



Short communication

## Rapid determination of anhydride content in *trans*-polyisoprene-graft-maleic anhydride by double-shot pyrolysis gas chromatography–mass spectrometry

Kanokwan Jumtee Takeno<sup>a,b</sup>, Shinya Takeno<sup>a,b</sup>, Isao Yuki<sup>a,b</sup>, Shuhei Yamaguchi<sup>a,b</sup>, Nobuaki Suzuki<sup>a,b</sup>, Yoshihisa Nakazawa<sup>a,b,\*</sup>

<sup>a</sup> Technology Development Headquarters, Hitachi Zosen Corporation, Osaka, Japan

<sup>b</sup> Hitz Research Alliance Laboratory, Graduate School of Engineering, Osaka University, Japan

## ARTICLE INFO

## Article history:

Received 16 June 2015

Received in revised form 9 October 2015

Accepted 11 October 2015

Available online 23 October 2015

## Keywords:

Double-shot

PyGC/MS

*trans*-polyisoprene-graft-maleic anhydride

(sTPIgMA)

Maleic anhydride

## ABSTRACT

A rapid method for determination of anhydride content in synthetic *trans*-polyisoprene-graft-maleic anhydride (sTPIgMA) by double-shot pyrolysis gas chromatography mass spectrometry (DS-PyGC/MS) has been developed. The sample preparation step was minimized and samples were easy to handle. Dissolution of the polymer in toxic solvents could be avoided, and solid specimens containing unreacted MA monomer could be analyzed without purification. Unreacted MA monomer, residual solvent, and other volatile substances were eliminated from sTPIgMA during the thermal desorption step. In the subsequent pyrolysis step, grafted anhydride moieties were thermally decomposed to carbon dioxide and quantified. The content of grafted anhydride, measured by the DS-PyGC/MS method, was compared with the values obtained from conventional titration and FTIR methods. The determination of grafted anhydride content in sTPIgMA by DS-PyGC/MS was shown to be fast, simple, accurate, and repeatable.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

Grafting modification using maleic anhydride has been used extensively in various polymers, including polyolefin, polystyrene, polysaccharides, polyesters, and synthetic and natural rubber [1–3]. Hydrophilicity in polyolefins and rubbers has been improved by grafting of MA molecules onto the non-polar polymer backbone [4,5]. MA-modified polyolefins and rubbers are used in various industrial applications such as compatibilizers, adhesives, and fillers. For example, MA-modified natural rubber is used as a compatibilizer in blends of polyamide 6 and natural rubber, resulting in an improvement in impact properties [6,7].

Two grafting mechanisms for introduction of the MA monomer to the polymer backbone have been suggested: radical-induced grafting and thermal grafting *via* an *ene* mechanism [1,8–11]. The grafting reaction can be carried out in solution, in a melt, or in the solid state [12]. Solid-phase grafting modification, which is carried out by mixing the polymer with MA monomer in a kneader, a roll mill, or an internal mixer, has been studied extensively for many

