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Direct Analysis of Tackifying Resins in Vulcanized Rubber by Simultaneous Pyrolysis Methylation-Gas Chromatography/Mass Spectrometry

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Vulcanized rubber containing three kinds of oligomeric resins such as cashew resin, t-octylphenol formaldehyde resin and terpene modified wood rosin has been characterized by simultaneous pyrolysis methylation-gas chromatography/mass spectrometry (SPM-GC/MS). After methylation by the SPM method using tetramethylammonium hydroxide, the methylated pyrolyzates of the corresponding resins were detected with higher sensitivity than underivatized pyrolyzates without any interferences from other ingredients of vulcanized rubber.

Introduction

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), a direct analysis method, is a powerful analytical technique for macromolecules and oligomers that are insoluble or not extractable from matrix by organic solvents. Simultaneous pyrolysis methylation (SPM) with tetramethylammonium hydroxide (TMAH) is frequently used as a derivatization method of macromolecules in analytical pyrolysis. The method improves the gas chromatographic analysis of polar pyrolysis products of natural, synthetic, and biological polymers with carboxyl, aromatic amino, and hydroxyl groups. There are many reports on structural analysis of resin and resinite since the method was first introduced by Challiner.[1-4] The latest works on analytical and applied pyrolysis of polymers, copolymers and blend, were reviewed

by Blazso.[5] Challinor has applied the SPM method for several types of rosin-based commercial resins[6] and alkyd resins[7] that are polyesters prepared by reaction of polyhydric alcohols with polybasic acids. According to the Challinor's report, the composition of *t*-butylphenol, *p*-nonylphenol formaldehyde condensates, and their rosin ester derivatives were successfully determined by the SPM method for the purpose of forensic uses. According to their reports, however, the SPM method gave more complex chromatographic profiles under the experimental condition, that is, somewhat high pyrolysis temperature of 770 °C.

Most studies concerning the SPM method were done for the structural examination of oligomers and macromolecules themselves. Commercial rubbers are quite complex materials. In addition to various polymers, rubber formulations contain a number of compounding additives that are plas-

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ticizers, extender oils, carbon black, inorganic fillers, antioxidants, antiozonants, tackifying resins, crosslinking agents, accelerators, adhesives, antifatigue agents, and others. These sophisticated formulations of rubber compounds cause complex chromatographic profiles, thus it is difficult to identify these tackifying resins in vulcanized rubber. Stearic acid of industrial grade, which is one of the components of rubber compound, is not pure but contains palmitic, oleic, and several fatty acids of low carbon numbers. These acids would be affected during *in-situ* pyrolysis of vulcanized rubber. TMAH would be competitively reacted with both the resins and the fatty acids. Other components in vulcanized rubber like basic amine antioxidants may affect methylation.

The purpose of this study is to get information about characteristic pyrolyzates by SPM as a direct analysis of the above resins in the vulcanized rubber based on natural rubber (NR) and butadiene rubber (BR). SPM was applied to the NR/BR vulcanized rubber containing three kinds of tackifying resins such as modified wood rosin of 10-15% terpene oil (Hi-Rosin™), *t*-octylphenol formaldehyde resin, and cashew resin (PR-YR-45™). One of the interesting points of this study is to see whether TMAH successfully methylates products in the complex mixture of pyrolyzates after pyrolysis. Effects of stearic acid, amine antioxidant, and other additives were studied, too. Another point is the identification of characteristic mass spectra of the resins obtained by SPM.

