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Composition and structure analysis of styrene–maleic anhydride copolymer by pyrolysis–gas chromatography

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Abstract

A pyrolysis–gas chromatography method has been developed to study composition and microstructure of a styrene–maleic anhydride (SMA) copolymer. Since the anhydride functional group is not stable under normal pyrolysis conditions, a derivatization technique has been developed to successfully study the composition and microstructure. Because of the unique structure of SMA copolymers, the number average sequence length can be used to indicate the polymer chain length or average molecular mass. The method developed in this report has demonstrated a feasible approach to studying the composition and structure by pyrolysis–GC for those polymers containing functional groups which are not stable under pyrolysis conditions.

Keywords: Pyrolysis; Styrene–maleic anhydride copolymer; Maleic anhydride

1. Introduction

Styrene–maleic anhydride (SMA) is a thermoplastic copolymer. It was commercially introduced in the early 1930s. SMA polymers have higher T_g values (glass transition temperature) and deflection temperatures under load in excess of 125°C. It can offer higher heat resistance compared with polystyrene and acrylonitrile–butadiene–styrene (ABS) while maintaining good impact, rigidity and dimensional stability. SMA polymers have several superior properties, such as low melt flow-rate, ease of coloring, and improved chemical resistance as compared to other engineering thermoplastics such as polycarbonate and modified polyphenylene oxide. The anhydride groups of SMA will hydrolyze in water, but the polymer dissolves only when converted to a salt. The low-molecular-mass SMA copolymer can be found as a levelling agent in floor

polishes, embattling/anti-resoil agents in rug shampoos, and pigment dispersants in paints [1]. SMA polymer is not particularly resistant to UV degradation. To stabilize it for outdoor use, a protective surface coating or a UV-resistant capping layer is required.

SMA copolymers have been widely used in automotive interiors [1]. The major area of application is instrument panel support components. The glass-reinforced SMA polymers are used extensively in supporting padded instrument panels. Unreinforced products are being used in a variety of interior trim parts and exterior mirror housings. Other applications for SMA polymer include housewares, small appliances, power tools, steam curlers and audio cassettes. SMA with flame-retardant materials added are being used in switch covers, modems, and a number of business-machine applications.

SMA copolymers are usually made by mass

copolymerization using a free-radical initiator. There is a strong tendency to form 1:1 equimolar copolymer [1] unless the maleic anhydride (MA) concentration is held at an extremely low level during the entire polymerization sequence. This starve feeding technique is used to make SMA resin containing 5–12% MA. When the number of styrene monomer units is larger than that of maleic monomer units, excess styrene units combine with each other to form blocks of styrene units in the polymer chain [2].

Polymer structure can be studied by the analysis of the dimers and trimers produced by pyrolysis–gas chromatography (Py–GC) [3–9]. The basic requirement is that the dimer and trimer peaks have to be detected and identified. The theory and the formulas can be found in the previous reports [3,7–9]. The composition and structure determination of underivatized SMA polymer by Py–GC has not been reported because the anhydride functional group in the SMA polymer will not survive under normal pyrolysis conditions [10]. In order to identify and quantify the anhydride containing polymer, the anhydride functional group has to be preserved either by esterification (form methyl ester) or by reacting the primary amine to form an imide. The composition and microstructure of SMA copolymer systems have been studied by ^{13}C -NMR [2] and by Py–GC [11] with methylation of the anhydride group.

In this study, the composition and the microstructure of SMA copolymers have been studied by derivatization (with methylamine) followed by Py–GC. The major pyrolysis fragments have been identified by Py–GC–MS in both electron ionization (EI) and chemical ionization (CI) modes. Py–GC has been used to produce very clear and distinguishable monomer peaks which are used in the determination of the composition. In addition, the number average sequence length for the styrene monomer has been further determined based on the trimer distribution. All Py–GC composition results have been in good agreement with the product composition label. The number average sequence length of styrene calculated from triad distribution (trimer peaks) is a reflection of the polymer chain length or average molecular mass. The method developed in this report has demonstrated a feasible approach to studying the composition and structure by Py–GC for those

polymers containing functional groups which are not stable under pyrolysis conditions.

