

# Determination Methods of the Grafting Yield in Glycidyl Methacrylate-Grafted Ethylene/Propylene/Diene Rubber (EPDM-g-GMA): Correlation Between FTIR and $^1\text{H-NMR}$ Analysis

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**ABSTRACT:** A normalized and universally applicable calibration function for the Fourier-transformed infrared (FTIR) quantification of the glycidyl methacrylate (GMA) grafting yield in polymers of known compositions having ethylene block sequences was established. The  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectroscopy results achieved on different GMA-grafted ethylene/propylene/diene rubber (EPDM-g-GMA) and ethylene/GMA copolymers were correlated to their FTIR data to calibrate the relative determination of the FTIR method. Both direct and indirect standardization approaches were followed and evaluated. The calibration deduced was used to investigate the free radical grafting reaction of GMA on EPDM rubber in the melt phase. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2616–2624, 1999

**Key words:** glycidyl methacrylate; grafting yield determination; ethylene/propylene/diene terpolymer (EPDM); melt functionalization; peroxide induced grafting; FTIR;  $^1\text{H-NMR}$

## INTRODUCTION

Although the synthesis of new polymeric engineering materials from new monomers is still possible, the chemical modification of already existing polymers has gained increasing research interest.<sup>1</sup> Functionalization of polyolefins with the introduction of polar groups to the polymer backbone has been performed intensively.<sup>2–5</sup> Maleic anhydride, maleic acid, dibutyl maleate, and various acrylic acids and esters are the main grafting monomers in such modifications. In recent years,

glycidyl methacrylate (GMA) has been increasingly used as grafting monomer because of its epoxide function, which is highly electrophilic and capable of reacting with a variety of functional groups as carboxylic acids, amides, and alcohols.<sup>6,7</sup>

Functionalized polymers are widely used as *in situ* compatibilizer<sup>8</sup> in polymer blends. Because only a few polymers are miscible, an effective compatibilizer is required to reduce the interfacial tension and increase the interfacial adhesion. Reduction of the dispersed phase particles size usually goes along with enhanced mechanical performance of these immiscible blends.

The evaluation of the grafting conditions (e.g., peroxide or monomer concentration, processing parameters like temperature and residence time) on the grafting reaction requires accurate analytical methods to determine the degree of functionalization in the final product. Various methods

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**Table I** Composition and Processing Parameters Used for the GMA Functionalization of the EPDM Rubber

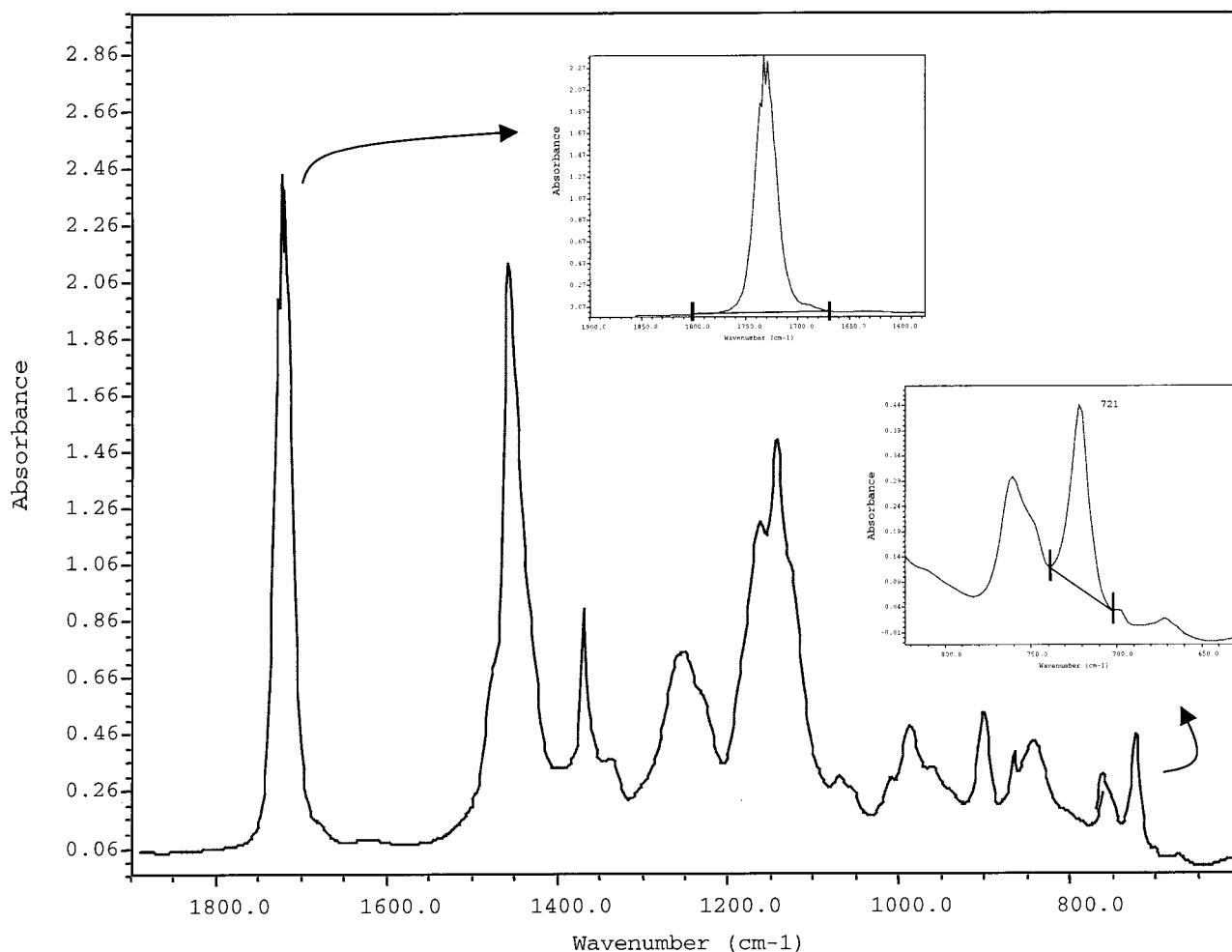
Sample Code	GMA (phr)	Peroxide (phr)	Torque <sup>a</sup> (rpm)	Temperature Settings <sup>a</sup> (°C)	$\Delta T^b$ (°C/min)
NMR-32	30	2.0	35, 55	110, 130	10
NMR-34	30	0.5	35, 55	110, 145	10
NMR-37	15	0.25	35, 55	110, 160	10