Experimental

The compositions of rubber compounds studied are listed in Table 1. The sample SPMRT 1, 2, and 3 contain the Hi-Rosin, *t*-octylphenol formaldehyde resin, and cashew resin respectively. Pyrolysis was carried out using a Model JHP-3 Curie-point Pyrolyzer (Japan Analytical Industry Co., Ltd.) which was combined with an on-line GC/MS (GC: Hewlett

Table 1. Compositions of cured rubber tested

Component	Samples unit: PHR*		
	SPMRT 1	SPMRT 2	SPMRT 3
Natural rubber	90	90	90
Butadiene rubber	10	10	10
Zinc oxide	3.0	3.0	3.0
Stearic acid	2.5	2.5	2.5
Carbon black	50	50	50
Antioxidant 6C	1.0	1.0	1.0
Antioxidant poly-TMDQ	0.5	0.5	0.5
Wax	1.0	1.0	1.0
Sulfur	1.4	1.4	1.4
t-Butyl-2-benzothiazole sulfenamide	1.4	1.4	1.4
PVI	0.3	0.3	0.3
Tackifying resin			
Modified wood rosin of			
10-15% terpene oil (Hi-Rosin™)	3.0		
t-Octylphenolformaldehyde resin		3.0	
Cashew resin (PR-YR-45™)			3.0

*PHR: part per hundred rubber ratio.

Packard 5890 II plus, MS: 5989B mass spectrometer). The GC/MS was equipped with a fused-silica capillary HP-5 column (Hewlett Packard, 0.25 mm i.d.×30 m) of 0.25 μm film thickness, and quadrupole mass spectrometer with an EI (70 eV) facility. The injector was operated in splitless mode at 250 °C. The column temperature was initially maintained at 90 °C for 2 minutes, and then enhanced to 290 °C at 10 °C/min. The small pieces of 0.2 mg of sample with Chromosorb-W powder as an absorbent of TMAH was wrapped in Pyrofoil® with tight contact and pyrolyzed for 5 seconds at 590 °C. The 0.5 μL TMAH (25% w/w aqueous solution) was injected on Chromosorb-W before wrapping with Pyrofoil. Chromosorb-W-DMCS-AW, about three times of the sample volume, was used as an absorbent because vulcanized rubber is not wetted by TMAH. The pyrolyzer chamber temperature and the needle temperature were set at 250 °C. The rubber compound tested was mixed in a small lab mixer and then sheeted out by an open roller.

Results and Discussion

Hi-Rosin, *t*-octylphenol formaldehyde resin, and cashew resin, which are studied in this report, are widely used as tackifying resins in rubber industry. These resins have reactive sites (hydroxyl group and carboxyl group) for TMAH.

Pyrolytic behavior and characteristic mass spectrum of Hi-Rosin (SPMRT 1). The characteristic mass spectrum of pyrolyzates of resin itself and vulcanized rubber containing the resin were compared in order to get information of mass spectral difference by SPM. First, the characteristic pyrolyzates of Hi-Rosin itself were identified in order to compare them to those of Hi-Rosin obtained by the SPM procedure. The total ion chromatogram (TIC) of
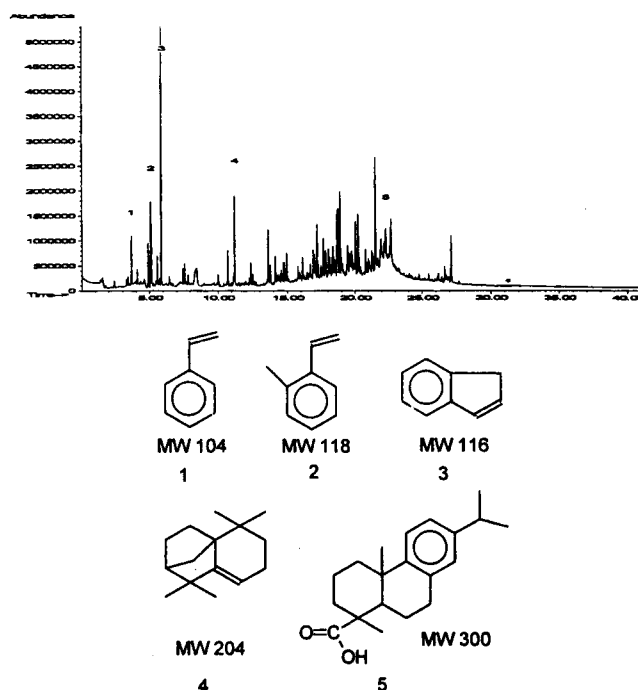

