the rubber powder by a gas-solid reaction with chlorine containing gas.<sup>5</sup> The redox method and grafting by gamma irradiation were used to reuse waste rubber.<sup>6</sup> Other surface treatment methods for improving filler-matrix adhesion such as plasma,<sup>7,8</sup> corona,<sup>9</sup> and electron beam radiation<sup>10</sup> were also extensively studied.

Among the surface-modification technologies, grafting reaction with a monomer is an efficient way to modify the surface characteristics of WTR.<sup>11–13</sup> Through grafting reaction, both surface characteristics of the particles and the particle agglomerates can be changed. The polymer grafting also provides possibilities for interfacial design. By selection of suitable monomers, functionalized WTR powder with various reactive groups can be obtained. Through graft copolymerization, the surface energetics and, therefore, the

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wettability by polymers of WTR are improved. Furthermore, the functional groups on WTR can react with those of the polymer matrix through the formation of covalent bonds.

In 1986, Pittolo and Burford<sup>14</sup> prepared a peroxide-cured BR/SBR blend filled with carbon black to simulate the tire rubber and used styrene to swollen these particles. By using peroxidation benzoin formyl or azobisisobutyronitrile as initiator, they obtained grafted rubber particles. The polystyrene chains grafting on ground tire rubber particles via styrene free radical polymerization initiated by thermal initiators was also reported in recent years.<sup>13</sup>

However, WTR contains a large ratio of carbon black (CB) particle. The presence of CB, which is known to be a strong radical scavenger due to the existence of polycondensed aromatic rings and quinonic and phenolic oxygen atoms, may act as trap radicals and thus affect the grafting process.<sup>12</sup> Therefore, it is necessary to create some "immobile" reactive points before grafting process.

Ozone induced surface grafting is widely applied in polymer modification because of the uniform and rapid creation of active peroxides on the polymer surface through simple equipment and low operation cost. The generated peroxides are capable of initiating the radical polymerization of vinyl monomers and result in surface grafting.<sup>15-17</sup>

In this article, the waste tire powder was subjected to ozone treatment to create some "immobile" reactive points (hydroperoxide groups) on the surface of WTR. Methyl methacrylate (MMA) was then grafted onto the surface of WTR powder. The grafted surface has been characterized by Fourier transform infrared spectra (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and contact angle measurements to characterize the surface modification. The effects of grafting conditions on the graft degree were also discussed.

## EXPERIMENTAL

### Materials

The waste tire rubber powder (60 mesh) used in this study was generated by pan-mill equipment according to the literature.<sup>18</sup> The WTR powder was extracted with acetone before use to remove plasticizing oils and other types of additives used during the vulcanizing process of the rubber for the production of tires, and then dried under vacuum until constant weight. The composition of the waste tires used in this paper is: 40% nature rubber, 45% butadiene styrene rubber and 15% *cis*-butadiene rubber.

Methyl methacrylate (MMA) (A.R. grade, Chengdu Kelong Chemical Reagent Plant of China) was vac-

uum distilled before use. Sulfuric acid, methanol, acetone, and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , were supplied by Tianjin Chengdu Kelong Chemical Reagent Plant of China and were used as received without purification.

### Ozone treatment of WTR powders

The ozone treatment of WTR was performed at room temperature for different times, the ozone concentration was 1.4 mg/L.

### Grafting of MMA onto WTR powder

The ozonized WTR was soaked in ethanol for 10 min and then placed in MMA solution and other additives. After removing oxygen by blowing nitrogen, the grafting reaction was carried out by placing the ampule in a water bath set at the relevant temperature. This graft copolymerization was initiated by radicals formed by the decomposition of peroxide on the WTR surface. After the grafting copolymerization reaction, the grafted WTR was taken out of the monomer solution in the glass ampule and extracted by hot acetone in a Soxhlet extractor for over 24 h to remove the unreacted remaining monomers or MMA homopolymers.

### Measurements and characterization

#### Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) was performed using a Nicolet 560 series FT-infrared spectrometer. The samples were prepared by mixing of 1 mg WTR powder and 100 mg of ground KBr and pressing it in a die, forming a pellet at pressure of 1 MPa for 1 min. All infrared spectra were scanned from 4000 to 400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

#### Contact angle measurement

WTR samples were pressed into films and then were investigated through the contact angles of water drops on films with Erma G-1 contact angle tester (Erma Optical Works Ltd. Japan) at room temperature. A 5 mL of distilled water droplet was deposited on the film surface with a microsyringe, and contact angle was measured. The value reported was the average of at least five measurements made at different positions of each film.

#### X-ray photoelectron spectroscopy

XPS spectra were recorded on a Kratos XSAM 800 spectrometer (Kratos analysis, UK) with an AlKa source (1486.6 eV). The  $\text{C}_{1s}$  peaks were fitting according to a Gaussian distribution.

### Scanning electron microscopy (SEM) observations

SEM micrographs were performed with a JSM-6390LV (Jeol, Japan) instrument equipped with an Oxford X-ray energy dispersive spectrometer (EDXS) microprobe.