<sup>a</sup> 1st value: setting at charge; 2nd value: setting at homogenization.

<sup>b</sup> Linear temperature increase up to the final temperature.

have been described in the literature like infrared (IR) spectroscopy, titration, elemental analysis,<sup>9</sup> and nuclear magnetic resonance (NMR).<sup>10–12</sup> The most widely used method for qualitative analysis of the functionalization,<sup>13,14</sup> however, is the IR spectroscopy. Quantitative approaches by means

of Fourier-transformed infrared (FTIR) also followed “preestablished calibration curves.” In such cases, blends of predefined compositions with the monomer<sup>15</sup> or similarly structured polymers showing akin absorption signals, were used for the calibration.

**Figure 1** Characteristic peaks in the FTIR spectra of EPDM-g-GMA.

**Table II** CHN Elemental Analysis of the EPDM Rubber (Buna AP 447)

Element	Measured Values (%)	Calculated Values (%)
H	13.85	14.16
C	83.86	85.84
N	0	0

Titration methods have also been applied.<sup>16,17</sup> However, all of these methods exhibit major shortcomings. The monomer might be volatile, as it is in the case of GMA. The determination of hydrolyzed epoxides in the GMA grafted polymer is encountered by difficulties related to the accurate end point detection and phase separation between aqueous and organic phases.

The target of this work was to correlate the results of the fast and routinely used FTIR technique to the more specialized and time-consuming NMR technique.

