

# Photoinitiated Grafting of Glycidyl Methacrylate and Methacrylic Acid on Ground Tire Rubber

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Received 24 September 2002; accepted 16 November 2002

**ABSTRACT:** Ground tire rubber (GTR) films and GTR particles were surface-functionalized by glycidyl methacrylate and methacrylic acid through photoinitiated grafting. The grafting yield of GTR films was determined by Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR). For the calibration of the FTIR-ATR data, X-ray photoelectron spectroscopy was used. The presence of

epoxy and carboxyl groups on the GTR surface was demonstrated by contact-angle measurements. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1622–1630, 2003

**Key words:** ESCA/XPS; infrared spectroscopy; photochemistry; rubber

## INTRODUCTION

Nowadays, the recycling of worn-out tires is a great technical and scientific challenge. Considerable efforts have been devoted to finding new applications for ground scrap tires.

Finely ground scrap tires, so-called ground tire rubber (GTR) particles, may be used as fillers and property modifiers in thermoplastic, elastomer, and thermoset blends.<sup>1</sup> However, the incorporation of GTR particles into a number of polymer matrices significantly impairs the mechanical and viscoelastic properties of the resulting systems.<sup>2</sup> This is because of the poor matrix–filler adhesion and the lack of reactive sites on the GTR particle surface.<sup>2–5</sup> Furthermore, the use of GTR in polar polymers has not yet been solved. The nonpolar nature and relatively low surface energy of GTR restricts the wetting of GTR by polar matrices.

Various surface treatments of GTR have been proposed for overcoming this problem. In the literature, several strategies for the chemical surface treatment of GTR are described:

- High-energy radiation, such as plasma, corona, and electron-beam radiation. The interfacial adhesion to various polymers can be improved by these methods because of the creation of oxidized species on the GTR surface.<sup>6</sup> However, the use of such methods is limited at present for economic reasons.

- Reactive gas treatment. Surface activation by a reactive gas treatment (e.g., a mixture of halogens and oxygen) increases the polarity of the surfaces of GTR particles and, therefore, improves their compatibility with polar matrices, such as polyurethane. The toxicity of the gas mixture does not favor the use of this technique.<sup>7,8</sup>
- Chlorination. Chlorination with trichloroisocyanuric acid has been reported to be a very effective way of modifying the GTR surface and making it more polar. However, it is not widely used because of environmental concerns.<sup>9</sup>
- Surface grafting. The interfacial adhesion can also be improved by the grafting of different monomers onto the GTR surface.<sup>10–13</sup> This grafting process results in a functionalized GTR powder with various reactive groups by the selection of suitable monomers. In this way, the surface energetics and, therefore, the wettability by polymers of GTR are improved. Furthermore, the functional groups on GTR can react with those of the polymer matrix through the formation of covalent bonds.

Naskar et al.<sup>10</sup> and Pramanik and Baker<sup>11</sup> grafted the GTR surface in the presence of thermoinitiators. The surface grafting of the monomer was initiated by the decomposition of the thermoinitiator at elevated temperatures. Adam et al.<sup>12</sup> and Abdel-Bary et al.<sup>13</sup> used high-energy radiation for the initiation of the grafting process.

Surface grafting initiated by ultraviolet (UV) light with photoinitiators is an interesting alternative approach to the surface modification of GTR particles. The procedure is very simple in comparison with other grafting procedures. When a photoinitiator is

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Contract grant sponsor: Deutsche Forschungsgemeinschaft; contract grant number: Ka 1202/7-1.

excited by UV irradiation, it abstracts hydrogen atoms from the polymer (i.e., GTR) and generates a polymer radical there. Polymer radicals act as initiation sites for grafting. A great advantage of this grafting method is that the polymer radicals can be produced directly at the GTR surface, so that the time-consuming diffusion of the initiator molecules into the GTR is omitted. Additionally, the initiation of the grafting occurs independently of the temperature and can be controlled by the UV radiation intensity.

Photoinitiated grafting has been used widely to improve specific surface properties of polymers. Its efficiency depends on many factors, such as the type of reaction, solvent, photoinitiator, UV-irradiation time, polymer substrate, and monomer.<sup>14–24</sup> Yu and Ryu<sup>14</sup> described the UV-initiated photografting of glycidyl methacrylate (GMA) onto styrene–butadiene rubber (SBR) with benzophenone (BP) as a photoinitiator.

The objective of this study was to analyze the possibility of the photoinitiated grafting of GMA and methacrylic acid (MAA) onto GTR with a commercial photoinitiator mixture. A further goal of the investigation was to find a reliable method of assessing the grafting yield.