Figure 1. Total ion chromatogram of modified wood rosin with 10-15% terpene oil. 1, Styrene (C8H8); 2, 1-ethenyl-2-methylbenzene (C9H10); 3, Indene; 4, Isolongifolene; 5, Dehydroabietic acid.
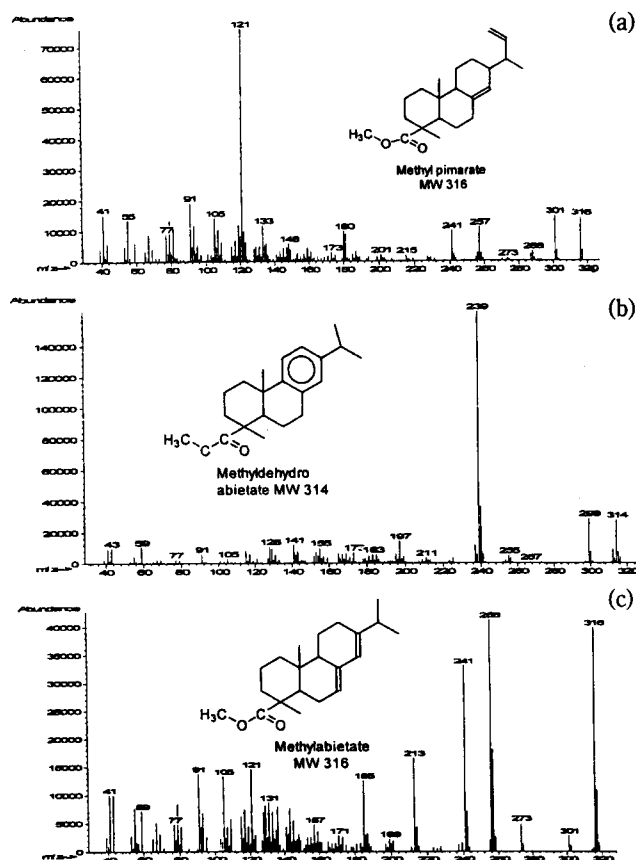
Figure 2. Mass spectrum of rosin ester of Hi-rosin by SPM. (a) methyl pimarate, (b) methyl dehydroabietate, (c) methyl abietate.
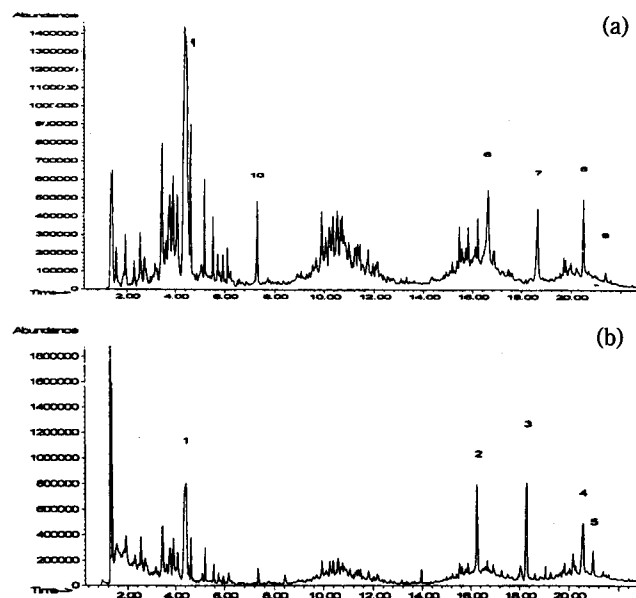