## EXPERIMENTAL

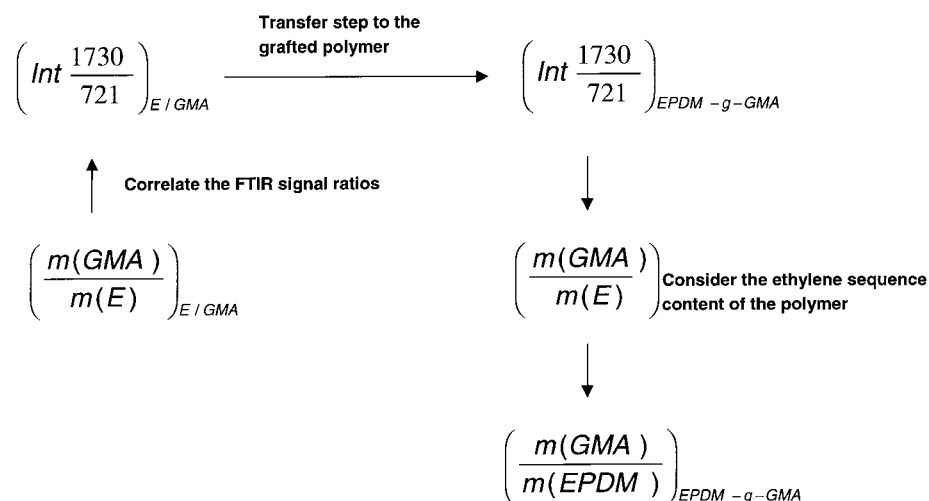
### Materials

The ethylene/glycidyl methacrylate (*E/GMA*) copolymers Igetabond 2C (6 wt % GMA; melt flow index (MFI), 3 g/10 min) and Igetabond E (12 wt % GMA; MFI, 3 g/10 min) were kindly supplied by Sumitomo Chemical Company, Ltd. (Tokyo, Japan). Another *E/GMA* copolymer, Lotader AX 8840 (8 wt % GMA,

MFI 190°/2.16 Kg: 4–6 g/10 min), was supplied by Elf Atochem Deutschland GmbH (Düsseldorf, Germany). The ethylene/propylene/diene terpolymer (EPDM) Buna AP 447 (74 wt % ethylene, 21 wt % propylene, 5 wt % ethylenenorbornene, density = 0.87 g/cm<sup>3</sup>) was provided by Bayer AG (Leverkusen, Germany). Reagent grade GMA, chloroform-*d* (CDCl<sub>3</sub>, bp = 61°C) and 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, bp = 146°C) were purchased from Sigma-Aldrich Chemie GmbH (Deisenhofen, Germany) and used without further purification. The used dicumylperoxide (DCP) Perkadox BC-40B-pd (DCP content: 40 wt %) was purchased from Akzo Nobel (Düren, Germany).

### Free Radical Grafting of GMA onto EPDM

The grafting reaction of GMA onto EPDM was performed in an internal batch mixer (Brabender Plasticorder). Torque and temperature were monitored and recorded online. The required amount of EPDM (Buna AP 447) was charged into the preheated mixing chamber. After 2 min of pre-mixing the liquid, GMA and the DCP were introduced in an EPDM melt at ≈120°C and homogenized with 35 rpm. The mixing chamber was kept closed by a ram. Then the temperature was raised by external heating to 160°C (20°C/min). The mixing speed was increased to 55 rpm to start the decomposition of DCP introducing the free radical grafting reaction. After the reaction had completed (assessed by torque measurement), the samples were discharged from the mixing chamber and cooled to room temperature. The batch mixer feedings and settings are listed in Table I.



**Figure 2** Standardization concept to determine the GMA grafting degree in polymers with high ethylene content.

### <sup>1</sup>H-NMR Measurement

The sample materials were dissolved in boiling solvent by means of ultrasonics. The <sup>1</sup>H-NMR spectra of the *E*/GMA and GMA-grafted EPDM (EPDM-g-GMA) were performed at 400.13 MHz on a Bruker AMX 400 spectrometer. The *E*/GMA were additionally measured on a Varian Gemini 2000 (300 MHz) BB spectrometer. The EPDM-g-GMA were measured in CDCl<sub>3</sub> at 60°C (64 scans), whereas the *E*/GMA copolymers were measured in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 125°C (64–1024 scans). These conditions were selected after testing several solvents and temperatures. In all cases, tetramethylsilane (TMS) was used as internal standard. The composition of all copolymers was calculated by integration of the related signals.

### FTIR Measurement

Thin films (≈100 μm) of the samples were prepared by pouring the NMR solutions onto polytetrafluoroethylene foil. The solvent was evaporated under vacuum. Absorbance spectra of all films were acquired using a Nicolet P 510 FTIR spectrometer after 50 scans at a resolution of 4 cm<sup>-1</sup>. The spectra were recorded four times per film at different positions and baseline corrected (“auto-correct-tilt”-mode). The characteristic signals in the spectra (Fig. 1) are found at ν = 1730 cm<sup>-1</sup> for the carbonyl stretching vibration of GMA and at ν = 721 cm<sup>-1</sup> for the CH<sub>2</sub>-rocking vibration of —[CH<sub>2</sub>]<sub>n≥4</sub> corresponding to the EPDM polymer chain. Following the methodology described by Fodor et al.,<sup>18</sup> who used FTIR to analyze oxidized

polyethylene, the quantity of the functional units was determined by integration of the appropriate signals. For the carbonyl stretching vibration the integration limits were 1800–1665 cm<sup>-1</sup>. This signal is well separated from other bands. The signal at 721 cm<sup>-1</sup> is not obviously separated from other peaks. The limits were symmetrically selected around the maximum with 740.94–702.34 cm<sup>-1</sup>. To eliminate the film thickness dependence, the integral absorption ratio was formed. The four determined values per sample were averaged to consider statistic deviations.