### The amount of peroxide on the surface

The amount of peroxide introduced onto the WTR surface by ozone treatment was determined using an iodometric method.<sup>19</sup> In brief, WTR sample was placed in one flask and 25 mL of isopropanol was added, and then followed by 1 mL of saturated potassium iodide and 1 mL of glacial acetic acid. The mixture was heated up to nearly boiling point, kept at incipient boiling for 2 to 5 min with occasional swirling and without cooling, and titrated with standard sodium thiosulfate until yellow color disappeared. The data reported was the average value for three specimens. The concentration of peroxide  $G_{\text{POOH}}$  (mol/g) was determined as follows:

$$G_{\text{POOH}} = (V \times C) / (m \times 1000)$$

where  $V$  was the volume of consumed  $\text{Na}_2\text{S}_2\text{O}_3$  solution (L),  $C$  was concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  solution (mol/L),  $m$  was the weight of WTR (g)

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out with a TG Q500 thermogravimetric analyzer (TA). Samples (1–3 mg) were placed in an alumina sample pan and runs were carried out at a standard rate of  $20^\circ\text{C}/\text{min}^{-1}$ . The WTR and MMA graft-WTR particles were heated under nitrogen atmosphere from 50 to  $600^\circ\text{C}$ .

### Elemental analysis

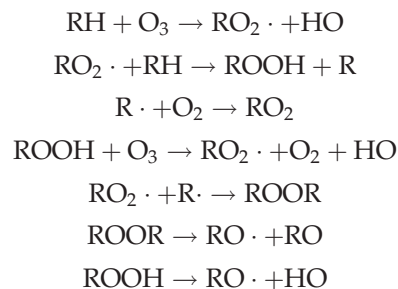
To determine the graft degree onto the WTR surface, elemental analysis of WTR and MMA-g-WTR sample were performed using an Elementar Vario EL Elemental Analyzer (Elementar, Germany). The estimation of carbon and oxygen was undertaken. The graft degree was determined by a comparison of the measured oxygen content with the calculated value for the pure monomer with the following formulas:

$$\text{Graft degree} = (7 \times R) / (2 + 2 \times R)$$

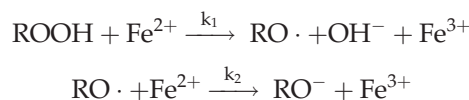
where  $R$  was the O/C ratio obtained from elemental analysis result.

## RESULT AND DISCUSSION

When WTR was subjected to ozone treatment, the trapped radicals or peroxides such as diperoxides (ROOR) and hydroperoxides (ROOH) were generally formed by the dissociation of the polymer backbone or hydrogen, which were described as follow.



During grafting reaction, the peroxides on the WTR surface were decomposed into free radicals HO and  $\text{RO} \cdot$ , RO could initiate the grafting of MMA monomers onto the surface of the WTR powder and formed graft copolymers. However, it was inevitable that HO induced the homopolymerization of the monomers. For declining the decomposing temperature of peroxides and inhibiting the homopolymerization of the monomers,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was used in this grafting reaction.  $\text{Fe}^{2+}$  ions acted as follows:<sup>20</sup>



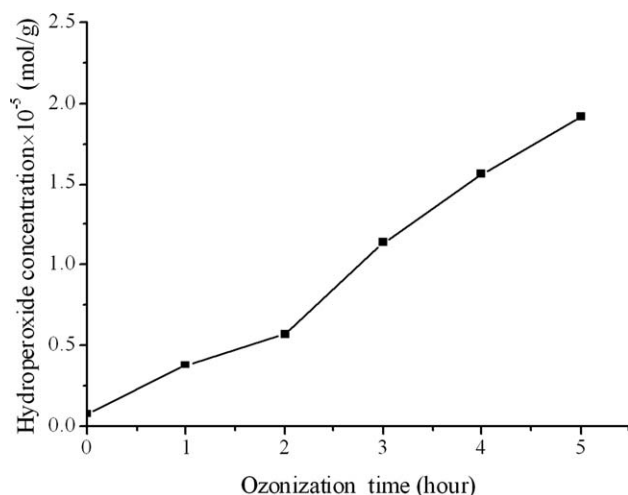
The ROOH was reduced by  $\text{Fe}^{2+}$  to  $\text{OH}^-$  which could not initiate polymerization and therefore inhibit the forming of the homopolymers.  $\text{Fe}^{2+}$  could also reduce RO which could initiate the grafting polymerization, but the reaction rate constant  $k_2$  is much smaller than  $k_1$ . As a result, homopolymerization was restrained.

### Effect of ozonization on the WTR powder surface

The concentration of peroxide introduced onto the WTR powder by ozone treatment was investigated using an iodometric method. The result was shown in Figure 1, it could be seen that at room temperature, the concentration of peroxide increased with the increase of ozone treatment time, indicating that more peroxides were introduced onto the surface of WTR.

### Surface characterization of MMA-g-WTR powder

Figure 2 showed the absorption spectra of the WTR powder before and after graft process and the main peak assignments were summarized in Table I. After graft process, new absorption peaks situated at



**Figure 1** Effect of ozonization time on hydroperoxide concentration of ozonized WTR.

1730  $\text{cm}^{-1}$  were observed in FTIR spectra. Furthermore, compared to weak peaks appeared at 2925 and 2856  $\text{cm}^{-1}$  for WTR, a relatively strong absorption peaks were observed at these positions for grafted MMA-g-WTR. All these information confirmed that MMA was grafted onto WTR and MMA-grafted-WTR was obtained.

