Determination of wet-strength resin in paper by pyrolysis-gas chromatography

Tatsuya Yano, Hajime Ohtani, and Shin Tsuge*

Dept. of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Fro-cho, Chikusa-ku, Nagoya 464-01, Japan

Takao Obokata

Laboratory of DIC-Hercules Chemicals Inc., Ichihara-shi, Chiba 290, Japan

ABSTRACT *Polyamide-epichlorohydrin resin (PAE), which is one of the paper additives to develop wet-strength, is determined by pyrolysis-gas chromatography equipped with a flame ionization detector. Cyclopentanone derived from the adipic acid moiety in PAE is used as the key product for determining PAE in paper. The reproducibility of analyses was 4.8% relative standard deviation. The observed results are also interpreted in terms of the possible mechanisms to develop the wet strength of paper.*

KEYWORDS
Additives
Analysis
Gas chromatography
Pyrolysis
Resin
Wet strength

Paper is composed chiefly of cellulose, but it contains various additives such as sizing agents, wet- and dry-strength resins, surface treatment agents, pigments, and fixing agents. Usually, the additives are added into pulp slurry and are partially lost with white water.

Sizing agents, such as higher fatty acid salts, rosin, and alkyl ketene dimers, have been analyzed by infrared spectroscopy, absorption spectrophotometry, and gas chromatography after conventional solvent extraction from paper matrices. However, the extraction and subsequent enrichment steps are not only time-consuming, but they can also cause some contamination or loss of the components. Furthermore, it is difficult to extract polymer additives such as wet- and dry-strength resins from paper, and the additives are present in very small quantities. Therefore, it is not an easy task to analyze reliably the paper for its additives.

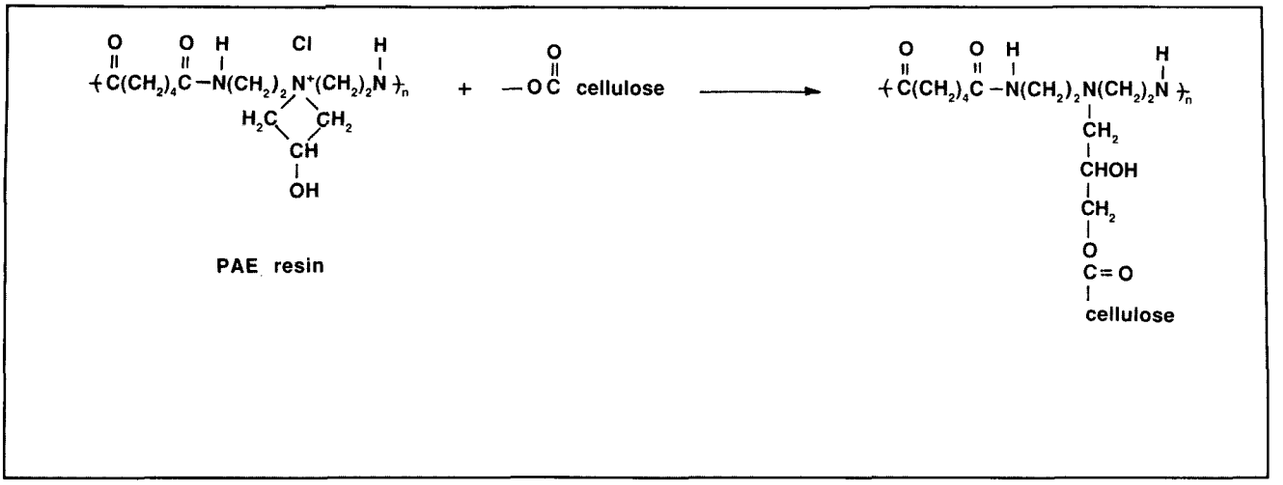
One of the most representative analytical pyrolysis techniques is pyrolysis-gas chromatography (PyGC). This technique can be used to extract the structural information from the mixture of the specific degradation products formed from the sample materials by a well-defined thermal fragmentation method. PyGC has been successfully applied to characterize the microstructures of polymers (*1-5*). The thermal degradation mechanisms of wood and cellulosic products have also been studied by PyGC (*6-8*). Moreover, Smith and Beaver (*9*) determined the content of a styrene-butadiene copolymer in paper by PyGC with a packed separation column. Levy and Wampler (*10, 11*) analyzed inks and photocopy toner in paper by PyGC equipped with a fused silica capillary column. In their reports, they demonstrated that PyGC should be a powerful tool for industrial quality-control and forensic laboratories.