### CHN Elemental Analysis

To check the supplied information about the composition of the EPDM rubber, a Carbon, Hydrogen and Nitrogen (CHN) analysis was performed using a Perkin Elmer EA 240 elementary analyser. The results are shown in Table II.

## RESULTS AND DISCUSSION

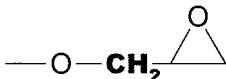
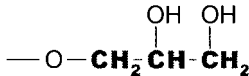
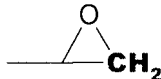
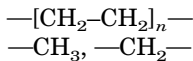
### Calibration of FTIR Measurements

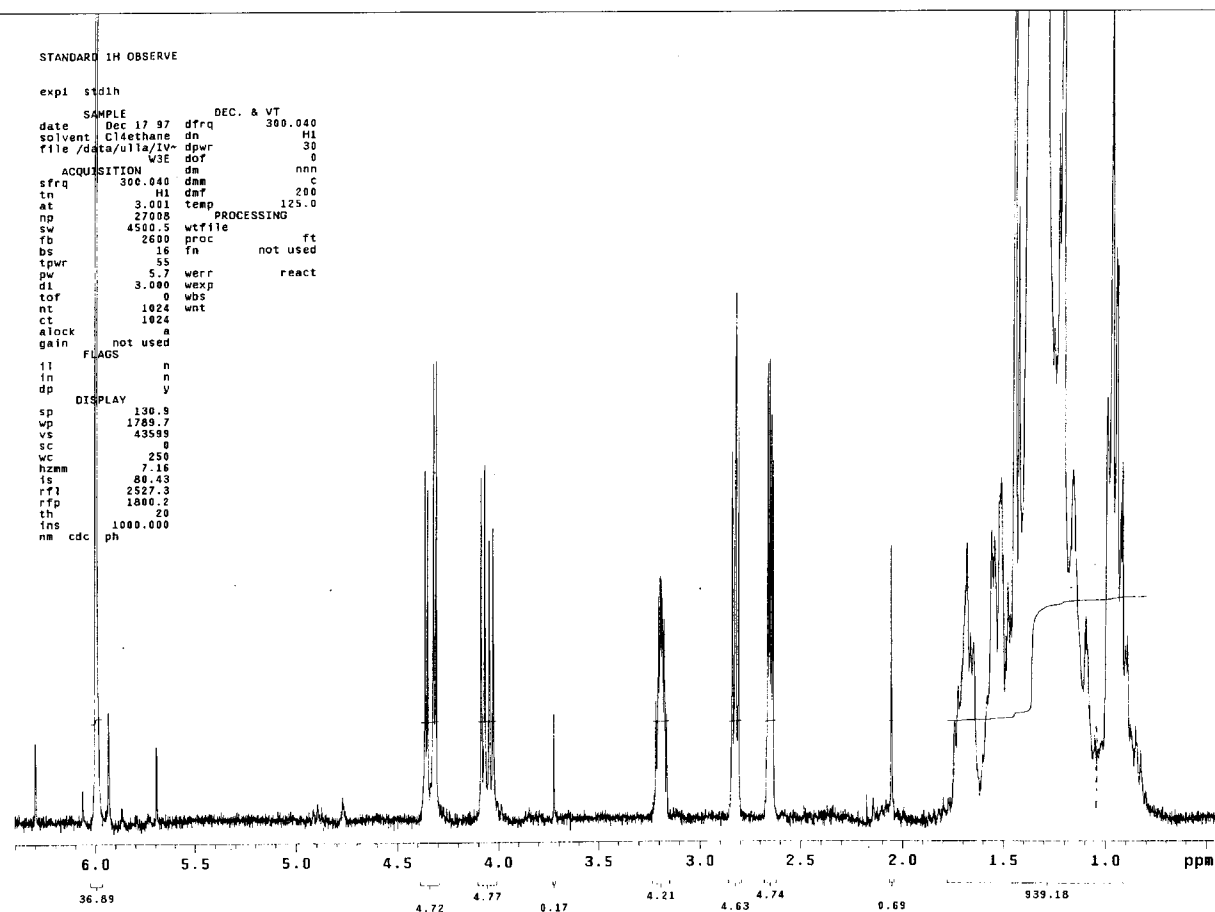
#### Indirect Standardization with *E*/GMA

*E*/GMA copolymers consist of the same functional units that are responsible for the characteristic signals in the FTIR spectra of EPDM-g-GMA. Although GMA is not grafted but copolymerized, it can be assumed that the related FTIR spectra show the same absorption properties.