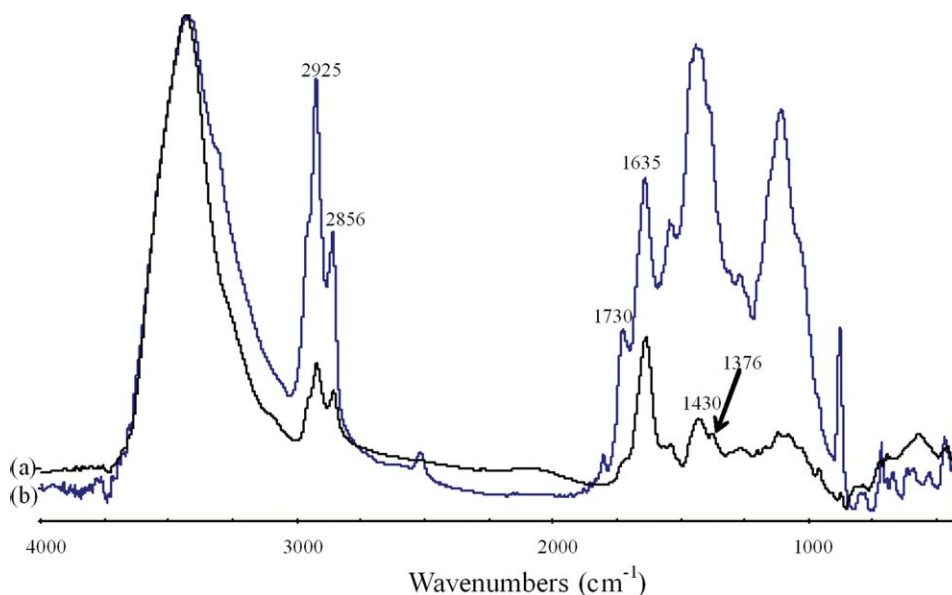
XPS was a useful tool for studying the surface properties of polymer surfaces due to its small analysis depth (<10 nm on the surface).<sup>21</sup> Therefore, the XPS analysis was performed to characterize the chemical structure changes of WTR surface after grafting. The XPS spectra of the WTR powder, ozone-treated WTR powder, and the MMA-g-WTR powder were shown in Figure 3(a–c), respectively.

**TABLE I**  
Positions and Assignment of Peaks in FTIR Spectra of WTR and MMA-g-WTR

Wavenumber( $\text{cm}^{-1}$ )	Group	Remark
2925	Methylene	C-H unsymmetrical stretch
2856	Methylene	C-H symmetrical stretch
1730	Carbonyl	C=O stretch
1430	Methyl methylene	C-H unsymmetrical bend
1376	Methyl	C-H symmetrical bend

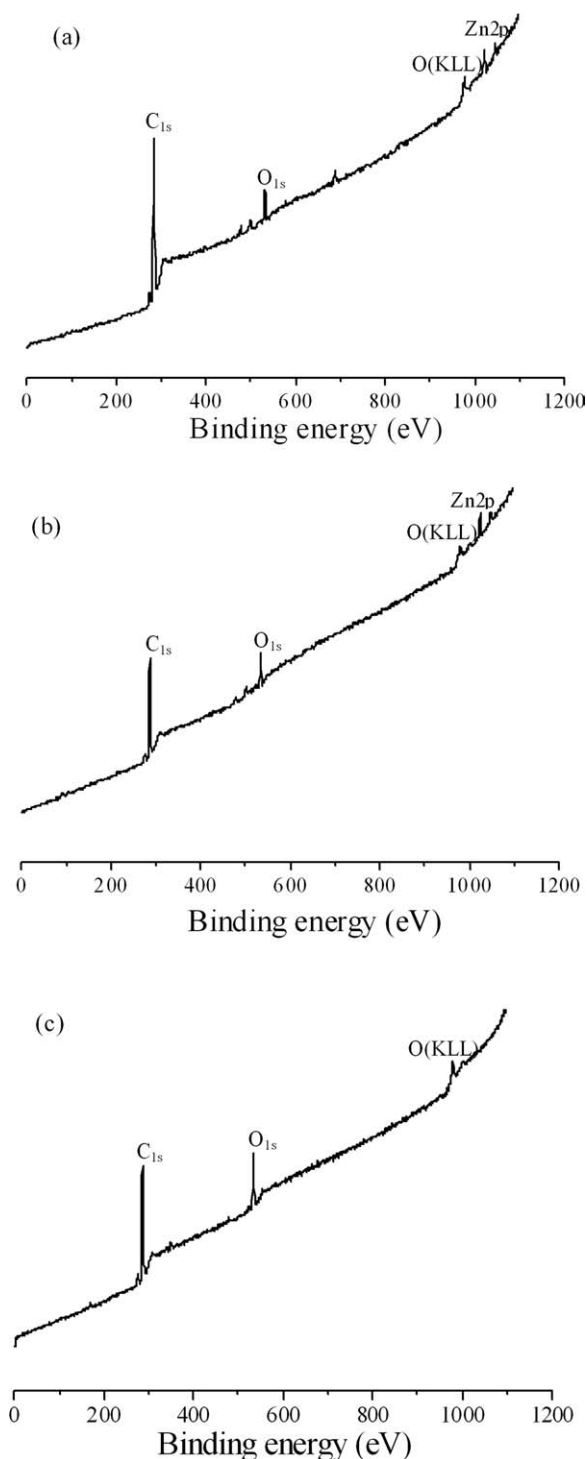
As shown in Figure 3, after graft modification, the peak height of  $\text{C}_{1s}$  decreased but the peak height of  $\text{O}_{1s}$  increased.