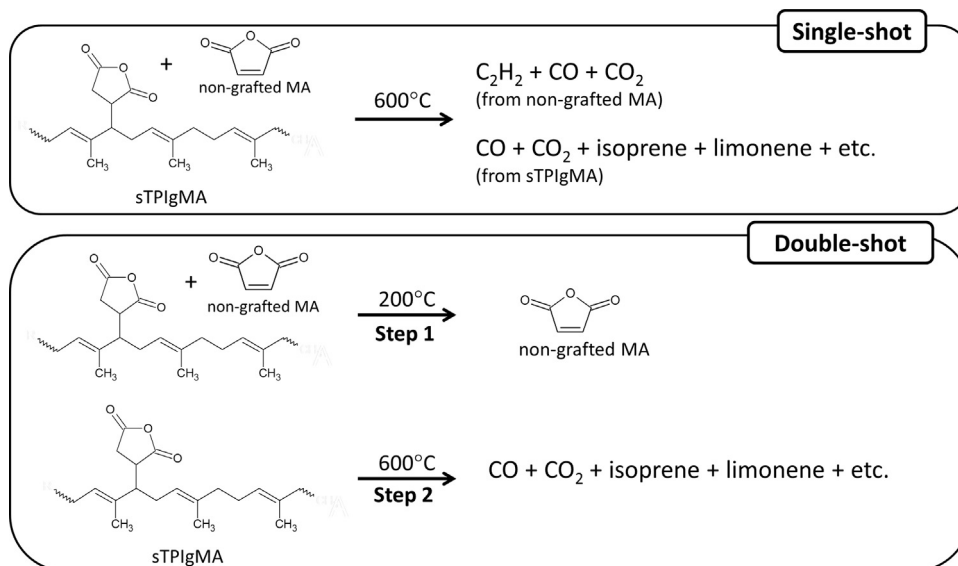
years [6,13,14]. However, the graft copolymer products from these techniques have a relatively low content of grafted MA (generally less than 0.5 wt%) due to the low solubility of MA in the molten non-polar polymer. Moreover, gel formation due to crosslinking reactions has been observed in several cases [1,15,16].

The absolute quantity of MA grafted onto the polymer backbone is generally determined by conventional colorimetric titration [17,18]. However, this method requires extensive sample preparation and the use of toxic solvents. In addition, because the graft copolymer must be completely dissolved in the solution, it is impracticable for polymers that contain a non-soluble gel fraction. The titration method is also difficult to apply to dark-colored polymer solutions due to the obscurity of the color-indicated endpoint.

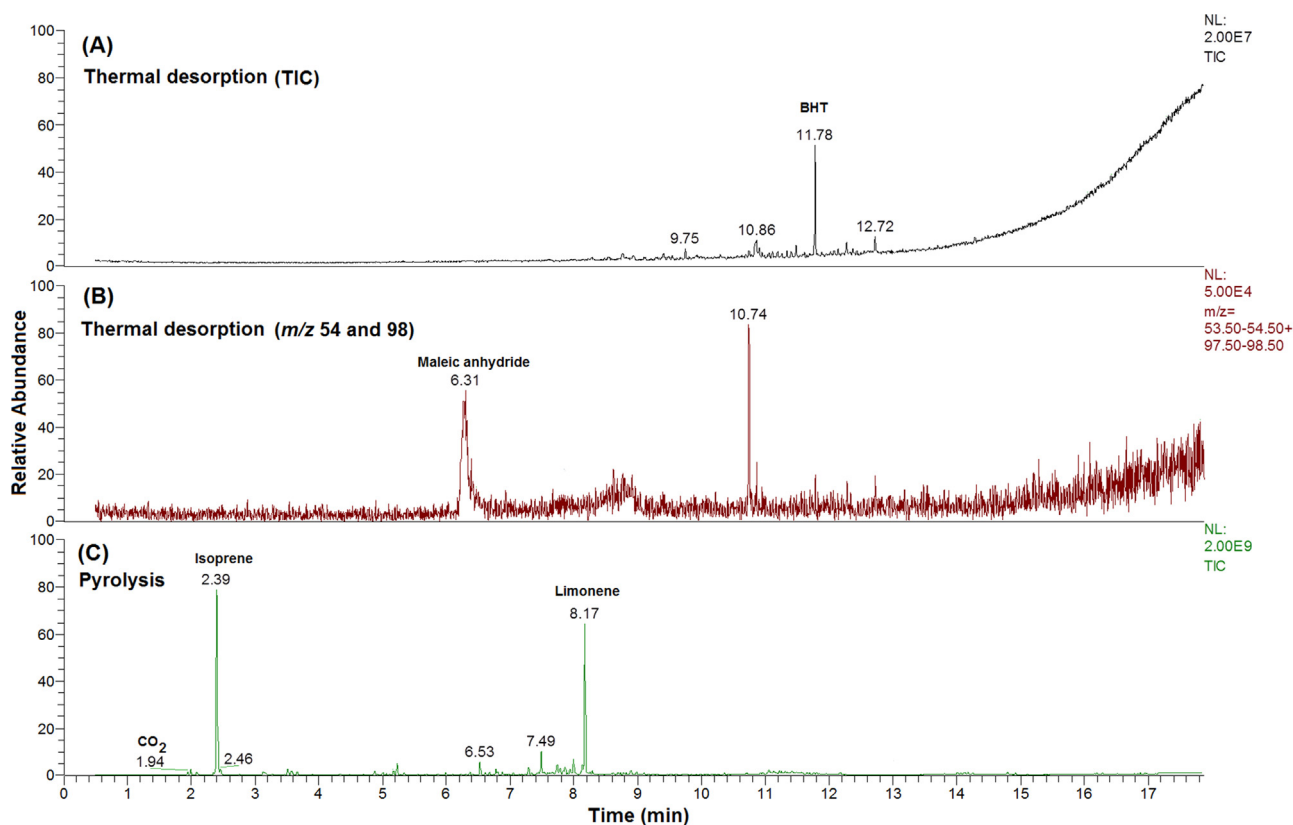
The characteristics of the grafted anhydride linkage, together with the degree of MA grafting, have been determined by FTIR and NMR spectroscopy [11,14,16–21]. FTIR has proved to be superior to titration for quantification of grafted MA in polypropylene-graft-maleic anhydride (PPgMA), but it requires thermal treatment of the sample at 130 °C for at least 24 h to convert the acid groups to aldehydes [20]. A recently developed method for determination of MA content, based on a combination of methylation using supercritical methanol and high-sensitivity <sup>1</sup>H NMR spectroscopy, can determine MA contents as low as 0.01 wt% [21]. It should be noted that purification of graft copolymers to remove