In the following, the grafting degree will be expressed as:

**Table III** Assignment of the Characteristic Signals in the <sup>1</sup>H-NMR Spectra for the *E*/GMA Copolymers

<i>A</i> <sub>3.6–4.4</sub>	3.87 ppm, 4.30 ppm	[2H]		GMA
		[5H]		GMA
<i>A</i> <sub>2.6–2.9</sub>	2.63 ppm, 2.83 ppm	[2H]		GMA
<i>A</i> <sub>0.5–2.4</sub>		[4H] [5H]		( <i>E</i> ) <sub>n</sub> GMA



**Figure 3**  $^1\text{H-NMR}$  spectra of the E/GMA copolymer: Igetabond E (experimental conditions: Varian Gemini 200 BB, 300 MHz).

$$\text{phr GMA onto EPDM} = \frac{m(\text{GMA})}{m(\text{EPDM})} \cdot 100 \quad (1)$$

wt % GMA onto EPDM

$$= \frac{[m(\text{GMA})]/[m(\text{EPDM})]}{1 + [m(\text{GMA})]/[m(\text{EPDM})]} \cdot 100 \quad (2)$$

The basic idea behind the concept is to transfer  $\left(\text{Int} \frac{1730}{721}\right)_{E/GMA}$ , which belongs to  $\left(\frac{m(\text{GMA})}{m(\text{E})}\right)_{E/GMA}$ , into  $\left(\text{Int} \frac{1730}{721}\right)_{EPDM-g-GMA}$  with its corresponding  $\left(\frac{m(\text{GMA})}{m(\text{E})}\right)_{EPDM-g-GMA}$ . Provided the constitution of the EPDM is known, the next transfer step is from  $\left(\frac{m(\text{GMA})}{m(\text{E})}\right)_{EPDM-g-GMA}$  to  $\left(\frac{m(\text{GMA})}{m(\text{EPDM})}\right)_{EPDM-g-GMA}$ .

A sketch of this standardization concept is depicted in Figure 2.

The method requires a precise knowledge of:

1. The composition of the E/GMA copolymer to determine  $\left(\frac{m(\text{GMA})}{m(\text{E})}\right)_{E/GMA}$ .
2. The EPDM's composition. This information is needed to calculate  $\left(\frac{m(\text{GMA})}{m(\text{EPDM})}\right)_{EPDM-g-GMA}$  from  $\left(\frac{m(\text{GMA})}{m(\text{E})}\right)_{EPDM-g-GMA}$ .

The composition of the copolymers was determined by quantitative  $^1\text{H-NMR}$  analysis from the relative areas of the following signals as shown in Table III. A corresponding  $^1\text{H-NMR}$  spectra of a E/GMA is shown in Figure 3.

The E/GMA composition  $\left(\frac{m(\text{GMA})}{m(\text{E})}\right)_{E/GMA}$  is calculated (with:  $M(\text{GMA}) = 142.15$  g/mol;  $M(\text{E}) = 28.05$  g/mol) according to:

**Table IV** Compositions and Related FTIR Integral Absorption Ratios Along with the GMA Contents Determined by the  $^1\text{H-NMR}$  Spectra

Sample	$[m(\text{GMA})]_{\text{total}}/[m(E)]$	$[m(\text{GMA})_{\text{Epoxyde}}]/[m(E)]$	Int (1720)/(721)	$\text{GMA}_{\text{Epoxyde}}$ (wt %)	$\text{GMA}_{\text{total}}$ (wt %)
Lotader AX 8840	0.09315	0.06615	2.47	6.205	8.53
Igetabond 2C	0.05895	0.05255	1.59	4.99	5.57
Igetabond E	0.1014	0.0935	2.77	8.28	9.20
NMR-32	0.3320	—	11.89	19.60	19.72
NMR-34	0.3032	—	10.18	18.27	18.33
NMR-37	0.1142	—	3.72	7.60	7.79

$$[n(\text{GMA})]/[n(E)]$$

$$= \frac{(A_{2.6-2.9})/(2) + (A_{3.6-4.4} - A_{2.6-2.9})/(5)}{(A_{0.5-2.4} - 5 \cdot A_{2.6-2.9})/4} \quad (3)$$

$$\Rightarrow \frac{m(\text{GMA})}{m(E)} = \frac{n(\text{GMA})}{n(E)} \cdot \frac{M(\text{GMA})}{M(E)} \quad (4)$$

Table IV shows the compositions ascertained by  $^1\text{H-NMR}$  and the FTIR integral absorption ratios. The NMR analysis reveals the great differences between the total amount of GMA units in the polymer and the amount of GMA having intact (i.e., not opened) epoxide rings.