Figure 3. Total ion chromatogram of cured rubber containing Hi-rosin; (a) without SPM and (b) with SPM. 1, Isoprene dimer MW 136; 2, Haxadecanoic acid methyl ester MW 270; 3, Octadecanoic acid methyl ester MW 298; 4, Methyl dehydroabietate MW 314; 5, Methyl abietate MW 316; 6, Hexadecanoic acid MW 256; 7, Octadecanoic acid MW 284; 8, Antioxidant 6C MW 268; 9, Dehydroabietic acid MW 300; 10, Benzothiazole MW 135.
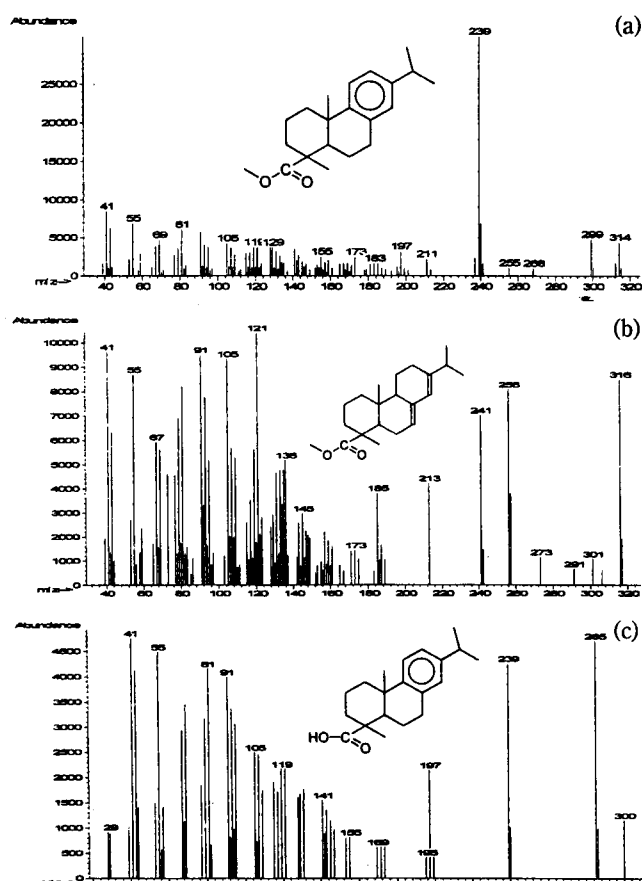

Figure 4. The characteristic mass spectra of Hi-Rosin in vulcanized rubber After SPM. (a) Mass spectrum of peak 4 of methyl dehydroabietate (m/z 314), (b) Mass spectrum of peak 5 of methyl abietate (m/z 316), Before SPM (c) Mass spectrum of peak 9 of dehydroabietic acid (m/z 300).

Hi-Rosin and the chemical structures of its pyrolyzates were shown in Figure 1. The Hi-Rosin is a modified resin. It is made by the reaction between C_5, C_9 series of aromatic monomers and a rosin acid like dehydroabietic acid[8] (MW 300). Some isomers of the resin acid such as methyl pimarate (MW 316: $C_{21}H_{32}O_2$), methyl dehydroabietate (MW 314: $C_{21}H_{30}O_2$), and methyl abietate (MW 316: $C_{21}H_{32}O_2$) were detected in Hi-Rosin using the SPM method, and their mass spectra and chemical structures are shown in Figure 2. In this study, the pyrolysis was done at somewhat lower temperature (590 °C×5 sec) to reduce the pyrogram complexity. The vulcanized rubber SPMRT 1, 2, and 3 were also pyrolyzed with TMAH under this condition.