### CONCEPT OF PHOTOCHEMICALLY INDUCED SURFACE GRAFTING

Likely the best way of achieving the optimum mechanical performance of compounds containing GTR fractions is to promote the interfacial interaction between the GTR powder and the polymers selected as matrix materials. The creation of polar functional groups on the GTR surface should result in increased reactivity and improved interfacial adhesion between the GTR and matrix polymers.

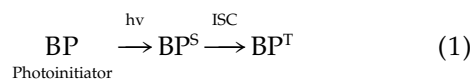
#### Mechanisms of photochemically induced surface grafting and related side reactions

Because of the complex recipe and high content of carbon black in tire mixtures, the GTR surface grafting reactions are greatly limited. One possibility is to create hydroperoxide and peroxide groups on the GTR surface before the grafting. This can be achieved in a two-step process, such as irradiation in air and mixing with functional monomers at elevated temperatures (grafting). In this case, the grafting is started by the decomposition of the peroxide and hydroperoxide groups.

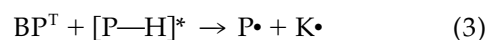
The other opportunity is to generate macroradicals directly on the GTR surface; this may induce the grafting of a liquid monomer with which GTR is pre-soaked. If there is intimate contact between the GTR and photoinitiator, a photochemically induced grafting process also becomes viable.<sup>25–27</sup> This technique seems to be the most straightforward one for GTR

functionalization. The mechanism of the photochemically induced surface grafting technique is similar to that of photocrosslinking with BP as a photoinitiator.

The BP molecules are excited to a singlet state (BP<sup>S</sup>) by absorbing near-UV irradiation. The short-lived singlet state is transformed into a triplet state (BP<sup>T</sup>) by intersystem crossing (ISC).<sup>15,25,26</sup>



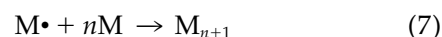
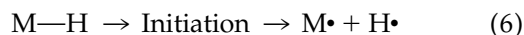
Via an inelastic collision with the polymer substrate surface (PH), some PH groups are excited to [P–H]\* by energy transfer. Furthermore, BP<sup>T</sup> abstracts hydrogen from the excited polymer surface, and polymer (P·) and ketyl radicals (K·) are formed.<sup>15,25,26</sup>



The free radicals on the GTR backbone formed by UV irradiation act as sites of attack for the monomer to be grafted. The P· macroradicals initiate the grafting reaction of the monomer (M):<sup>24–27</sup>



However, the homopolymerization of the monomer may occur as a side reaction:<sup>28,29</sup>



The grafting process according to eq. (5) results in a functionalized GTR that may possess various reactive groups by the selection of suitable monomers. In this way the surface energetics and, therefore, the wettability by polymer liquids of the GTR are improved. Furthermore, the functional groups on the GTR can react with those of the polymer matrix.<sup>30</sup> The feasibility of this concept was checked, and the first results are summarized later in this article.

## EXPERIMENTAL

### Materials and their characteristics

Grafting was performed on films of GTR and on GTR particles. The GTR was a ground summer truck tire tread mixture of Continental AG (Hannover, Ger-

**TABLE I**  
**Properties of GTR**

Property		Amount
Ingredients	SBR	55 phr
	BR	35 phr
	NR	10 phr
	Aromatic oil	35 phr
	Silica	30 phr
	Carbon black	4.3 phr
	Crosslinking ingredients	Traces
Particle size distribution	<0.1 mm	3%
	0.1–0.2 mm	57%
	0.2–0.3 mm	29%
	0.3–0.4 mm	11%
	>0.4 mm	Traces

many). This tire tread mixture was crushed by Pallmann GmbH & Co. KG (Zweibrücken, Germany). The properties of the GTR used in this study are summarized in Table I. The obtained GTR had a particle size between 0 and 400  $\mu\text{m}$ . GTR films about 1 mm thick were produced from these GTR particles by hot pressing between two pieces of aluminum foil (190°C and 10 bar).

For grafting, two monomers, GMA (Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) and MAA (Merck Eurolab GmbH, Darmstadt, Germany), were selected. Note that the grafting of GMA and MAA resulted in epoxy and carboxyl functionalities, respectively.

The photoinitiator Irgacure 1000 (Ciba Spezialitätenchemie GmbH, Lampertheim, Germany) was a mixture of 80% 2-hydroxy-2-methyl-1-phenyl-propan-1-one and 20% 1-hydroxy-cyclohexyl-phenyl-ketone. The monomer and initiator were used as received from their producers.

