Analysis of Polyester by a Combination of Curie-Point Heating Techniques and Preparative Liquid Chromatography

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A Curie-point heating technique has already been introduced to pyrolysis-gas chromatography, which was developed by us. We analyzed thecomponent ofa multi-component polyestercompletely by using acombination ofthe technique and preparative HPLC. We used Curie-point pyrolysis-GC/ MS, direct injection/ MS, headspace-GC/ MS and preparative HPLC for this study. We could thus determine the composition ofthe uncured polyester for manufacturing man-made marble consisting of an uncured polyester prepolymer, a crosslinking accelerator, an acrylate copolymer as the modification agent and some additives (surfactant and plasticizer). This analytical method is an available, convenient way for compositional analysis of complex polymers materials.

Pyrolysis gas chromatography-mass spectrometry(Py-GC/MS) has recently become popular for polymer analysis owing to its simplicity and capacity for providing important compositional and structural information, especially regarding multi-component materials. One of the advantages of this method is that all compositions of the polymer(s), and additive(s) employed in the material can be investigated without any pretreatment.[1][2] On the other hand, headspace-GC/MS is a powerful measurement technique for volatile compounds in solids.[3] Moreover, it is suggested that that data be compared with the Py-GC results for a distinction of volatile components from pyrolyzates on a pyrogram of a multi-component polymer material. An on-line direct injection/MS(D1/MS) technique could separate the pyrolyzates and volatile components of a polymer sample according to the mass on a liner scale with very high sensitivity; it thus enables a rapid analysis with a throughput of up to one sample per minutes.[4][5] For the most complex material system, fractional separation by preparative liquid chromatography is helpful, and sometime necessary, to obtain pure fractions and then identify them individually by Py-GC or pyrolysis-DI/MS in order to determine definite mass data.[6] Due to the high heating speed (less than 0.2 s of the temperature raise time), accurate temperature reproducibility (± 1°C) and a wide temperature range (160 - 1040°C), the Curie-point heating technique has successfully been applied to Py-GC/MS, Dl/MS and headspace-GC/MS.[2,3,7,8] In this work, all of the

measurements mentioned above were used to characterize a multi-component thermosetting polymer system composited by the uncured unsaturated polyester resin, curing agent modification agent and additives.

Experimental

Sample

A set of uncured unsaturated polyester resin (BX-923, Synthetic Resin Co. of Beijing, China) comprised two parts (coded as part A and B), including a prepolymer, reactive monomer, curing accelerator, modification material and additives in the sample. This polymer was mixed with marble powder, and used for manufacturing man-made marble.

Apparatus

Pyrolysis or headspace sampling was carried out using a Model JHP-3 Curie-point Pyrolyzer or a Model JHS-100 Curie-point Headspace Sampler (Japan Analytical Industry Co., Ltd.), which was combined with an on-line Model QP-2000A GC/MS system (Shimadzu Co., Japan). The GC/MS was equipped with a high-resolution, fused-silica capillary column (J&W Sci., DB-1, 0.25mmi.d.X30m) coated with immobilized poly(dimethyl silicone) of 0.25urn thickness, and a quadrupole mass spectrometer with an El ionization source(70eV). A JDI800Curie-point DI Probe(Japan Analytical Industry Co., Ltd.) was inserted in a QP

2000A mass system up to the position where the sample cell (9 mmX2mm i.d.) at the tip of the probe could be connected to the ion source.[8] The sample was wrapped in Pyrofoil® with tight contact. The amounts of samples to be injected were less than 2ug, 0.1 mg and 0.4 mg for DI/ MS, Py-GC/ MS and headspace-GC/ MS, respectively. The GC column temperature was initially maintained at 35°C for 5 min, and then programmed to 300°C at 8°C / min. From the carrier gas of helium, 50ml/min was split at a ratio of 50:1. The volatile fractions of the headspace samples extracted at 220°C for 10 min were transferred to an adsorbent, (Tenax®) at -40°C, and then desorbed at 255°C for 10 s by Pyrofoil® with Curie-point heating. A Model LC-908, preparative liquid chromatograph (HPLC) was equipped with the series of columns (GPC) of ModelJaigel-1 H and Jaigel-2H and a refractive index detector (Japan Analytical Industry Co., Ltd.). Chloroform was used as the solvent (40kg/cm2, 3.8 ml/min). The sample size injected was 50 mg in 3 ml of the chloroform.