2. Experimental

2.1. Sample preparation

2.1.1. Styrene–maleic anhydride copolymer resins

A laboratory grade of 50:50, 67:33 and 75:25 mol% SMA copolymer resin (labeled SMA50/50, SMA67/33 and SMA75/25) was purchased from Polysciences (Warrington, PA, USA). The resin in powder form was used without any further purification. A 10% polymer solution was prepared by dissolving SMA copolymer into a 10% methylamine–water solvent. The industrial grade SMA copolymers SMA1000 (50:50 mol%), SMA2000 (67:33 mol%) and SMA3000 (75:25 mol%) were obtained from Elf Atochem (Berkeley, IL, USA). The sample preparation was the same as laboratory grade SMA copolymer as previously mentioned.

2.2. Pyrolysis–GC and pyrolysis–GC–MS

Samples of polymer solution (approx. 300 μm) were deposited on a Pt ribbon and equilibrated for 10 min in a 250°C interface connected to the injection port of a HP5890 gas chromatograph equipped with a flame ionization detection (FID) system. Samples were pyrolyzed (CDS 120 Pyroprobe Pt coil) at a set temperature of 700°C. The coil was heated to 700°C with 20°C/ms and held at 700°C for a 5 s interval. The pyrolysis products were split in the 250°C injection port, with 10 p.s.i. head pressure, 30:1 split ratio, separated on a fused-silica capillary column (J&W DB-5, 30 m \times 0.25 mm I.D., 1.0- μm film) using a linear temperature program (40 C°/4 min., 20 C°/min., to 120 C°/10 min. then 20 C°/min. ramp to 300 C°/23 min.), and detected by FID (1 p.s.i. = 6894.76 Pa).

In GC–MS, the FID system was replaced with a VG Trio-1 mass spectrometer. The GC output was transferred through a transfer line (280°C) to the ion source of the mass spectrometer. EI mass spectra were obtained every second over the mass range of 29–500 u. Methane was used as reagent gas in the CI mode.

2.3. Test of temperature dependence and reproducibility

A series of pyrolysis runs of SMA copolymer in the temperature range from 500°C to 900°C were performed. The 700°C pyrolysis temperature was chosen based on optimized yield of monomer and trimers for both monomers. The reproducibility of pyrolysis data was always a concern when applying the technique to any kind of quantitative study. Based on eight consecutive runs of a 50:50 industrial grade SMA copolymer, the normalized monomer peak intensity shows a relative standard deviation of 5% from the average value. This indicates the reliability of the pyrolysis method applied to the analysis of derivatized SMA copolymers.

3. Results and discussion

Fig. 1 shows the typical pyrograms of a 50:50 mol% and a 75:25 mol% SMA copolymer without derivatization. All major fragments in the pyrograms are styrene-related products [12] as shown in Table 1 which demonstrated that the anhydride functional group has no contribution to any fragment detected. Due to a lack of anhydride fragments, neither compositional nor structural information can be extracted from these pyrograms. Knowing the composition of the SMA copolymer, the 75:25 mol% SMA pyrogram does show a sharp and clear styrene dimer and trimer peaks which indicated that there are grouped styrene monomer units distributed in the polymer chain.

Fig. 2 shows a pyrogram of a 75:25 mol% SMA copolymer derivatized with methylamine. The methylamine reacts with an anhydride functional group to form a series of imide compounds. All derivatization-related major fragments in the pyrograms are listed in Table 2. The compound C (as indicated in Table 2) is chosen for the composition study because this peak (component) is the most stable derivatized pyrolysis product. Rows 3 and 4 in Table 3 show the calculated composition of the SMA copolymers. The composition calculated for laboratory grade copolymers are in very good agreement with NMR results as well as with the product specification values supplied from the manufacture.

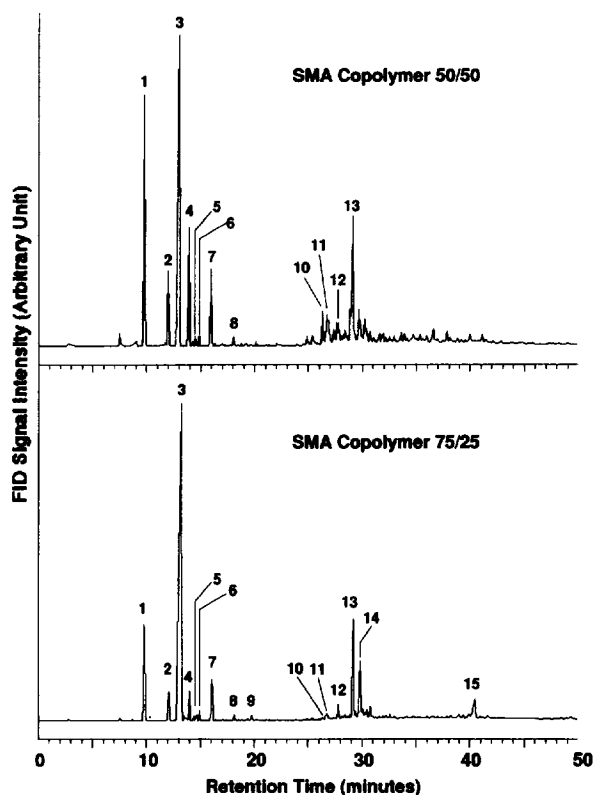




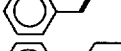
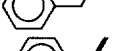