Figure 3 presents the difference between characteristic pyrolyzates of vulcanized rubber containing the Hi-rosin before and after SPM. The in-situ methylation by TMAH led to enhance intensities of each ester derivative. The peak 4 of methyl dehydroabietate (molecular ion at m/z 314) and peak 5 of methylabietate (m/z 316) were detected after SPM in vulcanized rubber (SPMRT 1). The intensity of peak 9 of the vulcanized rubber (before SPM) which is dehydroabietic acid (molecular ion at m/z 300) would be too small to identify when the sample size and/or content is below the amount of this experiment. The identified mass
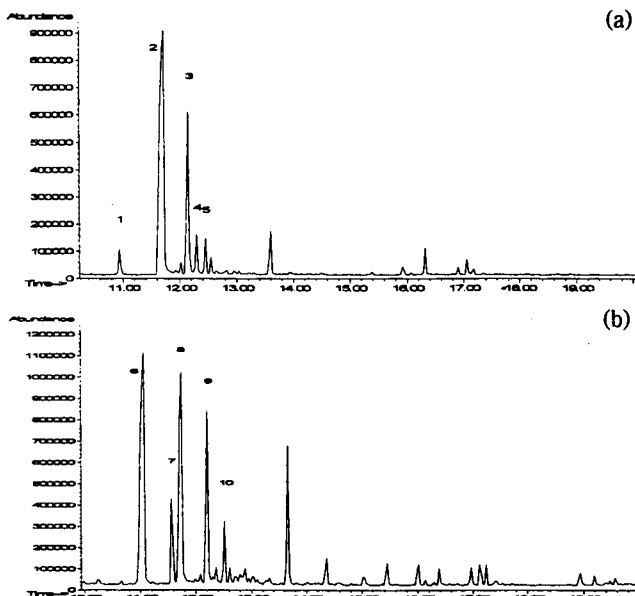
(a)

(b)

Figure 5. Total ion chromatogram of *t*-octylphenolformaldehyde resin. (a) without SPM, (b) with SPM. Peak 1: m/z 220, 149, 121; Peak 2: m/z 206, 135, 107 of *t*-octylphenol; Peak 3: m/z 220, 149, 121 of 2-methyl-4-*t*-octylphenol; Peak 4: m/z 206, 135, 107 of octylphenol isomer; Peak 5: m/z 234, 163, 135 of 2,6-dimethyl-4-*t*-octylphenol; Peak 6: m/z 220 of methyl ether of *t*-octylphenol by SPM; Peak 7: m/z 234, 163 of isomer of peak 5, Peak 8, 9, and 10 corresponding to the peak 2, 3, and 5.

Table 2. Characteristic ions of *t*-octylphenol formaldehyde before and after SPM

Peak number	Ion (m/z)	Assign	Remark
1	220, 149, 121	Methyl substituted *t*-octylphnol	Before SPM (Py-GC/MS)
2	206, 135, 107	4-*t*-octylphenol	
3	220, 163, 149, 121	2-Methyl-4-*t*-octylphenol	
4	206, 135, 107	Octylphenol isomer	
5	234, 163, 135	2,6-dimethyl-4-*t*-octylphenol	
6	220, 149, 121	Methylated *t*-octylphenol	After SPM (SPM-GC/MS)
7	234, 163, 135		
8	206, 135, 107	Peak 8, 9 and 10	
9	220, 149, 121	correspond	
10	234, 163, 135	to peak 2, 3, 5	