Results and Discussion

Resin and its additives

A total ion current (TIC) pyrogram obtained from Py-GC/MS of the uncured resin (part A) pyrolyzed at 500°C, as shown in Fig. 1. The structures assigned to the mass signals of the pyrolyzates are listed in Table 1; the identification was carried out mainly on basis of mass spectral fragmentation patterns. The code numbers of
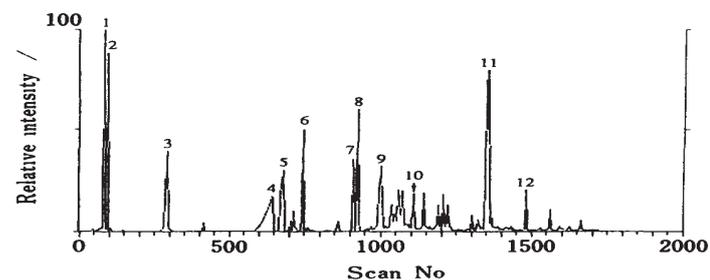
the pyrolyzate peaks in Fig. 1 corresponded to the numbers in Table1. Peaks 2 and 3 (with shorter retention times) indicate unsaturated hydrocarbon and alcohol derived from the hexylene sequences in the polymer chains. In particular, the , -diens are most likely formed through the predominant pyrolysis mechanism involving a cyclic transition state at two neighboring ester linkages for the polyester (Scheme 1[9]). The 1, 5, and 7 peaks correspond to benzene, phthalic anhydride, and cyclohexenyl phthalate, respectively, which were also the main peaks on the pyrogram of the polyester synthesized by phthalic acid and hexenediol.10 A mostly characteristic pyrolyzate, dihexenyl phthalate as the monomer (peak 11), was reflected on the repeat units of poly(dihexenyl phthalate). The relationship between the polymer structure and the pyrolyzates is summarized in Scheme 2. The presence of phenyl benzoate (peak 8) and polycyclic aromatic pyrolyzates (peak 6, 9 and 10) on the pyrogram ofthe resin would be caused either by the secondary and tertiary thermal processes ofthe polyester, or by a thermal decomposition of other aromatic component mixed with the polyester. To distinguish the different conclusions, part A of the sample was separated and collected into two fractions (F-1 and F-2),as shown in Fig. 2, by preparative HPLC with high-performance columns; F-1 and F-2 were then identified by Py-GC individually. The pyrogram of F-1 also showed all of the characteristic pyrolyzates of

Table 1 Pyrolyzates assignments of part A of the sample

1	Benzene	7	Cyclohexenyl phthalate
2	Hexadiene	8	Phenyl benzoate
3	Hexenol	9	Methoxydibenzofuran
4	Benzoic acid	10	Dihydronaphthacene
5	Phthalic acid	11	Dihexenyl phthalate
6	Acenaphthene	12	C_{16} aliphatic alcohol

Fig 1   TIC pyrogram of part A obtained by Py GC/MS
The peak notations correspond to those in Table 1
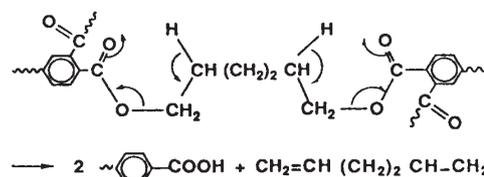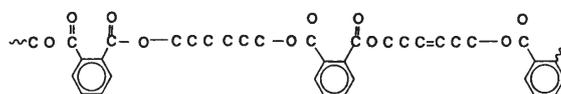
Scheme 1