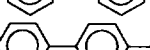
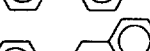



Fig. 1. The typical pyrograms of SMA50/50 and SMA75/25 copolymers without derivatization.

The composition calculated for SMA2000 and SMA3000 differ by 3% and 4%, respectively, from the specification. These differences may be due to the variation in concentration by different lots from the manufacture.

Based on the reactivity of styrene monomer and maleic anhydride monomer, the SMA copolymer has a tendency to form alternating copolymer [1]. The number average sequence length for the monomer which is less than 50 mol% (in this study, it is maleic anhydride) will just equal 1.0. The number average sequence length for the other monomer (styrene, in this case) can be calculated in two ways. One way is to calculate via the composition. For a randomly distributed copolymer with monomer S and M, the number average sequence length of S and M can be calculated by composition with equations expressed as:

Table 1
Py-GC-MS peak assignment of SMA copolymer without derivatization

Peak label	Retention time (min)	Molecular mass (u)	Structure
1	9.80	92	
2	12.06	106	
3	13.23	104	
4	13.94	120	
5	14.61	118	
6	14.91	120	
7	16.12	118	
8	18.14	118	
9	19.76	132	
10	26.34	168	
11	26.76	168	
12	27.84	182	
13	29.18	202	Undetermined Styrene Dimer Styrene Trimer
14	29.80	208	
15	40.45	312	

$$\text{mol\% S} = \frac{\tilde{n}_S}{\tilde{n}_S + \tilde{n}_M} \cdot 100\% \quad (1)$$

$$\text{mol\% M} = \frac{\tilde{n}_M}{\tilde{n}_S + \tilde{n}_M} \cdot 100\% \quad (2)$$

Another way to calculate the number average sequence length is by the dyad/triad distribution. For the same copolymer system, the number average sequence length calculated through triad distribution can be expressed as:

$$\tilde{n}_S = \frac{N_{SSS} + N_{MSS+SSM} + N_{MSM}}{\frac{1}{2}N_{MSS+SSM} + N_{MSM}} \quad (3)$$

$$\tilde{n}_M = \frac{N_{MMM} + N_{SMM+MMS} + N_{SMS}}{\frac{1}{2}N_{SMM+MMS} + N_{SMS}} \quad (4)$$

where \tilde{n}_S and \tilde{n}_M are the number-average sequence length of monomers S and M. N_{SSS} , $N_{SSM+MSS}$, N_{MSM} , N_{SMS} , $N_{SMM+MMS}$, N_{MMM} , are the experimentally derived six distinguishable triad molar fractions or number of molecules. In this study, the actual calculation based on the styrene unit and MA unit are alternating in the copolymer structure. The terms, such as N_{MMM} , $N_{SSM+MSS}$ and $N_{SMM+MMS}$ will be approximately 0, N_{MSM} will be equal to N_{SMS} . The number average sequence calculation for maleic anhydride is always equal to 1 and the number average sequence calculation for styrene is dependent on the terms N_{SSS} and N_{MSM} . Fig. 3 shows the pyrograms of 50:50, 67:33 and 75:25 mol% SMA copolymer in the trimer region. The trimer peak SSS and SMS are overlapped. The peak area of these two trimers were obtained by curve fitting of unresolved peaks.

In Table 3, row 5 shows the number average sequence length of styrene calculated directly from the composition which was generated from monomer intensities. Row 6 is the results of the number average sequence length of styrene calculated from the triad distribution (trimer peaks). The number average sequence length using two different methods do not always agree. This phenomena indicates the effect of the polymer chain length or average molecular mass on the number average sequence length when the monomer unit in the copolymer is not a random distribution. The SMA copolymer in this study is a very good example.