It is interesting to note the deviation between the real  $E/\text{GMA}$  compositions determined by  $^1\text{H-NMR}$  and the material data provided by the manufacturers. Table IV contains the experimental reaction data.

#### Direct Standardization

In contrast to the previously described method, it is also possible to work without external standard substances. The grafted material itself functions as standard material. Again, an absolute method like  $^1\text{H-NMR}$  is needed to determine the grafting degree beside the relative FTIR measurement.

The  $^1\text{H-NMR}$  analysis was performed as described for  $E/\text{GMA}$ , but with differing signal intervals as shown in Table V. The number of hydrogens in the region 0.5–2.4 ppm ( $A_{0.5-2.4}$ ) deriving from the EPDM polymer chain are calculated

**Table V** Assignment of the Remaining Characteristic Signals in the  $^1\text{H-NMR}$  Spectra of EPDM-g-GMA

$A_{0.5-2.4}$	[14.0036 H] [5H]	See Figure 5 — $\text{CH}_3$ , — $\text{CH}_2$ —	EPDM GMA
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according to Figure 4 and Table VI. A typical spectra of EPDM-g-GMA is shown in Figure 5.

The position of GMA grafted to the EPDM chain by free radical grafting does not influence the analysis of the NMR spectra, as can be seen in Figure 6. The double bonds of GMA are formally “inserted” into the P–H (P: macromolecule) bonds during the grafting reaction. This hydrogen, now on the new terminal carbon atom, will still be found at  $\approx 2.2$  ppm.<sup>19,20</sup> That means within the defined peak area 0.5–2.4 ppm. The ratio is calculated with respect to the EPDM’s composition (Table VI) as follows:

$$[n(\text{GMA})]/[n(\text{EPDM 447})]$$

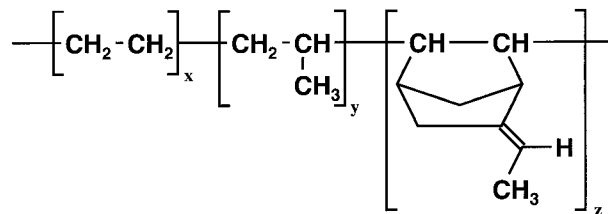
$$= \frac{(A_{2.6-2.9})/(2) + (A_{3.6-4.4} - A_{2.6-2.9})/(5)}{(A_{0.5-2.4} - 5 \cdot A_{2.6-2.9})/(14.0036)} \quad (5)$$

$$\Rightarrow \frac{m(\text{GMA})}{m(\text{EPDM 447})}$$

$$= \frac{n(\text{GMA})}{n(\text{EPDM 447})} \cdot \frac{M(\text{GMA})}{M(\text{EPDM 447})} \quad (6)$$

$$\Rightarrow \frac{m(\text{GMA})}{m(E)} = \frac{100}{74} \cdot \frac{m(\text{GMA})}{m(\text{EPDM 447})} \quad (7)$$

The resulting correlation of FTIR and the corresponding  $\left(\frac{m(\text{GMA})}{m(E)}\right)_{\text{EPDM-g-GMA}}$  values is shown in Figure 7.

**Figure 4** Constitution of EPDM (Buna AP 447).



**Table VI** Composition of EPDM Buna AP 447

Unit	Ethylene	Propylene	Ethylidenenorbornene
wt %	74	21	5
Sum formula	C2H4	C3H6	C9H12
Unit weight	28.05	42.08	120.19
Number of units	74/28.05 = 2.638	21/42.08 = 0.4990	5/120.19 = 0.0416
Unit relationship	63	12	1
Number of H deriving from this unit	4 × 2.638 = 10.552	6 × 0.4990 = 2.994	11 × 0.0416 = 0.4576
Total		14.0036	

### Comparison of the Two Standardization Methods

The indirect and direct methods resulted in the two equations:

$$E/GMA \text{ copolymer: } \frac{m(\text{GMA})}{m(E)} = 0.0371 \cdot \text{Int} \frac{1730}{721} (R^2 = 0.9962) \quad (8)$$

$$EPDM-g-GMA: \frac{m(\text{GMA})}{m(E)} = 0.0288 \cdot \text{Int} \frac{1730}{721} (R^2 = 0.9908) \quad (9)$$

The indirect standardization method yields 28.8% higher values for  $[m(\text{GMA})/m(E)]$ , i.e., higher GMA grafting rates onto EPDM, than the direct standardization. Another consideration is that the  $\left(\text{Int} \frac{1730}{721}\right)_{EPDM-g-GMA}$  values are higher than those of  $E/GMA$  at the same  $[m(\text{GMA})/m(E)]$  value.