Scheme 2
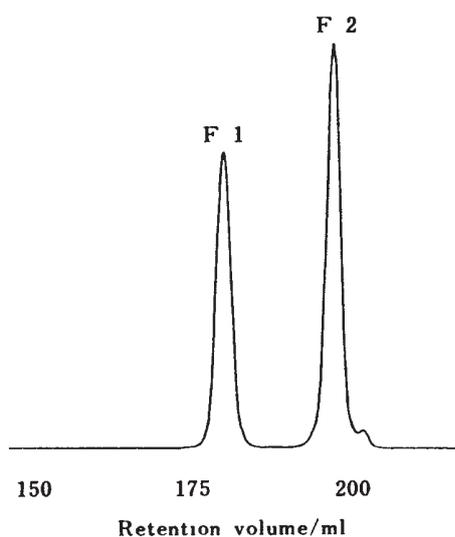
Fig 2 HPLC chromatogram of part A

(BPO)

rearrangement & cyclization

Scheme 3
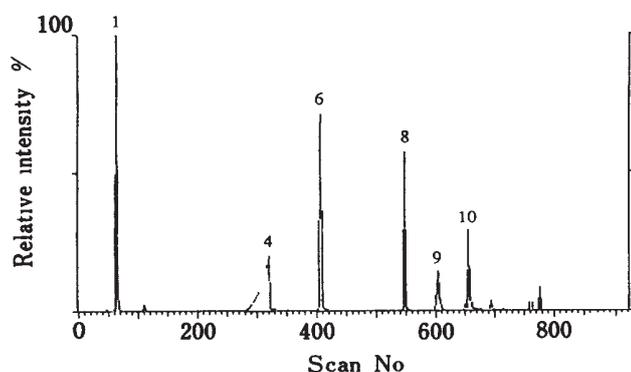
Fig 3 TIC pyrogram of F 2 obtained by Py GC/MS   The
peak notations correspond to those in Table 1

Fig 4 TIC pyrogram of part B obtained by Py GC/MS
1 methacrylate 2 methyl methacrylate 3 isohexyl
methacrylate 4 dioctyl phthalate 5 C_{16} aliphatic alcohol

poly(dihexenyl phthalate) and reconfirmed the same
results mentioned above. The pyrogram of F-2,
performed at a relatively lower temperature of 220°C for
3 s, is shown in Fig. 3. The sufficient decomposition of
F-2 in a weaker thermal environment indicated that it
could be a thermally labile compound. Some of the
assigned pyrolyzates of F-1 (see Table 1) corresponded to
benzoic acid (peak 4) and phenyl benzoate (peak 8) and
implied the scission, elimination, and recombination of a
aromatic peroxide. A rearrangement of the peroxide
with subsequent cyclization to polycyclic compuuds
(acenaphthene, methoxydibenzofuran and dihydrona-
phathacene, as peak 6, 9, and 10 on the pyrogram) has
also been considered to a significant extent.
Summarizing all of this information, F-2 was identified
as benzoyl peroxide (BPO), a crosslinking accelerator for
the unsaturated polyester. The decomposition
mechanism of BPO is shown in Scheme 3. In addition,
a broadly exothermic peak with a maximum temperature
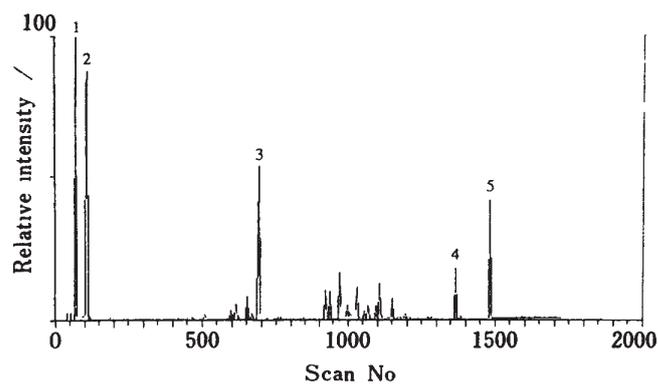of 133°C was observed in the differential scanning
calorimetry (DSC) profile of F-2,which was identical
with the thermal decomposition behavior of BPO.
Finally, a weaker mass signal(peak 12) with a longer
retention time in Fig. 1 indicated the presence of a high
aliphatic alcohol in the resin, implying that component as
a kind of additives (a surfactant, perhaps).