Assuming the copolymer has X mol% maleic anhydride, there will be $2X$ mol% monomer units in the polymer chain which are in the alternating form and $100 - 2X$ mol% monomer units in the styrene block. If the total monomer units is T and each polymer chain contains Y units, therefore the system has T/Y polymer chains. The number average sequence length of styrene can be calculated from the definition:

$$\begin{aligned} \tilde{n}_S &= \frac{\text{Total number of styrene units}}{\text{Total number of styrene blocks}} \\ &= \frac{\frac{T}{Y} \cdot 2X \cdot Y \cdot \frac{1}{2} + \frac{T}{Y} \cdot (100 - 2X) \cdot Y \cdot 1}{\frac{T}{Y} \cdot 2X \cdot Y \cdot \frac{1}{2} + \frac{T}{Y} \cdot (100 - 2X) \cdot 1} \end{aligned}$$

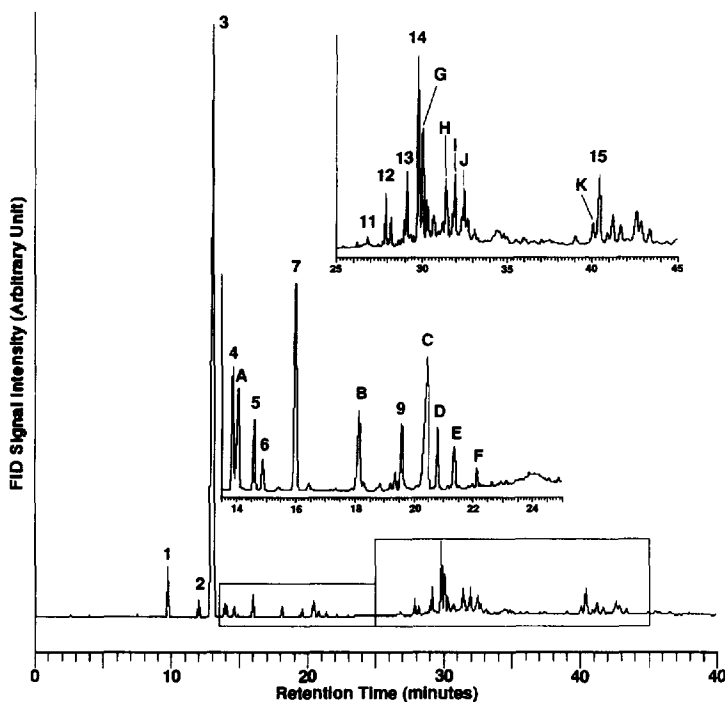


Fig. 2. The typical pyrograms of a SMA75/25 copolymer with methylamine derivatization.

$$= \frac{X \cdot Y + (100 - 2X)Y}{X \cdot Y + (100 - 2X)}$$

$$= \frac{100 - X}{X + \frac{100 - 2X}{Y}}$$

where X should be greater than 0 and not greater than 50. Table 4 tabulates the effect of polymer chain length or average molecular mass to the number average sequence length for the SMA copolymer with composition of 67:33 and 75:25 mol%. Based on the formula and Table 4, the lower the maleic anhydride content, and the shorter the chain length (lower average molecular mass), the number average sequence length calculated from dyad or triad distribution will be significantly lower than the values reflected by the composition.

Owing to a small amount of styrene trimers being detected in the SMA copolymer SMA1000, the number average sequence of styrene in this copolymer are slightly greater than 1.0. This is an indication that the copolymer is not a perfect alter-

nating copolymer. The number average sequence length of styrene for copolymer SMA67/33 and SMA75/25 show that the polymer chain length of these polymers are approximately 10–20 and 20–30 monomer units long or average molecular mass of 1000–2000 and 2000–3000. Similar conclusions cannot be made from SMA2000 and SMA3000 copolymers in this study because of possible relative large errors in the composition determination as discussed in the previous paragraph.

This discussion emphasizes that in order for Eq. (1) and Eq. (2) to be true, the monomer distribution in the copolymer has to be random. If the monomer units are not randomly distributed in the copolymer, then Eq. (1) and Eq. (2) cannot be used. The relationship between number average sequence length and composition is dependent on the concentration of monomers and the polymer chain length (average molecular mass). From the other point of view, the polymer chain length information can be obtained if both composition and number average sequence length information can be actually generated.