There are several possible explanations for this finding. First, this deviation derives from the different composition of the polymers. Not all ethylene units in the studied polymers cause the  $A_{721}$  signal. Only the  $-\text{[CH}_2\text{]}_{n \geq 4}$  units, e.g., at least two ethylene units are required for the  $\text{CH}_2$ -rocking vibration. Alternating monomer units do not contribute to this signal. In this case,  $A_{721}$  will be measured as too small and therefore  $\text{Int}(1730)/(721)$  determined too high.

Comparing the molar ratio of ethylene with the other monomeric units in the polymers exhibit the following ratios for  $E/GMA$  and  $EPDM-g-GMA$ , respectively:

$$\left(\frac{n(E)}{n(\text{GMA})}\right)_{E/GMA} : 50 \text{ to } 86 \quad (10)$$

$$\left(\frac{n(E)}{n(\text{GMA})}\right)_{EPDM-g-GMA} : 5.9 \quad (11)$$

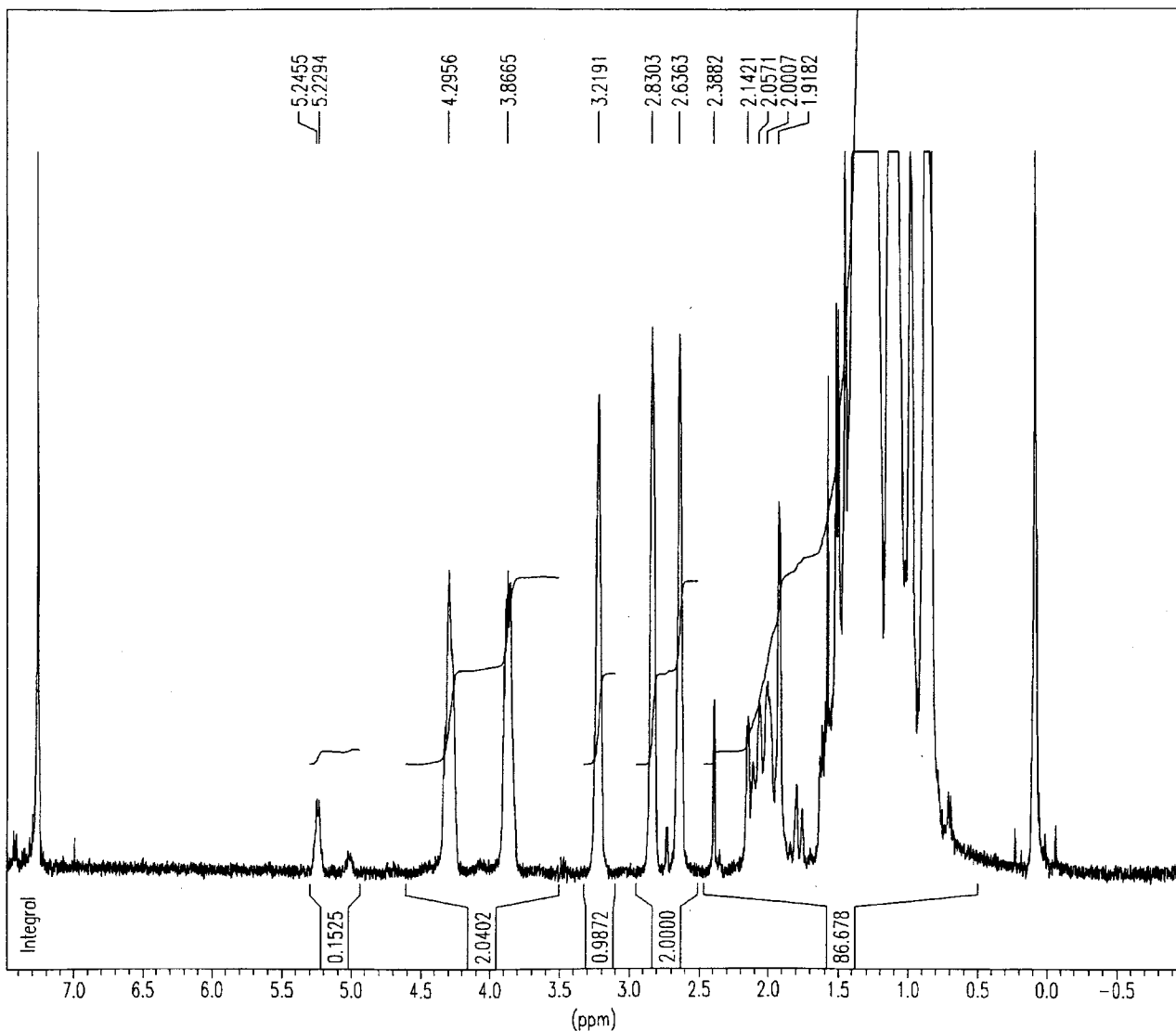
The EPDM rubber has only 10% of the ethylene units compared with  $E/GMA$ . Therefore this effect influences the EPDM much stronger.