Table II was the elemental compositions and the ratio of O/C obtained from the spectra of the WTR, ozonied WTR and MMA-g-WTR powders. As shown in Table II, the O/C ratio obtained by the XPS study for the WTR powder was 0.07. Since the main components of WTR were nature rubber, butadiene styrene rubber and *cis*-butadiene rubber, it should not contain oxygen in the polymer. The presence of oxygen on the surface of the untreated WTR powder suggests that the WTR surface was attached by the oxygen atom or probably contained low-level surface oxidation. When the WTR powder was treated by ozone, the ratio of O/C was increased to 0.14. The increase of the O/C ratio was due to that, during the ozone treatment, free radicals were formed on the surface of the WTR. These radicals reacted almost immediately with an oxygen molecule and finally introduced oxygen-containing groups onto



**Figure 2** FTIR spectra of (a)WTR and (b)MMA-g-WTR. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]





**Figure 3** XPS wide-scan of (a) WTR, (b) ozonized WTR, (c) MMA-g-WTR.

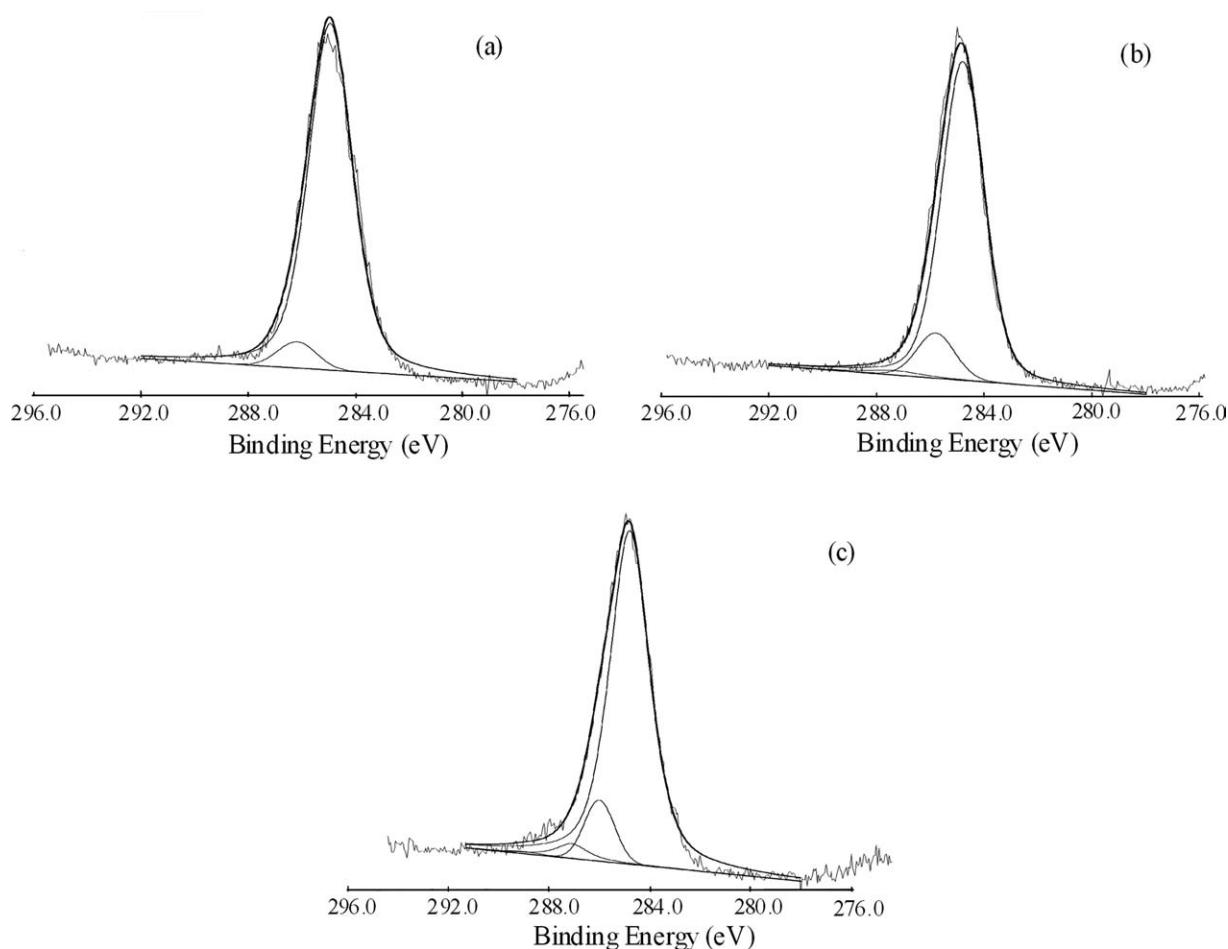
the surface of WTR. After grafting with the MMA monomer, the O/C ratio of WTR powder increased further and reached to 0.18. The higher O/C ratios for MMA-g-WTR graft powders in Table II may be related to the higher O/C contribution from the MMA.