Recently, Crockett *et al.* (*12*) analyzed various polymer additives in paper by PyGC equipped with a packed column. To avoid the interference from the complex pyrolysis products of paper, they first prepyrolyzed only the cellulose matrix at a relatively low temperature of around 400°C, then pyrolyzed the polymer additives in the resulting char at a higher temperature of about 850°C.

Though much work has been done using the pyrolysis-gas chromatography technique, quantitative determination of the additives in paper has not been carried out. We applied PyGC to the quantitative determination of polyamide-epichlorohydrin (PAE) resin in paper.

*To whom correspondence should be addressed.

1. Reaction of PAE resin with cellulose



PAE resin structure

The structure of PAE is shown in **Fig. 1**. The wet strength of paper is increased simply by adding PAE, without developing any reaction with the cellulosic hydroxyl group which might cause loss of the water-absorption nature of the paper. Furthermore, it is known that the wet strength of the paper with PAE is much improved by thermal curing. The development of wet strength has been interpreted as follows:

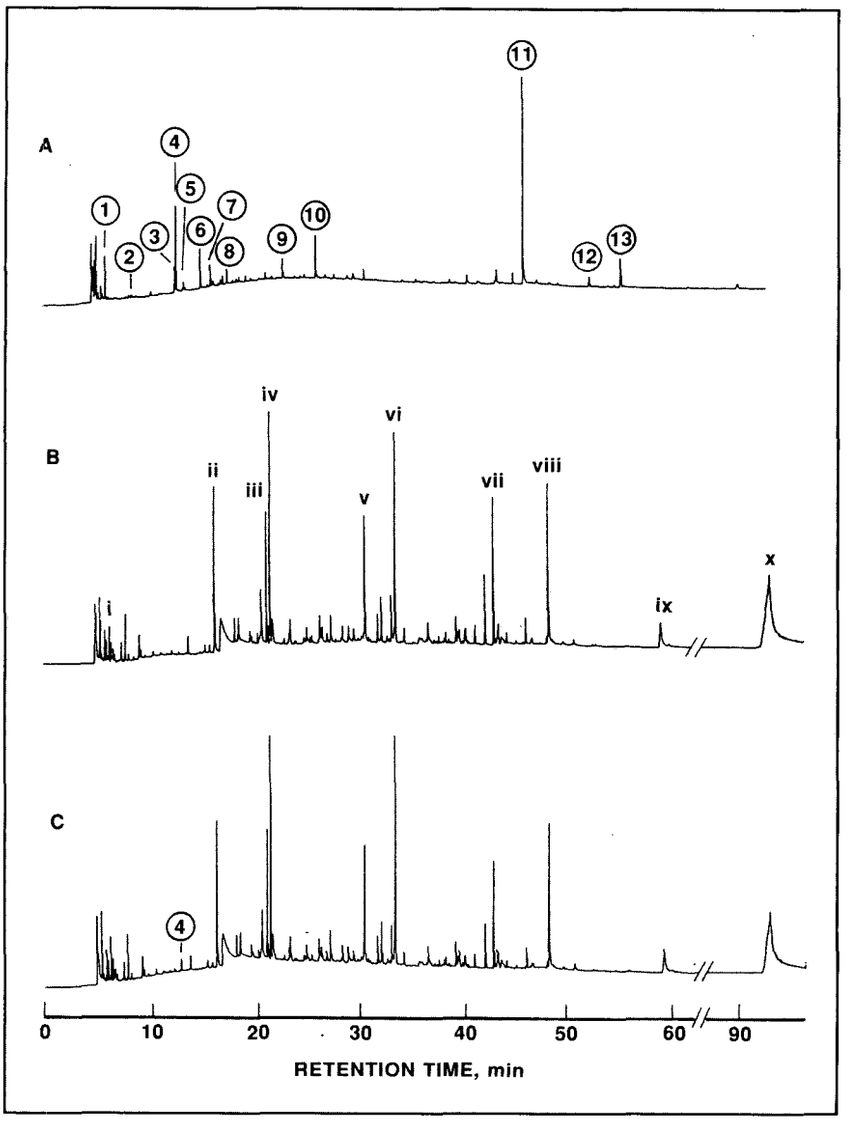
1. Protection of fiber-fiber contacts by a network of crosslinked resin molecules
2. Crosslinking of cellulose by the formation of resin-cellulose chemical bonds, as shown in Fig. 1.