spectra of peak 4, 5, and 9 in vulcanized rubber containing Hi-Rosin before and after SPM are shown in Figure 4. The peak 2, 3, 4, and 5 of Figure 3 show that stearic acid and rosin acid were simultaneously reacted with TMAH. This implies that the SPM reaction did not disturb methylation each other in 0.5 μL level of TMAH. Other remarkable difference of both pyrograms in Figure 3 lies on the intensity of antioxidant 6C. The peak 8 of amine antioxidant 6C™ generally appears closely to that of Hi-Rosin and the 6C peak disturbs the identification of the small Hi-Rosin peak before SPM. However, the peak intensity of 6C[9] (ion at m/z
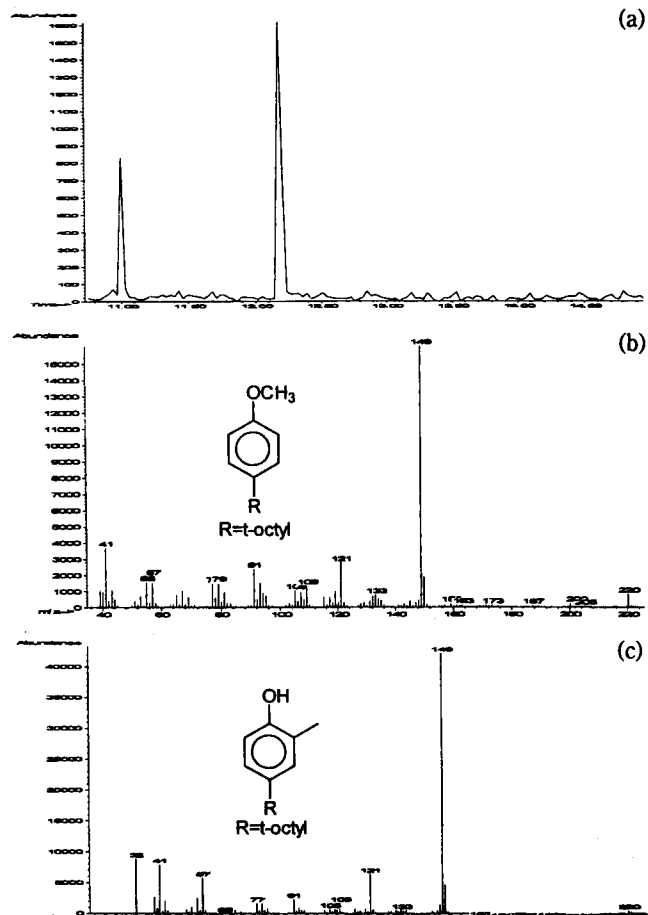

(a)

(b)

R=t-octyl

(c)

R=t-octyl

Figure 6. Extracted ion current chromatogram with m/z 220 in vulcanized rubber (SPMRT2) 1: m/z 220 of methyl ether of the resin, mass spectrum (a), 2: pyrolysate with methylene bridge on *t*-octylphenolformaldehyde resin, mass spectrum (b).

268, 211) which corresponds to the marked number 8 was dramatically decreased to the baseline level after SPM. The 6C peak did not disturb the identification of Hi-Rosin peak after SPM. The peak 10, bezothiazole (ion at m/z 135) was formed from fragmentation of *t*-butyl-2-benzothiazole sulfenamide, a vulcanization agent.

Pyrolytic behavior and characteristic mass spectrum of *t*-octylphenolformaldehyde resin (SPMRT 2). The *t*-octylphenol formaldehyde resin[10] is divided into two classes, that is, novolc and resol types according to catalysts and the component ratio between alkylphenol and formaldehyde. This resin is widely used as tackifying resins in rubber industry. Tackifying resins have autohesion effect that promote the tackiness between two materials. As mentioned earlier, Challinor has characterized *t*-butylphenol and *p*-nonylphenol formaldehyde resin by Py-GC and SPM-GC.

In this study, characteristic pyrolyzates of a vulcanizate containing *t*-octylphenol formaldehyde resin have been studied. The TIC of *t*-octylphenol formaldehyde resin obtained with or without the SPM procedure was shown in Figure 5. Several peaks were obtained from *t*-octylphenol formaldehyde resin by Py-GC/MS without SPM as shown in Figure 5a. Those are peak 1 of m/z 220, 149, 121 (methyl-4-*t*-octylphenol), peak 2 of m/z 206, 135, 107 (*t*-oc-