Figure 4(a)–(c) showed the C<sub>1s</sub> spectra of the WTR, ozonized WTR and MMA-g-WTR powders and Table III listed the binding energy, relative area and relative content found in the deconvolution of the C<sub>1s</sub> spectra. For untreated WTR particles, the C<sub>1s</sub> signal can be fitted with two peaks centered at 284.9 eV and 286.1 eV, which attributed to C-H/C-C and C-O bonds, respectively. In the case of ozone-treated WTR powders, the C<sub>1s</sub> signal was peak-fitted with four components. Except the peaks centered at 284.8 eV and 285.8 eV, two new peaks centered at 287.3 eV and at 288.9 eV appear. This mainly corresponded to C = O group. It suggested that when WTR powder was subjected to ozone treatment in air, the peroxides such as diperoxides (ROOR) and hydroperoxides (ROOH) are generally formed by the dissociation of the polymer backbone or hydrogen. The C<sub>1s</sub> signal of MMA-g-WTR was peak-fitted with four components, centered at 284.8 eV, 286.0 eV, 287.1 eV, and 288.9 eV, respectively. According to literature,<sup>22</sup> these four peaks represented different carbons in MMA: (1) aliphatic hydrocarbon (C-C/C-H, at a binding energy of 284.8 eV), (2) an ester-induced-shifted carbon (C-COO at 286.0 eV), (3) the methyl side ester (C = O at 287.1 eV), and (4) the carboxyl carbon (-COO at 288.9 eV).

The presence of the PMMA layer covering the WTR particles surface was confirmed by EDXS X-ray microanalysis (Fig. 5). The surface composition data determined by EDXS analysis were summarized in Table IV. The relative increase in the O signal intensity indicated that the rubber particle surfaces were covered with a layer of grafted PMMA. A backscattered electron imaging analysis was achieved for the unmodified WTR powder and MMA-g-WTR graft powders (Fig. 5). According to literature,<sup>23</sup> this analysis provided elemental composition variation as well as surface topography since the efficiency of production of backscattered electrons was proportional to the average atomic number of the material (the elements with higher atomic number appear brighter than those with low atomic number). In Figure 5(a), some bright points were observed on the surface of unmodified WTR, these points probably due to Ca atoms which has high atomic number. In case of MMA-g-WTR graft powders, few bright points could be observed, which suggested that the presence of the PMMA layer

**TABLE II**  
Elemental Composition of WTR Surface Determined by XPS

sample	C (%)	O (%)	Zn (%)	O/C
WTR	90.6	6.7	1.7	0.07
Ozonized WTR	86.9	11.8	1.3	0.14
MMA-g-WTR	85.0	15.0	0	0.18



**Figure 4** XPS carbon 1s core-level spectra of (a) WTR, (b) ozonized WTR, and (c) MMA-g-WTR.

hindered the backscattered electrons to reach the depth where Ca atoms existed.

#### Thermal stability of MMA-g-WTR powder

The TG and DTG curves of WTR and MMA-g-WTR were plotted and compared in Figure 6. The thermal degradation of WTR powder was composed by two principal steps under nitrogen flow. Compared with

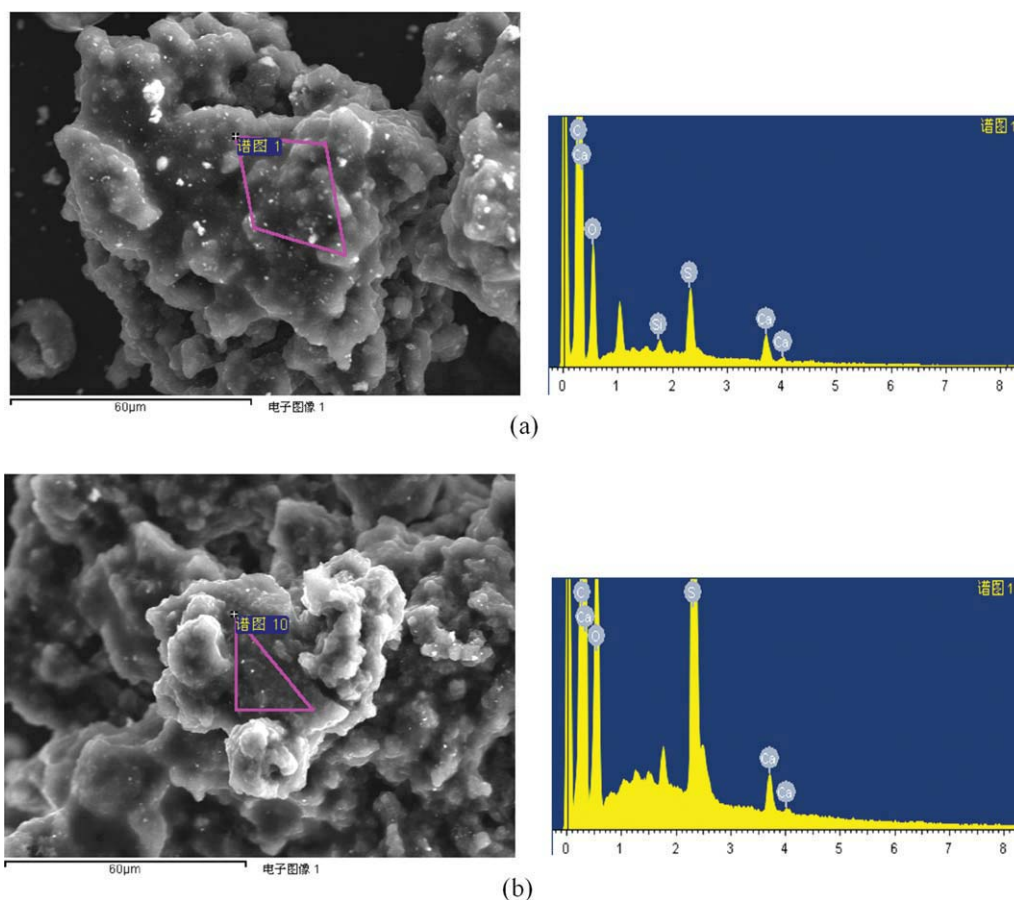
the TG and DTG plots of the tire samples reported by others,<sup>24</sup> the weight loss center at 360°C should attribute to the degradation of NR and the weight loss center at 460°C is corresponding to the degradation of the SBR/BR. In the thermograms of the MMA-g-WTR sample, TGA curve was composed by three stages. The first stage of weight loss at 150°C, corresponded to the loss of the water which attached on the surface of the powder sample. The second stage in mass loss at about 200°C should correspond to depolymerization initiated by weak H-H linkages together with weak peroxides and/or hydroperoxides linkages of PMMA.<sup>25</sup> However, this stage was insignificant, suggesting that there were few of the above-mentioned linkages. The third stage (around 420–430°C maximum of the DTG curve) included the radical transfer to unsaturated chain ends and random scission of PMMA<sup>25</sup> and WTR degradation step.