As solvents, ethanol and acetone (Merck Eurolab) were used as received.

### Surface grafting of GTR

The GTR films and GTR particles were treated with a patented photografting procedure.<sup>31</sup> This treatment involved the soaking of the GTR films or GTR particles in an ethanol solution containing the monomer and photoinitiator before UV irradiation. Grafted GTR grades were produced after UV irradiation under nitrogen at ambient temperatures (designated further on as GMA-g-GTR and MAA-g-GTR). A schematic of this process is given in Figure 1.

For the determination of the monomer grafting yield on the GTR, first the unreacted monomer and the respective homopolymer [poly(glycidyl methacrylate) (PGMA) or poly(methacrylic acid) (PMAA)] were separated by Soxhlet extraction. This occurred by the extraction of the gross product for 12 h with boiling acetone (for PGMA and GMA) or water (for PMAA

and MAA). Finally, the grafted product (GMA-g-GTR or MAA-g-GTR) was filtered and dried in an oven to a constant weight.

### Analysis

#### Grafting yield of the GTR films

Fourier transform infrared (FTIR) analysis (Nicolet P 510; Nicolet Instrument Co., Madison, WI) was carried out by attenuated total reflection (ATR) to identify the surface composition of the grafted GTR films. A germanium crystal at an incident beam angle of 45° was used. Five hundred scans were collected for each spectrum to improve the signal-to-noise ratio in the FTIR-ATR measurements.

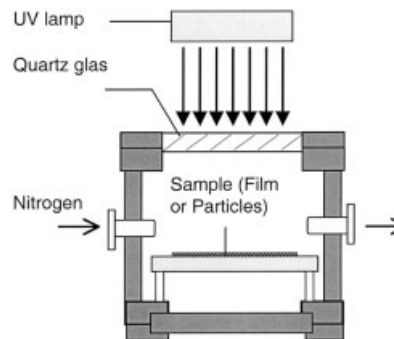
As it was difficult to measure the absolute amount of monomer grafting, the assessment of the relative graft ratio was targeted. For GMA-g-GTR and MAA-g-GTR, the relative graft ratio was determined with the relative absorbance of the carbonyl peak against that of the peak of C—H bending (disclosed later) as an internal standard:

$$\text{Relative GMA graft ratio} = \frac{A_{1735\text{cm}^{-1}}}{A_{1451\text{cm}^{-1}}} \quad (1) \quad (8)$$

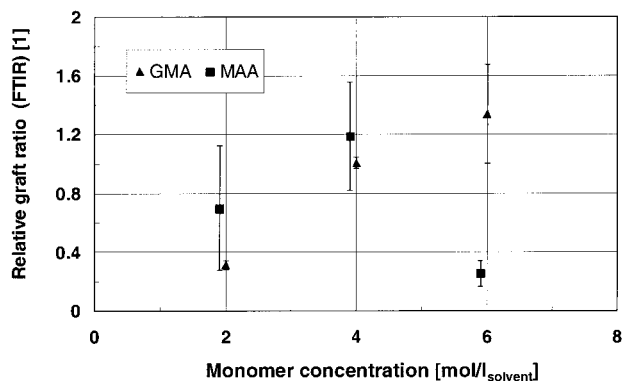
$$\text{Relative MAA graft ratio} = \frac{A_{1700\text{cm}^{-1}}}{A_{1451\text{cm}^{-1}}} \quad (1) \quad (9)$$

Three different samples were used to obtain the graft ratio data. The FTIR-ATR data were very reproducible.

To determine the absolute grafting yield onto the GTR surface, we needed to calibrate the FTIR-ATR results. For this calibration, the method of direct standardization was used.<sup>32</sup> Accordingly, samples with different relative graft ratios assessed by FTIR-ATR were analyzed also by X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded on an Axis Ultra XPS spectrometer (Kratos Analytical, Manchester, UK) with a mono-Al  $K\alpha_{1,2}$  X-ray radiation source. The atomic concentrations of the elements were calcu-



**Figure 1** Schematic of the surface photografting process.



**Figure 2** Influence of the monomer concentration in the wetting solution on the relative graft ratio of the GTR films (grafting conditions: 0.2 mol of Irgacure/L of solvent, 30 s of UV irradiation, 20°C, and N<sub>2</sub>).

lated from their peak areas and standard photoionization cross sections. The amount of the grafted monomer was determined by a comparison of the measured oxygen content with the calculated value for the pure monomer with the following formulas:<sup>15,16</sup>

$$\text{Amount of grafted GMA} = \frac{\frac{O}{O+C}}{\frac{3}{3+7}} \quad (1) \quad (10)$$

$$\text{Percentage grafted GMA} = \frac{10 \cdot O/C}{3 + 3 \cdot O/C} \times 100 \quad (11)$$

$$\text{Percentage grafted MAA} = \frac{6 \cdot O/C}{2 + 2 \cdot O/C} \times 100 \quad (12)$$

The calibration plots contained the percentages of the grafted monomers derived from XPS as a function of the relative graft ratios from the FTIR-ATR analysis.