Second, high grafting degrees are always accompanied by increased crosslinking. Even though macroradical formation is more likely to take place at unsaturated sites or ternary carbon atoms,<sup>21</sup> there is still a certain probability for this side reaction to occur which leads to macroradical coupling. This might interrupt the ethylene sequences additionally and therefore increase the FTIR absorption ratio.

This deviation lies in the method itself.  $A_{721}$  represents all rocking vibration intensities of  $[\text{CH}_2]_{n \geq 4}$ . That means at least two ethylene units need to be located as neighbors to yield such a vibration. Alternating ethylene/comonomer sequences within the polymer backbone will not be detected by this vibration and yield higher  $\text{Int}(1730)/(721)$  values.

### CONCLUSIONS

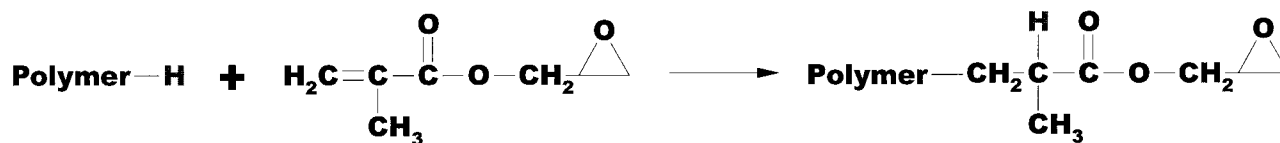
If the precise ethylene content of the EPDM rubber or any other polymer of high ethylene content (that is EPM, ethylene/ $\alpha$ -olefin copolymers, etc.) is known, eq. (8) provides a normalized and universally applicable calibration method for GMA grafted polymers having ethylene block sequences.



**Figure 5**  $^1\text{H-NMR}$  spectra of the EPDM-g-GMA (NMR-32) (experimental conditions: Bruker AMX 400 400.13 MHz).

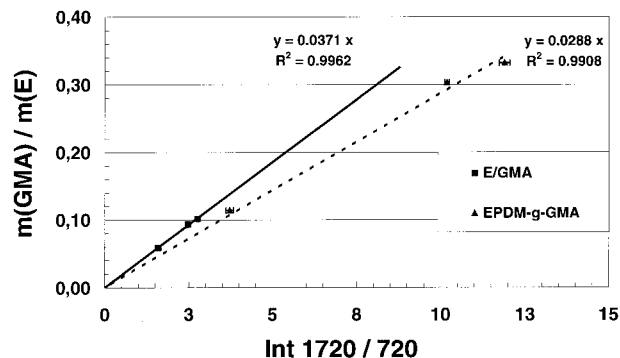
If the rubber's constitution is not entirely known, the indirect standardization method, using well known mixtures of *E*/GMA and EPDM, is still feasible and may deliver the grafting degree. The experienced absolute error, especially in the lower grafting range, is acceptable as can be seen in Figure 7.

It is interesting to note that almost the entire GMA grafted to the EPDM rubber in the described way still has the epoxide function intact (Table IV). For the intended use as a compatibilizing agent in polymer blends the intact (not opened) epoxide plays a crucial role coupling two polymer phases via chemical bonding together.



**Figure 6** Formal insertion of GMA in a carbon-hydrogen bond of a polymer.





**Figure 7** Comparison of direct and indirect standardization.

Because the hydrolyzed and ring-opened share of the grafted GMA is less reactive toward polar groups (like  $-\text{COOH}$ ,  $-\text{OH}$ ) its compatibilizing efficiency would be decreased drastically.

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