Curing agent and modification agent

Figure 4 shows a TIC pyrogram of part B carried out
by Py-GC/MS, pyrolyzed at 500 C for 5s, on which
some acrylate monomer peaks, methyl acrylate (MA,
peak 1), methyl methacrylate (MMA, peak 2) and
isohexyl methacrylate (HMA, peak 3), were identified.

As is well known, acrylate polymers and copolymers thermally degrade mainly to the correlative monomers in the absence of oxygen.[12-13] Based on that information, a solid sample of part B was reasonably deduced as being a copolymer of MA, MMA and HMA. Otherwise, peak 4 and 5 on the pyrogram assigned to a high aliphatic alcohol and dioctyl phthalate (DOP) would reflect the thermal volatilization of some additives, which are considered to be a surfactant and a plasticizer in the material, respectively.

Pyrolysis-DI/ MS is a simple, rapid analytical pyrolysis measurement technique without any chromatographic separation process. Since the mass profiles of all pyrolyzates are labeled on a linear mass scale, it is suitable for fingerprint identification purposes.[78] Figure 5 is the TIC pyrogram of part B pyrolyzed at 500°C for 3 s by

DI/MS. The corresponding mass spectrum indicated that the observed species was a co(MA-MMA-HMA)polymer identified by the related monomer fragments with m/z values of 86(MA), 100(MMA), and 170(HMA), respectively. Though the conclusion is the same as that by Py-GC, since the throughput of up to one sample was within a few minutes, the analysis is more effective.

An important point remained regarding the previous discussion, i.e. the monomer peaks of MA, MMA and HMA on both of Py-GC and DI/MS pyrograms of the part B must have originated from two considerable ways; thermal pyrolysis of the copolymer to the corresponding monomers or / and thermal volatilization of the free monomers dissolved in the copolymer.[14] To confirm that, headspace GC/MS was carried out at a purging temperature of 220°C with in 1 min for both part B and a
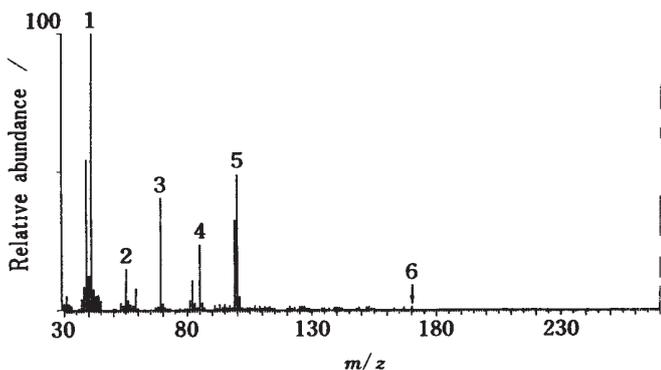

Fig 5 Mass spectrum of part B obtained by pyrolysis DI/MS 1 propyrene 2 acrolein 3 2 methyl acrolein 4 methacrylate 5 methyl methacrylate 6 isohexyl methacrylate
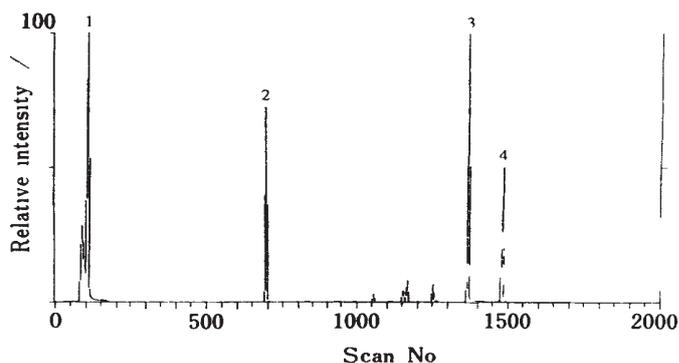