### Grafting yield of the GTR particles

For the determination of the grafting yield of GTR particles, only XPS spectroscopy was applied. The absolute grafting yield was calculated according to eqs. (11) and (12).

### Contact-angle measurements

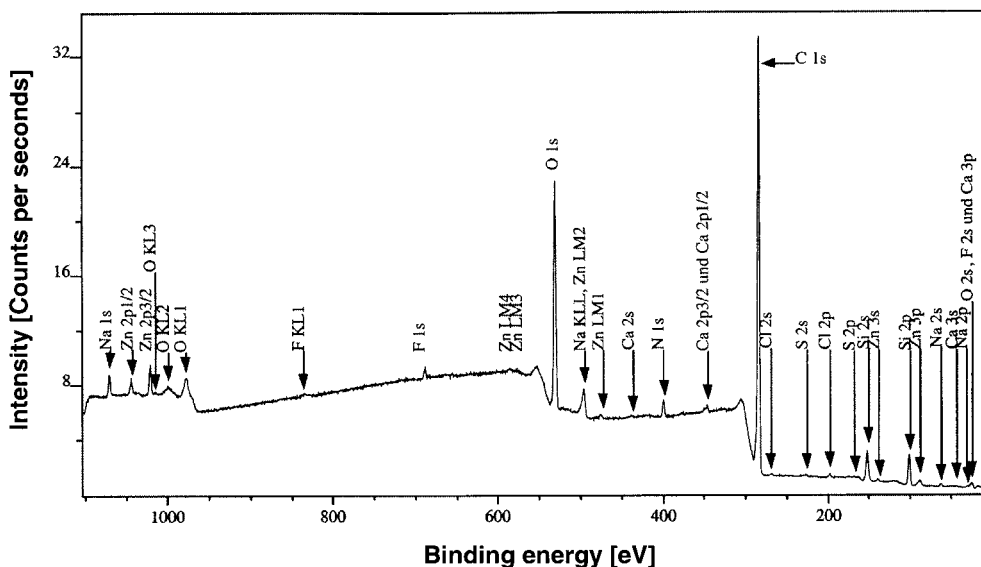
To characterize the surface properties, we also performed contact-angle measurements (with the sessile drop technique). The average contact angle of 10 drops of deionized water on the surface of the GTR film was determined with a goniometer from Ramé Hart, Inc. (model A-100; Mountain Lakes, NJ).

## RESULTS AND DISCUSSION

### Grafting yield and its determination

The GTR films were grafted with both GMA and MAA. The extent of grafting, as measured by FTIR-ATR at different monomer concentrations, is shown in Figure 2. The monomer concentration means the concentration of the monomer in 1 L of ethanol (wetting solution). The UV irradiation time was 30 s.

As shown in Table I, the GTR consisted of SBR, natural rubber (NR), and butadiene rubber (BR). To detect the total grafting ratio of the GTR surface, we selected as a reference signal for GTR the (C—H) bending vibration,  $\delta_{sy}(\text{CH}_2)$ , at 1451 cm<sup>-1</sup>. For the



**Figure 3** Overview XPS spectrum of the untreated GTR film.

TABLE II  
GMA and MAA Grafting Yield of GTR Films Calculated from XPS Results

Sample	Monomer	Monomer concentration [mol/L of solvent]	XPS O/C ratio (1)	Grafting yield (%)
1	GMA	2	0.0085	2.81
2	GMA	4	0.0204	6.66
3	GMA	6	0.1447	42.14
4	MAA	2	0.0467	13.38
5	MAA	4	0.0677	19.02
6	MAA	6	0.0371	10.73

monomers GMA and MAA, the carbonyl stretching  $\nu(\text{C}=\text{O})$  at 1735 and 1700  $\text{cm}^{-1}$ , respectively, was considered.

As can be seen in Figure 2, no uniform tendency for the grafting of GMA and MAA on the GTR films could be concluded. The relative graft ratio of GMA increased with the monomer concentration, whereas the MAA-grafted samples showed the highest graft ratio at a concentration of 4 mol/L of solvent. This suggests that homopolymerization dominated at high MAA concentrations, and so an optimum monomer concentration existed for MAA grafting.