#### Effect of grafting conditions on the graft degree of MMA-g-WTR powder

The effect of ozone treatment time on the graft degree was studied. As can be seen from Figure 7, with the prolonging of ozone treatment time, the

**TABLE III**  
The Relative Area and Relative Content of WTR, Ozonized WTR, and MMA-g-WTR

Sample	Binding energy (ev)	Relative area	Relative content (%)
WTR	284.9	2420.0	94.7
	286.1	136.1	5.3
Ozonized WTR	284.8	2358.9	87.7
	285.8	276.8	10.3
	287.3	51.1	1.9
	288.9	2.2	0.1
	284.8	1262.7	86.6
MMA-g-WTR	286.0	137.8	9.5
	287.1	49.1	3.4
	288.9	7.9	0.5
	284.8	1262.7	86.6



**Figure 5** SEM images and EDXS of (a) ozonized WTR (b) MMA-g-WTR. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

amount of grafted methyl methacrylate on the WTR powder increased gradually. When the ozone treatment time was 4 h, the graft degree reached a maximum value, and then decreased. This was because prolonging ozone treatment time could increase the amount of peroxide, which resulted in more reactive sites on WTR surface. However, when the ozone treatment time was too long, it was easier for the free radicals generated by thermodecomposition reacted with each other and lead to chain termination. Graft degree was thus decreased reversely.

The influence of polymerization time on graft degree of MMA-g-WTR was shown in Figure 8. It was obvious that the graft degree initially increased

with the grafting time, and then tended to level off after 4 h.

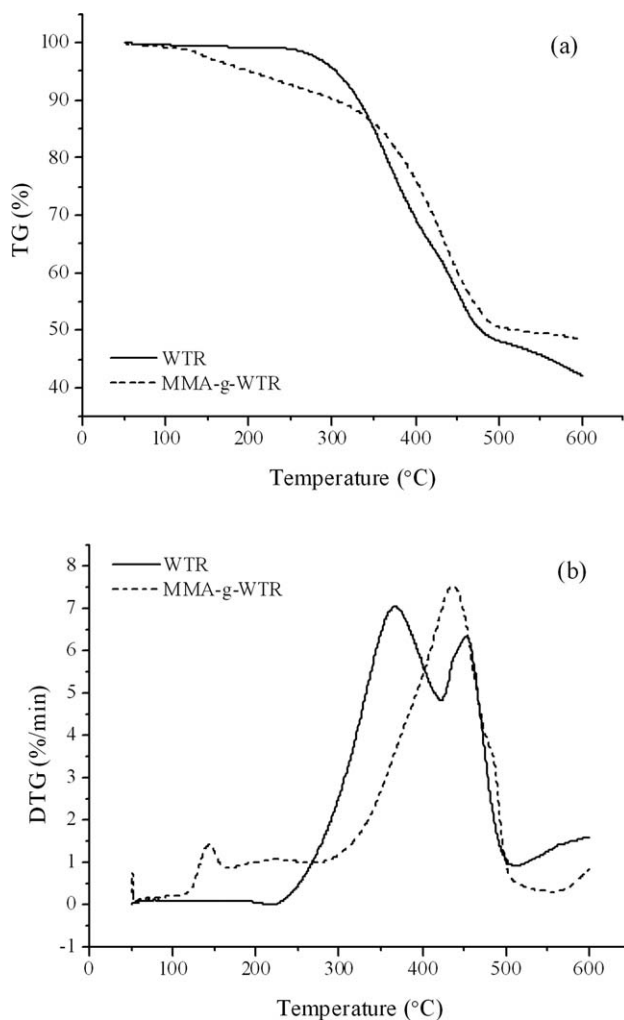
The polymerization temperature was one of the important factors controlling the grafting. Therefore the effect of temperature on the graft degree of MMA-g-WTR was investigated. As shown in Figure 9, the graft degree at 70°C was much higher than that at 50°C, while the graft degree was remarkably low at 30°C. The reason why the graft degree was low at low temperatures might attribute to the extremely low decomposition rate of peroxide at low temperatures.