Fig 6 TIC chromatogram of part B by headspace GC/MS 1 methyl methacrylate 2 isohexyl methacrylate 3 dioctyl phthalate 4 C₁₆ aliphatic alcohol
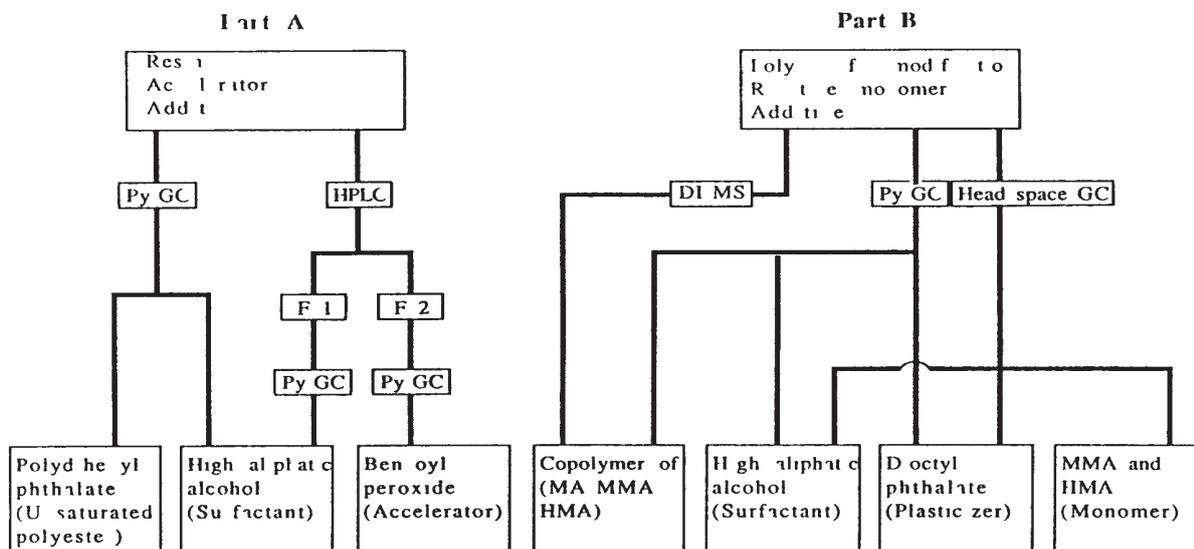

Fig 7 Flowchart diagram of the analytical measurements in this work

monomer-free co(MA-MMA) polymer for the same sample size and condition. Since no significant peak showed on the headspace chromatogram of the monomer-free copolymer, this indicated that no detectable pyrolyzate formed at that temperature for the purified co(MA-MMA)polymer. A headspace TIC chromatogram of part B at 225°C is shown in Fig. 6, in which the monomer peaks of MMA and HMA presented with the obvious intensities are compared to the standard copolymer. The results show that there were some reactive monomers (MMA and HMA) dissolved in the copolymer as the crosslinking agents of the unsaturated polyester. Therefore, it could be deduced that the copolymer in part B acted as a modification material and an adsorbent for the reactive monomers.

In conclusion, all of the components in a set of uncured unsaturated polyester system, including an unsaturated polyester prepolymer, a crosslinking accelerator, an acrylate copolymer as the modification agent and some additives (surfactant and plasticizer) were well identified by a combination of Curie-point Py-GC/MS, DI/MS, headspace-GC/MS and preparative HPLC. A flowchart diagram of the analytical measurements used in this work is illustrated in Fig. 7. The results showed that the Curie-point heating technique combined to multi-chromatographic and mass spectroscopic methods is an available and convenient way for the compositional analysis of complex polymer materials.

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