Figure 3 shows the complete XPS overview spectrum of the untreated GTR film (reference sample). This spectrum shows many signals, which refer to multiple elements in the surface region and, in addition, various possible chemical linkages with carbon. Beside the major elements (carbon and oxygen), nitrogen, fluorine, sodium, silicon, sulfur, chlorine, calcium, and zinc were detected in the surfaces of the ungrafted GTR films.

The untreated GTR film also indicated an O/C value ( $\{\text{O}/\text{C}\}_{\text{R}}$ ). It was likely due to Si, Al, and Zn, which were present as their oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{ZnO}$ , respectively). Therefore, this value should be deduced from the values of the grafted GTR samples ( $\{\text{O}/\text{C}\}_{\text{G}}$ ) to determine the organically bound oxygen:

$$\text{O}/\text{C} = \{\text{O}/\text{C}\}_{\text{G}} - \{\text{O}/\text{C}\}_{\text{R}} \quad (1) \quad (13)$$

Table II lists the grafting yield on the examined GTR films based on XPS results [see eqs. (11) and (12)]. The absolute grafting yields of the GTR films showed the same tendency determined by FTIR-ATR. The highest grafting yield was found for GMA with a concentration of 6 mol/L of solvent, whereas for MAA grafting, an optimum was noticed at a concentration of 4 mol/L of solvent.

To calibrate the relative grafting ratio determined by FTIR-ATR [eqs. (8) and (9)], we took XPS spectra of the same samples. Figure 4 shows the calibration function derived. It was assumed that there was a linear correlation between FTIR-ATR and XPS data:

$$\text{GMA grafting yield (\%)} x_{\text{GMA}} = 22 \cdot \frac{A_{1735\text{cm}^{-1}}}{A_{1451\text{cm}^{-1}}} \quad (14)$$

$$\text{MAA grafting yield (\%)} x_{\text{MAA}} = 17 \cdot \frac{A_{1700\text{cm}^{-1}}}{A_{1451\text{cm}^{-1}}} \quad (15)$$

However, the experimental data deviated from the ideal linear function. This deviation was due to the moderate signal-to-noise ratio of the FTIR-ATR analysis. Recall that carbon-black-filled GTR films showed some inherent absorbance in the interesting IR wave-number range. A further source of the deviation was the multiplicity of elements in the surface regions of the GTR films and their pollution. Accordingly, a universal calibration for the FTIR-ATR results based on XPS investigations could hardly be given.

With a comparison of the C1s spectra of ungrafted GTR films with those of GMA- and MAA-grafted ones (Fig. 5), the occurrence of grafting became obvious.

The C1s spectra were deconvoluted into six constituting peaks (A–F). These peaks were assigned to various chemical linkages according to the related binding energies. This was done by a consideration of literature data<sup>33</sup> (Table III).

Figure 5(b,c) clearly shows that the ratios of the component peaks E and F (referring to the presence of esters and carbonic acids, respectively) to the refer-

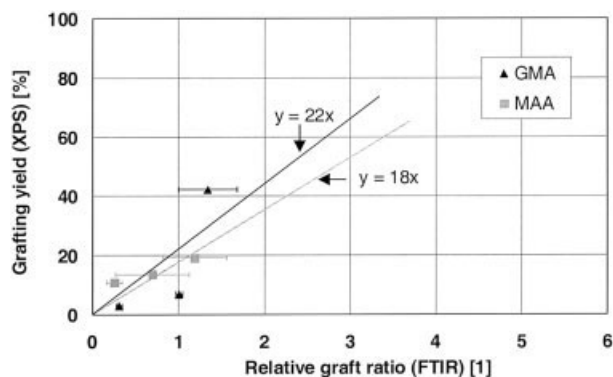


Figure 4 Calibration of FTIR-ATR results for the GTR films based on the corresponding XPS results.