Espy *et al.* (*13, 14*) reported that the first mechanism, which they termed "homo-crosslinking," predominated over the second mechanism, or "co-crosslinking," and that the first mechanism was accelerated by thermal curing.

Since the network structure thus formed makes it difficult to extract PAE from paper samples, its determination has been difficult. So far, the content of PAE in paper has been mostly estimated indirectly by measuring the total nitrogen content by the conventional Kjeldahl method.

In the PyGC technique, however, the paper samples can be directly pyrolyzed without any pretreatment. The characteristic peaks of PAE can be separated from those of complex cellulosic products by using a high-

2. Pyrograms of PAE resin and paper by flame ionization detector (A) PAE resin, (B) blank paper, and (C) paper with 3.2% PAE resin added



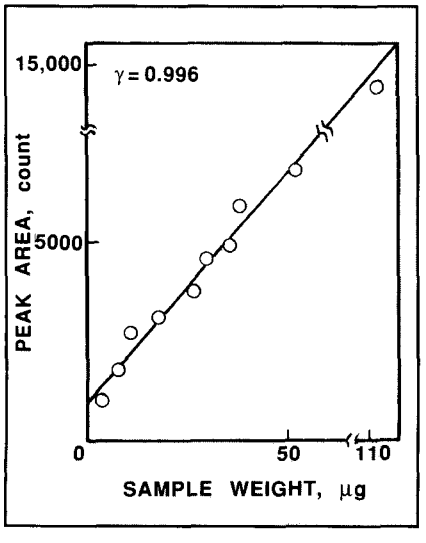
I. GC/MS peak assignment of the PAE pyrolysates

No.	Name
1	Chloroethane
2	Allylamine
3	1-cyano-1,3-butadiene
4	Cyclopentanone
5	1,4-diazine (pyrazine)
6	2-methyl-1,4-diazine
7	Aniline
8	Phenyl-1,2-diamine
9	Not identified (MW = 94)
10	$C_7H_6N_2$
11	Not identified (MW = 152)
12	Not identified
13	Not identified

II. GC/MS peak assignment of the pyrolysates of paper without PAE

No.	Name
i	furan
ii	1-hydroxy-2-propanone
iii	1-hydroxy-2,3-butadione
iv	2-furaldehyde
v	$C_5H_6O_2$
vi	2-tetrahydrofuraldehyde-5-one
vii	5-hydroxymethyltetrahydrofuran-2-one
viii	1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose (levoglucosenone)
ix	1,4-dideoxy-D-glycero-hex-1-enopyranos-3-ulose
x	1,6-anhydro-β-D-glucopyranose (levoglucosan)

3. Relationship between amounts of PAE and peak intensities of cyclopentanone in the pyrograms of PAE alone



resolution, fused-silica capillary column. On the basis of the intensities of the characteristic peaks, it is possible to estimate the contents of PAE in paper.

Results and discussion

Estimation of retained PAE resin

In **Fig. 2**, Pyrogram A is the pyrogram of PAE at 500°C. The PAE pyrolysates identified by gas chromatography-mass spectroscopy (GC/MS) are summarized in **Table I.** The main pyrolysis products are cyclopentanone (Peak 4) and an unknown compound (molecular weight = 152, Peak 11). Cyclopentanone is known to be formed from the adipic acid portions in the polymer chain at elevated temperature (*15, 16*). We proposed that the most intense peak, Peak 11, is constituted from a product formed from the portions of diethylene triamine and epichlorohydrin.

Pyrogram B is that of paper without PAE additives. The pyrolysates of paper identified by GC/MS are summarized in **Table II.** In addition to an intact pyrolysis product (Peak X), 1,6-anhydro-α-D-glucopyranose (levoglucosan), a large number of more fragmented polar compounds formed from cellulose are indicated in the pyrogram (*6, 8*).