Table 2
Py-GC-MS peak assignment of SMA copolymer derivatized with methylamine

Peak label	Retention time (min)	Molecular mass (u)	Structure
A	14.05	111	
B	18.13	125	
C	20.46	113	
D	20.79	127	
E	21.34	139	
F	22.12	125	
G	30.14	215	
H	31.39	231	
I	31.95	217	
J	32.42	229	
K	40.01	319	

Table 3

The composition and number average sequence length for different SMA copolymers from pyrolysis-gas chromatography method

Row	Sample identity	SMA50/50	SMA67/33	SMA75/25	SMA1000	SMA2000	SMA3000
1	mol% S (Designed)	50 ^{a,b}	67 ^{a,b}	75 ^{a,b}	50 ^a	67 ^a	75 ^a
2	mol% M (Designed)	50 ^{a,b}	33 ^{a,b}	25 ^{a,b}	50 ^a	33 ^a	25 ^a
3	mol% S (Calculated)	50.0	66.7	76.9	50.6	70.7	78.8
4	mol% M (Calculated)	50.0	33.3	23.1	49.4	29.3	21.2
5	N(S)-C ^c	1.00	2.00	3.33	1.02	2.41	3.71
6	N(S)-T ^d	1.00	1.87	3.06	1.04	1.90	3.62

^a The composition data from product specification.

^b The composition data from NMR.

^c The number-average sequence length calculated from composition.

^d The number-average sequence length calculated from triad distribution.

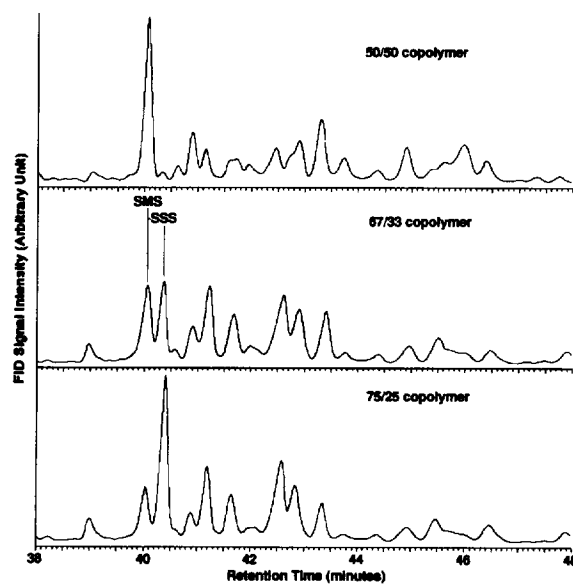


Fig. 3. The pyrograms (region of interest) of SMA50/50, SMA67/33 and SMA75/25 copolymers.

4. Conclusions

The composition and microstructure of SMA copolymer can be studied by derivatizing the copolymer with methylamine followed by Py-GC. Because the monomer units are not randomly distributed in the polymer, the number average sequence length of styrene calculated from triad distribution will not necessarily reflect the composition. Instead, by combining the composition and the number average sequence length information, the polymer chain length or average molecular mass may be explored. However, in order to predict the copolymer

Table 4

The number-average sequence length calculated from composition and the number average sequence length calculated from triad distribution for 50:50, 67:33 and 75:25 mol% of SMA copolymers from theory

SMA copolymer	Chain length	Average M_n	50:50	67:33	75:25
Mol% S ^a			50	67	75
Mol% M			50	33	25
N(S)-C ^a			1.00	2.00	3.00
N(S)-T ^b	10	1 000	1.00	1.82	2.50
N(S)-T ^b	20	2 000	1.00	1.90	2.73
N(S)-T ^b	30	3 000	1.00	1.94	2.81
N(S)-T ^b	40	4 000	1.00	1.95	2.86
N(S)-T ^b	50	5 000	1.00	1.96	2.88
N(S)-T ^b	60	6 000	1.00	1.97	2.90
N(S)-T ^b	70	7 000	1.00	1.97	2.92
N(S)-T ^b	80	8 000	1.00	1.98	2.93
N(S)-T ^b	90	9 000	1.00	1.98	2.93
N(S)-T ^b	100	10 000	1.00	1.98	2.94
N(S)-T ^b	1 000	100 000	1.00	2.00	2.99
N(S)-T ^b	10 000	1 000 000	1.00	2.00	3.00

^a The number-average sequence length calculated from composition.

^b The number-average sequence length calculated from triad distribution.

chain length or average molecular mass, the composition and triad distribution determination must be accurate. The main effort in this study is the method development to demonstrate a feasible approach to studying the composition and structure by Py-GC for those polymers containing functional groups which are not stable under pyrolysis conditions.

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