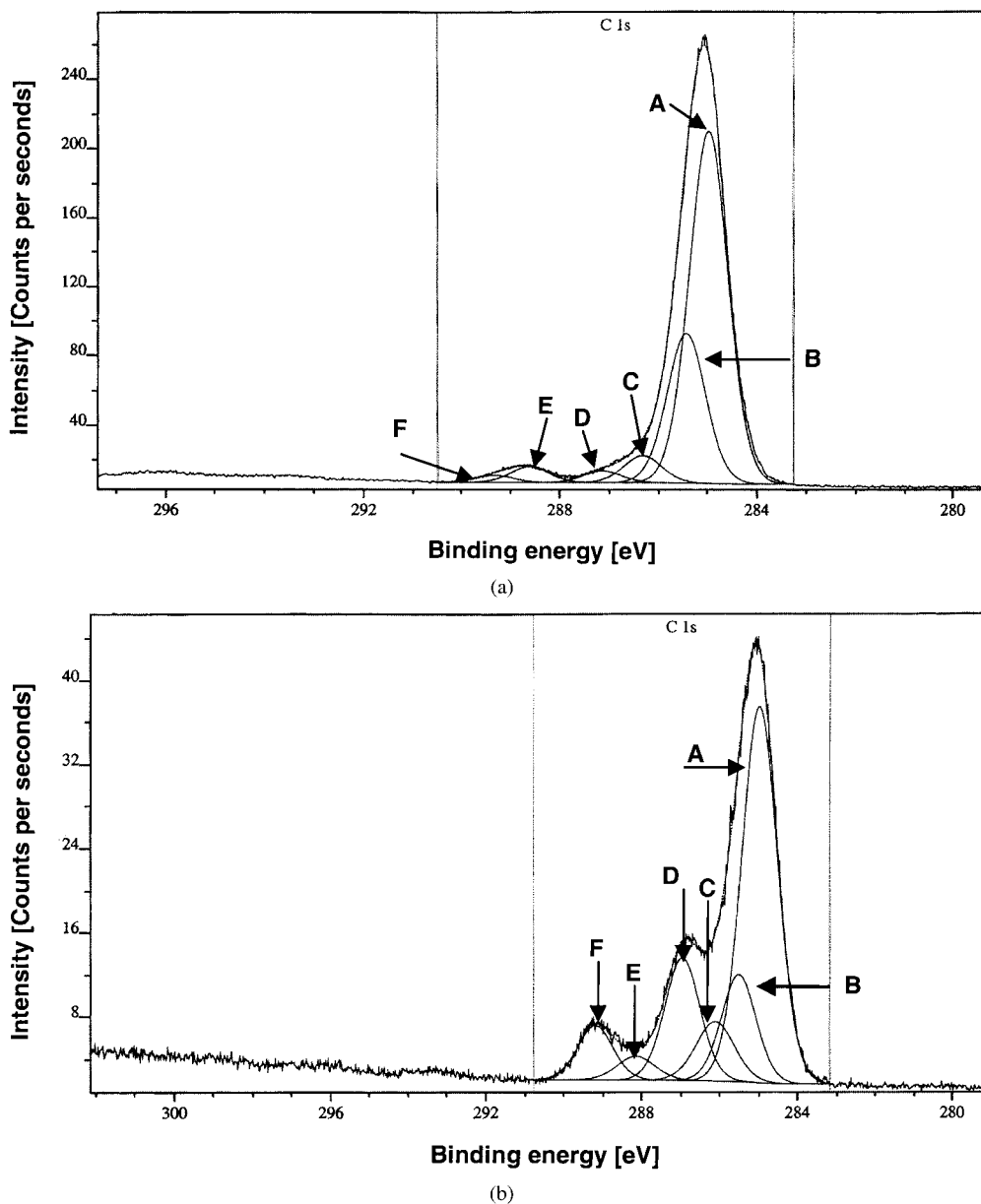


Figure 5 C1s spectra of (a) the ungrafted GTR film, (b) the GMA-grafted film, and (c) the MAA-grafted GTR film.

ence peak A (hydrocarbons) increased. This tendency became even more pronounced when the appropriate values of the reference sample in Figure 5(a) were considered.

Table IV summarizes the determined values and absolute grafting yields on the examined GTR particles. For the XPS analysis, the GTR particles were placed on an adhesive strip. The grafted monomer content was determined by a consideration of eqs. (11)–(13). With the selected monomer concentration of 6 mol/L of solvent, less MAA was grafted than GMA onto the GTR particles. This agreed with the results achieved on GTR films. Furthermore, the grafting yield of the GTR particles was considerably smaller than that on the GTR films. This effect could be attrib-

uted to the particle form irradiation (only one side of the GTR particles was irradiated). However, the information depth of the XPS measurement for particles was significantly smaller than for films because of the rough particle structure. Note that XPS informed us about grafting from a surface layer 5–8 nm thick.