Pyrogram C is that of paper containing 3.2% of PAE. Although many of the characteristic products of PAE overlap those of cellulose, the peak of cyclopentanone from PAE pyrolysis is distinctly observed in the pyrogram and was confirmed by GC/MS. However, Peak 11 is indistinguishable in the pyrograms of the paper samples, perhaps because its formation is depressed by the interaction between PAE and the cellulose matrix. Cyclopentanone is therefore used as the key product for the presence of PAE.

Figure 3 shows the relationship between the weight of PAE and the peak intensities of cyclopentanone in the pyrograms for weighted pure PAE samples. An almost linear relationship is observed up to 110 μg PAE. Moreover, the reproducibility (over six runs) of the peak intensities of cyclopentanone for the sample containing 0.5% of PAE was 4.8% relative standard deviation. These results suggest that the PAE retained in paper can be determined from the peak intensity of cyclopentanone in the pyrogram.

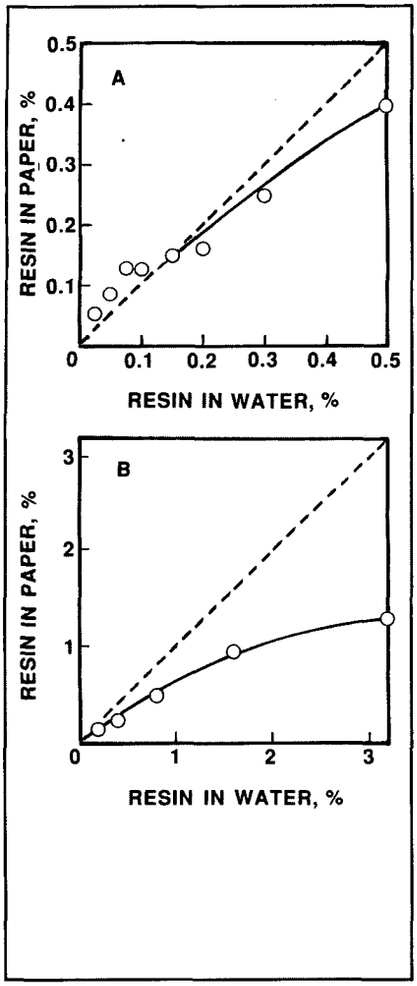
Here, the PAE content was calculated from the peak intensity of cyclopentanone normalized by the sample weight on the basis of that in the pyrogram for 50 μg PAE. **Figure 4** shows the relationship between the PAE fed into pulp slurry and the amounts retained in paper as estimated by PyGC. For a relatively small feed of PAE, the amounts of PAE in paper are nearly the same as the addition amounts (Fig. 4A). These results suggest that at least 80% of the PAE is retained in paper up to a feed of 0.5% PAE in water. On the other hand, the retention rate of PAE in the paper decreases almost exponentially at higher PAE addition levels (Fig. 4B). When 3.2% of PAE is added into pulp slurry, the amount of the PAE retained in paper is only about 40%.