\* Correspondence to: 8F Techno Alliance, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan. Fax: +81 6 6879 4165.

E-mail address: [nakazawa@bio.eng.osaka-u.ac.jp](mailto:nakazawa@bio.eng.osaka-u.ac.jp) (Y. Nakazawa).



**Fig. 1.** DS-PyGC/MS chromatograms of sTPIgMA in the presence of unreacted MA: (A) TIC chromatogram of the thermal desorption step; (B) SIM chromatogram at  $m/z$  54 and 98 for the thermal desorption step; and (C) TIC pyrogram at a pyrolysis temperature of  $600^\circ\text{C}$  after thermal desorption.



**Fig. 2.** Possible thermal desorption and pyrolysis reactions for single-shot and double-shot pyrolysis of sTPIgMA in the presence of unreacted MA monomer.

residual MA monomer and any remaining solvent must be carried out before determination of MA content by these methods [16,21]. Therefore, it is necessary to develop a simple, reliable, solvent-free, and less time-consuming analytical method to determine grafted MA in graft copolymers.

Pyrolysis gas chromatography/mass spectrometry (PyGC/MS) utilizes thermal depolymerization/degradation to characterize polymers and additives [22]. It is recognized that PyGC/MS is a reliable analysis method with high sensitivity, high accuracy and

good reproducibility. It is extensively used in industrial analytical laboratories for qualitative identification of plastics, rubber, and elastomers, especially non-soluble materials because it does not require a complicated sample preparation and chemical information can be obtained. Single-shot PyGC/MS has been applied to the characterization of a chloroprene-MA copolymer, a styrene-MA copolymer, and a graft copolymer of PP with styrene and MA [12,23,24]. Pyrolysis of *cis*-polyisoprene-*graft*-maleic anhydride (cPIgMA), polyethylene-*graft*-maleic anhydride (PEgMA), and

Download English Version:

<https://daneshyari.com/en/article/1196650>

Download Persian Version:

<https://daneshyari.com/article/1196650>

[Daneshyari.com](https://daneshyari.com)