**Influence of grafting on the wetting behavior**

Changes in the chemical surface structures of GTR films due to the grafting of functional monomers should also manifest in their wettability. The results of the contact-angle measurements (Fig. 6) show that the grafted samples always possessed lower contact angles with water than the ungrafted ones. Accordingly,

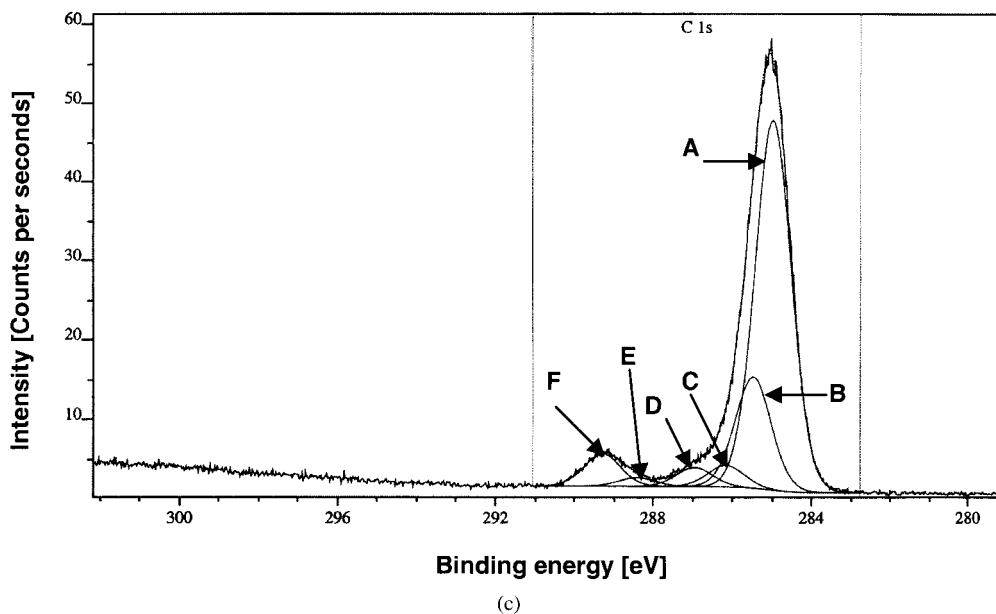


Figure 5 (Continued from the previous page)

the wettability of the films by water was improved by the grafted GTR surface. For MAA-grafted samples, the difference in the wetting behavior was more pronounced than for GMA grafting. With an increasing GMA concentration in the grafting solution, the contact angle of GMA-g-GTR with water decreased. However, for MAA, smaller contact angles were observed at lower monomer concentrations.

Figure 7 shows the contact angle with water as a function of the relative graft ratio for GTR films. The contact angle decreased with an increasing relative graft ratio. This was due to the polarity of GTR from grafting. The surface energy and its polar and dispersive constituents were determined on ungrafted and grafted GTR films with the method of Owens and

Wendt.<sup>34</sup> As shown in Figure 8, the surface energies of the GTR increased with GMA and MAA grafting. With respect to ungrafted GTR, a prominent increase could be recognized in the polar surface energy term.

#### Influence of the GTR type

The GTR used contained mostly silica reinforcements (cf. Table I). This is characteristic of the new generation of tire compounds. The question arises whether or not the aforementioned photografting procedure can be adopted to traditional GTRs containing solely carbon black as a filler (GTR-CB). GTR-CB was supplied by Scanrub AS (Viborg, Denmark) in a particle size range of 0.4–0.7  $\mu\text{m}$ . The average composition of this

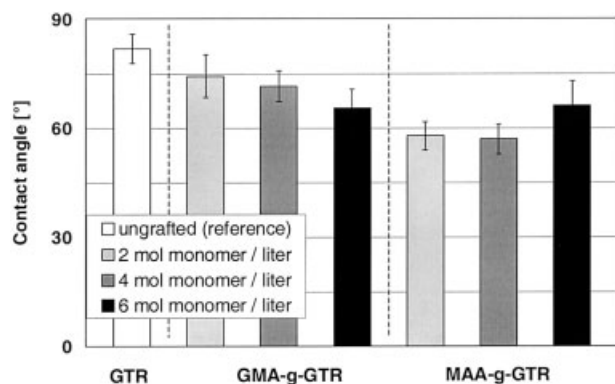
TABLE III  
Assignment of the Component Peaks in the C1s Spectra to Various Chemical Units

A	B	C	D	E	F
$\text{C}_x\text{H}_y^a$	$-\text{C}-\text{NH}_x$ $-\text{C}-\text{S}$ $-\text{C}-\text{C}(\text{O})-\text{O}-$	$-\text{C}-\text{OH}$ $-\text{C}-\text{O}-\text{C}-$	$-\text{C}=\text{O}$ (keto group)	$-\text{C}-\text{C}(\text{O})-\text{OR}$ (ester) $-\text{C}-\text{C}(\text{O})-\text{OH}$ (carboxylic acids)	

<sup>a</sup> Possible conjugated  $\text{C}=\text{C}$  linkages coincide here with the component peak A.