#### Effect of graft on the hydrophilicity of MMA-g-WTR powder

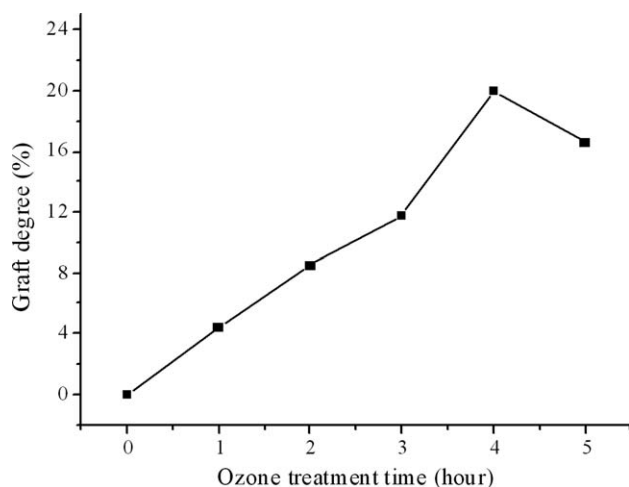
Figure 10 showed the water contact angle of the WTR as a function of the graft degree. The untreated WTR has a water contact angle equal to 115°. With the increase of the degree of grafting, the water contact angles of the grafted WTR sample decreased. The decrease in water contact angle indicated that the hydrophilicity of the WTR powder can be remarkably improved by grafting with MMA.

**TABLE IV**  
Surface Atomic Composition of Ozonized WTR and MMA-g-WTR Powder Determined by EDXS

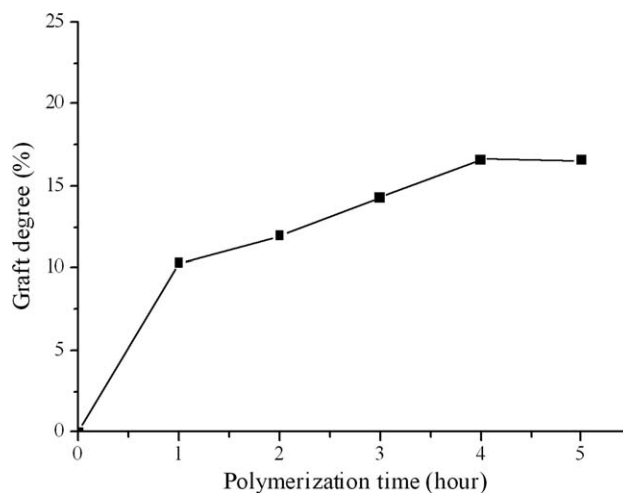
Sample	Atomic composition (%)				
	C	O	Si	S	Ca
Ozonized WTR	87.3	11.9	0.1	0.5	0.2
MMA-g-WTR	86.1	12.8	0	1.0	0.1



**Figure 6** TG (a) and DTG (b) curves of WTR and MMA-g-WTR.



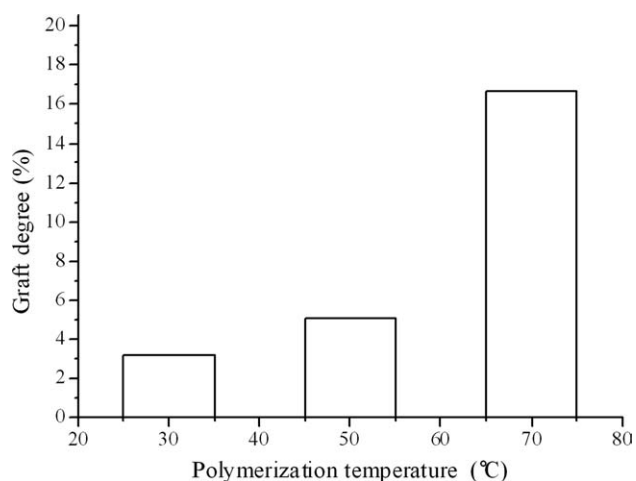
**Figure 7** Effect of ozone treatment time on the graft degree of MMA-g-WTR (polymerization time: 4 h, polymerization temperature: 70°C, MMA methanol solution concentration: 60 vol %, Mohr's salt concentration:  $2.5 \times 10^{-3}M$ ,  $H_2SO_4$  concentration: 0.1M).



**Figure 8** Effect of polymerization time on the graft degree of MMA-g-WTR (ozone treatment time: 5 h, polymerization temperature: 70°C, MMA methanol solution concentration: 60 vol %, Mohr's salt concentration:  $2.5 \times 10^{-3}M$ ,  $H_2SO_4$  concentration: 0.1M).