Wet-strength response to retained PAE resin

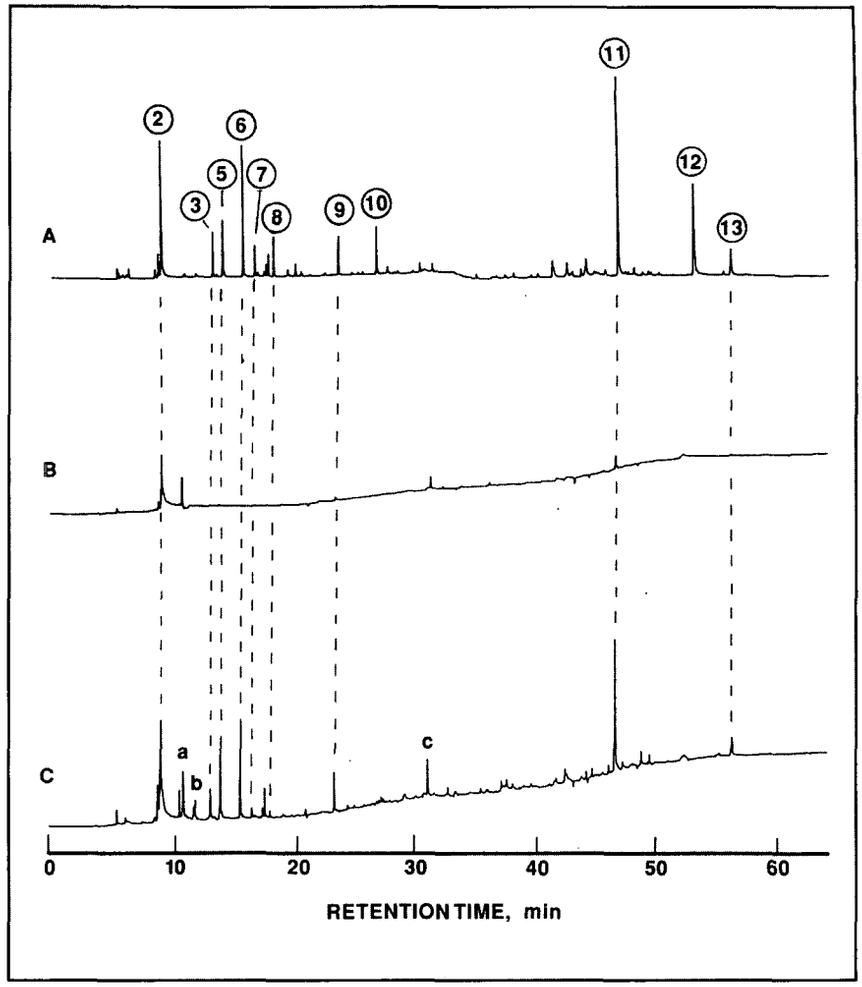
Figure 5 shows the relationship between PAE contents determined by PyGC and the wet tensile strength of paper samples (breaking length). The wet tensile strength is approximately proportional to the PAE content up to about 0.3% resin content. At higher resin retention, the slope of the curve rapidly falls off. Although at the first stage (below 0.3% resin retention) homo-crosslinking and co-crosslinking might occur simultaneously, co-crosslinking would be matured by a certain amount of the retained PAE when cellulosic or hemicellulosic carboxyl groups in the matrix are almost consumed. On the other hand, homo-crosslinking can still proceed in the second-stage region, in which more PAE is retained, and the wet strength would develop mostly by homo-crosslinking.

The ratio of the increase in wet strength in the first stage to that of the second stage in Fig. 5 is roughly 16:1. This fact suggests that the co-crosslinking might be about 15 times as effective as homo-crosslinking for development of wet strength under the conditions for sample preparations. Therefore, the increase of carboxyl groups in the matrices (by addition of carboxymethylcellulose, for example) may be more effective for the development of the wet strength than the increase of the retained PAE (*14*).

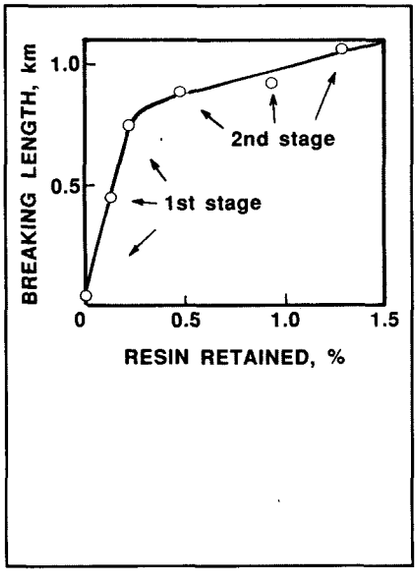
4. Relationship between retained PAE resin in paper determined by PyGC and feed of PAE resin in the pulp slurry: (A) paper samples with low PAE feed as in Table III and (B) paper samples with high PAE feed as in Table IV



6. Pyrograms of PAE resin and paper samples by flame thermionic detector (A) PAE resin, (B) blank paper, (C) paper with 3.2% PAE resin added



5. Relationship between wet-tensile strength and retained PAE resin



III. Paper samples containing PAE resin

No.	Resin dosage, % (dry basis)	Breaking length, km
1	0	0.07
2	0.025	0.17
3	0.05	0.28
4	0.075	0.39
5	0.1	0.47
6	0.15	0.60
7	0.2	0.70
8	0.3	0.81
9	0.5	1.06

Basis weight: 65 g/m².
Water: pH 6.5.
Freeness: 380 mL CSF.
Drying: 80°C, 120 s by drum dryer.