TABLE IV  
GMA and MAA Grafting Yield of GTR Particles Calculated from XPS Results

Name	Grafting conditions	XPS O/C (1)	Grafting yield (%)
GMA-g-GTR	6 mol of GMA/L of solvent 0.2 mol of Irgacure® 1000/L of solvent 20°C, $\text{N}_2$ , 30 s of UV irradiation	0.0276	8.95
MAA-g-GTR	6 mol of MAA/L of solvent 0.2 mol of Irgacure® 1000/L of solvent 20°C, $\text{N}_2$ , 30 s of UV irradiation	0.0103	3.06

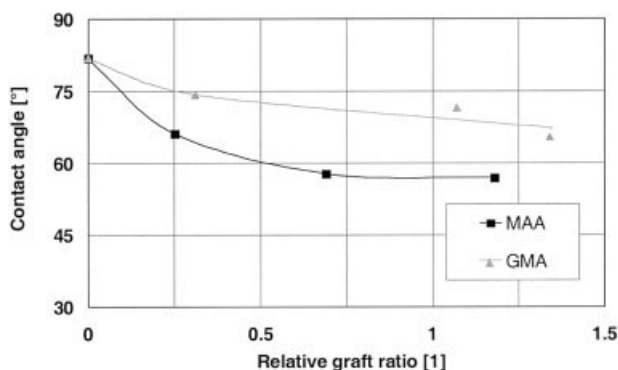


**Figure 6** Contact angle with distilled water for the ungrafted, GMA-grafted, and MAA-grafted GTR films.

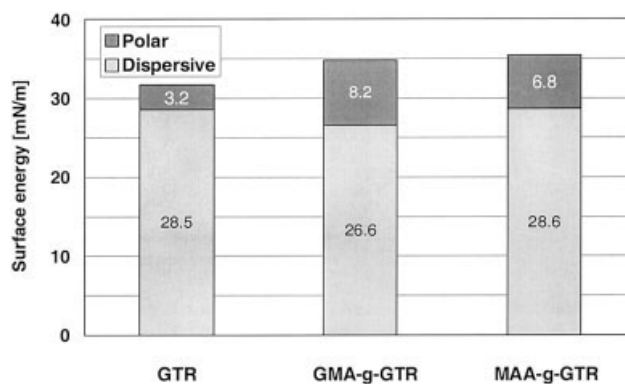
GTR-CB was as follows (data in parts): SBR, 40; BR, 20; NR, 30; butyl + carboxylated butyl rubber, 10; processing oil, 37; and high abrasion furnace (HAF)-type carbon black, 34. For its grafting, the same conditions indicated in Table IV were used. The relative graft ratio of this GTR-CB deduced from FTIR-ATR measurements was 0.15 for GMA grafting and 0.10 for MAA grafting. These values were markedly below those achieved on GTR with dominant silica filling; the relative graft ratios in that case were 1.3 and 0.23 for GMA and MAA, respectively (cf. Fig. 2). This finding suggests that the presence of carbon black greatly reduced the efficiency of the targeted photografting. This was obviously due to the UV screening and related effects of the carbon black. In a fundamental study devoted to clarifying the effect of carbon black, it was shown that at lower carbon black contents (<15 phr), this grafting process worked well, whereas at higher loadings (>30 phr), it practically did not work.<sup>32</sup>

## CONCLUSIONS

On the basis of this work devoted to the surface functionalization of GTR via the photochemically induced



**Figure 7** Relationship between the contact angle with distilled water and the relative graft ratio (FTIR) for the grafted GTR films



**Figure 8** Surface energy of the ungrafted, GMA-grafted, and MAA-grafted GTR films.

grafting of monomers (i.e., GMA and MAA), the following conclusions can be drawn:

- UV-irradiation-induced grafting works well for GTR as long as the GTR is silica-filled and/or contains only a small amount of carbon black ( $\leq 15$  phr).
- The grafting degree was determined by the FTIR-ATR technique with an inherent standard peak [C—H bending vibration  $\delta_{sy}(\text{CH}_2)$ ]. The FTIR results (relative graft ratio) were calibrated by XPS measurements. The occurrence of grafting was also demonstrated, apart from these spectroscopic methods, by wetting measurements (sessile drop technique).

Continental AG and Ciba Spezialitätenchemie GmbH are acknowledged for providing materials.

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