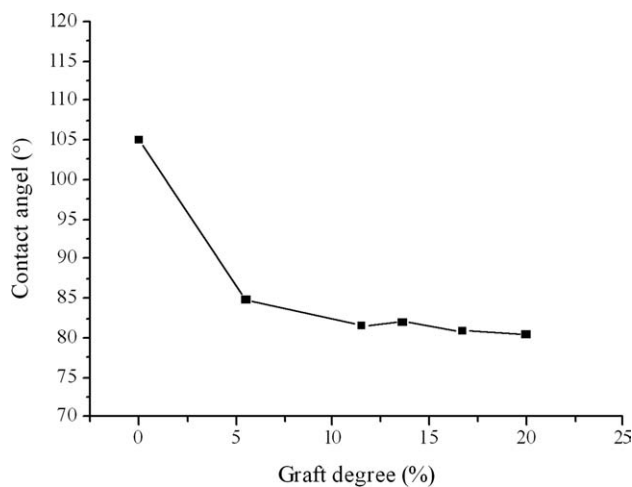
## CONCLUSION

1. Through ozone treatment, some "immobile" reactive points (hydroperoxide groups) were introduced on the surface of WTR. The free radical produced by heating and by catalyzing with ferrous ion of hydroperoxidized WTR, could successfully initiate graft polymerization of methyl methacrylate onto the surface of WTR powder. This approach provides a way to avoid the effect of CB, existing in vulcanized WTR and is known as trap radicals, on the grafting process.



**Figure 9** Effect of polymerization temperature on the graft degree of MMA-g-WTR (ozone treatment time: 5 h, polymerization time: 4 h, MMA methanol solution concentration: 60 vol %, Mohr's salt concentration:  $2.5 \times 10^{-3}M$ ,  $H_2SO_4$  concentration: 0.1M).





**Figure 10** Effect of graft degree on contact angle of MMA-g-WTR.

- Both of the concentration of hydroperoxide groups and the graft degree were increased with ozonization time. With increasing of polymerization time and polymerization temperature, the graft degree increased. By altering these grafting conditions, the graft degree could be controlled.
- After grafting with MMA, the hydrophilicity of the WTR was improved.

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## References

- Wu, D. Y.; Bateman, S.; Partlett, M. *Compos Sci Technol* 2007, 67, 1909.
- Tantayanon, S.; Juikham, S. *J Appl Polym Sci* 2004, 91, 510.
- Oliphant, K.; Baker, W. E. *Polym Eng Sci* 1993, 33, 166.
- Sipahi-Saglam, E.; Akovali, G.; Kaynak, C.; Akkas, N.; Yetmez, M. *Polym Eng Sci* 2001, 41, 514.
- McInnis, E. L.; Bauman, B. D.; Williams, A. US Patent 5, 506, 283, 1996.
- Adam, G.; Sebenik, A.; Osredkar, U.; Veksli, Z.; Ranogajec, F. *Rubb Chem Technol* 1990, 63, 660.
- Yasuda, H.; Marsh, C.; Brandt, S.; Reilly, C. N. *J Polym Sci Part A: Polym Chem* 1977, 15, 991.
- Zimmerman, C. J.; Ryde, N.; Kally, N.; Partch, R. E.; Matijeve, E. *J Mater Res* 1991, 6, 855.
- Dong, S.; Sapiha, S. In *Proceedings of the Annual Technology Conference. Society of Plastics Engineering (ANTEC 91)*; Montreal, Canada, 6–9 May 1991; p 1154.
- Rajalingham, P.; Sharp, J. B. *Rubber Chem Technol* 1993, 66, 664.
- Fuhrmann, I.; Karger-Kocsis, J. *J Appl Polym Sci* 2003, 89, 1622.
- Coiai, S.; Passaglia, E.; Ciardelli, F. *Macromol Chem Phys* 2006, 207, 2289.
- Coiai, S.; Passaglia, E.; Ciardelli, F.; Tirelli, D.; Peruzzotti, F.; Resmini, E. *Macromol Symp* 2006, 234, 193.
- Pittolo, M.; Burford, R. P. *Rubber Chem Technol* 1985, 58, 97.
- Yamauchi, J.; Yamaoka, A.; Ikemoto, K. *J Appl Polym Sci* 1991, 43, 1197.
- Dasgupta, S. *J Appl Polym Sci* 1990, 41, 233.
- Karlsson, J.; Gatenholm, P. *Polymer* 1996, 37, 4251.
- Zhang, X. X.; Lu, C. H.; Liang, M. *J Appl Polym Sci* 2007, 103, 4087.
- Kokatnur, V. R.; Jelling, M. *J Am Chem Soc* 1941, 63, 1432.
- O'Neill, T. *J Polym Sci Part A: Polym Chem* 1972, 10, 569.
- Briggs, D. In *Surface Analysis of Polymers by XPS and Static SIMS*; Clarke, D. R.; Suresh, S.; Ward I. M., Eds.; Cambridge University Press: Cambridge, 1998.
- Watts, J. F.; Leadley, S. R.; Castle, J. E.; Blomfield, C. J. *Langmuir* 2000, 16, 2292.
- Goldstein, J.; Newbury, D.; Joy, D.; Lyman, C.; Echlin, P.; Lifshin, E.; Sawyer, L.; Michael, J. *Scanning Electron Microscopy and X-ray Microanalysis*, 3rd ed.; Kluwer Academic Plenum Press: New York, 2003.
- Cui, H.; Yang, J. L.; Liu, Z. Y. *J Chem Ind Eng* 1999, 50, 826.
- Kandare, E. *Polym Adv Technol* 2006, 17, 312.