IV. Paper samples containing PAE resin

No.	Resin dosage, % (dry basis)	Breaking length, km
1	0	0.038
2	0.2	0.449
3	0.4	0.749
4	0.8	0.883
5	1.6	0.919
6	3.2	1.057

Basis weight: 64 g/m².
Water: pH 6.5.
Freeness: 390 mL CSF.
Drying: 100°C, 50 s by drum dryer.

Nitrogen-specific detection of the PAE fragments

Characteristic peaks of PAE, except for cyclopentanone, were interfered with severely by multiple products formed from the cellulose matrix in the pyrograms detected by the flame ionization detector, as Fig. 2 shows. Even in such a case, some of the peaks from PAE might be sensitively observed without interference by using a nitrogen-selective flame thermionic detector.

Figure 6 shows the pyrograms detected by the flame thermionic detector for the same samples as in Fig. 2. By comparing Fig. 6A with Fig. 2A, we see that almost all of the products from PAE include nitrogen except cyclopentanone. On the other hand, the flame thermionic detector does not respond sensitively to the products from cellulose matrix, as Fig. 6B shows. Therefore, the peaks originating from the PAE in paper can be selectively detected by the flame thermionic detector, as shown in Fig. 6C.

The relationships between the intensities of major peak in Fig. 6C and the amount of PAE in paper indicate almost the same tendency as that in Fig. 4. This fact suggests that the peak intensities detected by flame thermionic detector also reflect the amount of the retained PAE. Note the slight differences between the pyrogram of the paper-retained PAE (C) and that of PAE alone (A). Peaks 10 and 12 in A completely disappear, and Peaks 3, 7, 8 and 11 become smaller in C, while the new Peaks a, b, and c are observed.

This result suggests that these products might reflect the formation of resin-cellulose chemical bonds. Therefore, this technique would be expected to offer a new method for studying the degree and the mechanism of the reactions between cellulose and PAE. Further study along this line is now in progress.

Experimental procedures

Conditions for PyGC

A vertical microfurnace-type pyrolyzer (Yanagimoto GP-1018) was directly attached to a gas chromatograph (Shimadzu GC-9A) equipped with a flame ionization detector and a flame thermionic detector (*17*). About 0.5 mg of the paper sample or 0.05 mg of the resin sample was pyrolyzed under the flow of nitrogen or helium carrier gas. The pyrolysis temperature was set empirically at 500°C because lower temperatures caused peak broadening and poor reproducibility of the resulting pyrograms. Also, at higher temperatures, additional unknown peaks were observed, and the reproducibility was poor.

A fused-silica capillary column (50 m × 0.25 mm in internal diameter, Quadrex) coated with FFAP (free fatty acid phase; 0.25 μm thick) immobilized through chemical crosslinking was used. The 50-mL/min flow rate for the carrier gas at the pyrolyzer was reduced to 1.0 mL/min at the capillary column by a splitter. The column temperature was initially set at 40°C and then programmed to 240°C at a rate of 4°C/min. The pyrolysis chromatogram peaks were identified using a gas chromatograph-mass spectrometer (Shimadzu QP-1000) with an electron impact ionization source.

Materials

A PAE (Kymene 557H) produced by DIC-Hercules Chemicals Inc. was added to the pulp slurry to prepare paper samples. Then the paper samples were dried only by a drum dryer at 80°C for 120 s or at 100°C for 50 s without further thermal curing of the retained resin. The 15 paper samples containing various amounts of PAE are listed in **Tables III and IV**, together with the wet strength measured. Wet strength is expressed in terms of breaking length (km), calculated as 0.001 times the tensile strength (in kg of force) divided by the product of the width of the specimen (mm) times the basis weight (g/m^2). (The tensile strength is equal to the maximum load to a specimen of wet paper at fracture.)□

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