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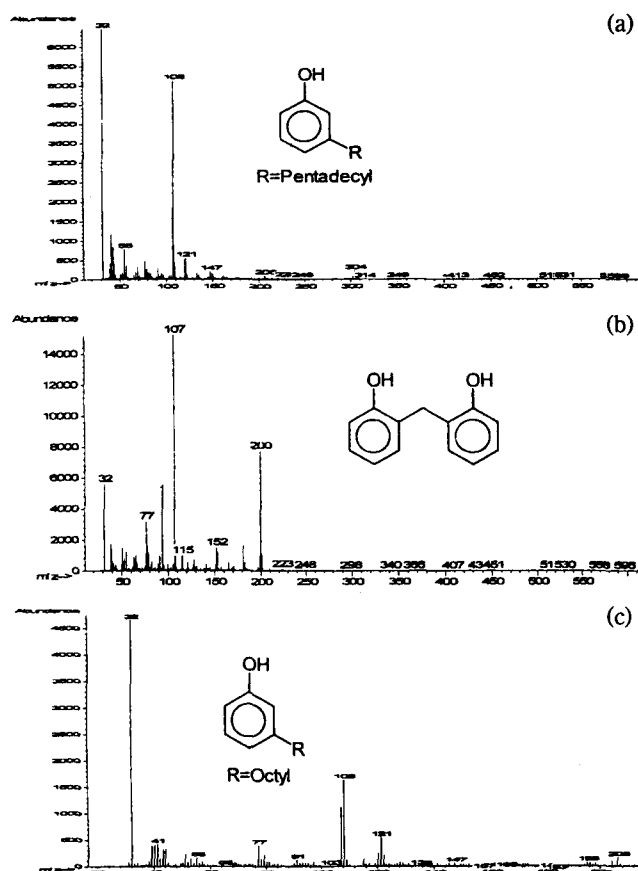
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Figure 7. Major characteristic mass spectrum of cashew resin. (a) m/z 304 of 3-pentadecylphenol, (b) m/z 200 of 2,2-methylene bisphenol (c) m/z 206 of 3-octylphenol.

Figure 8. Characteristic mass spectrum of cashew resin by SPM. (a) m/z at 318 of 1-metoxy-3-phentadecylbenzene, (b) m/z 228 of methoxy methylene bisphenol, (c) m/z 220 of 1-methoxy-3-oc-tylbenzene.

tylphenol), peak 3 of at m/z 220, 163, 149, 121 (2-methyl-4-*t*-octylphenol) and peak 4 of octylphenol isomers, and peak 5 of 2,6-dimethyl-4-*t*-octylphenol (m/z 234, 163, 135). After the SPM procedure (Figure 5b), the height of methylated *t*-octylphenol (m/z 220, 149, 121) of peak 6 corresponding to peak 1 was increased. The peaks 8, 9, and 10 correspond to peak 2, 3, and 5 based on their mass spectra. The compound corresponding to the peak 7 was thought to be an alkylated *t*-octylphenol based on its mass spectrum. Two pyrolyzates with m/z 220 (peak 1 and 3 of Figure 5a, peak 6 and 9 of Figure 5b) was found. The pyrolyzate with methylene bridge between the two phenyl rings of the resin leads to the ion at m/z 220. Another ion at m/z 220 was from etherification of the resin by SPM. The methyl ether (peak 6) of the resin seemed to be allowed by SPM of *t*-octylphenol formaldehyde. These characteristic m/z values of *t*-octylphenol formaldehyde resin are shown in Table 2. The SPM effect has been similarly observed in vulcanized rubber containing the resin (SPMRT 2). Extracted ions at m/z 220 and 149 of vulcanized rubber SPMRT 2 were shown in Figure 6. The peak 1 was identified as the ether form by SPM, corresponding to the peak 6 of Figure 5. The peak 2 of Figure 6 with m/z 220 has been identified as the pyrolyzate due to a methylene bridge between the two phenyl rings. However, the peak intensity of m/z 220 was not increased compared to that of peak 6 in Figure 5.

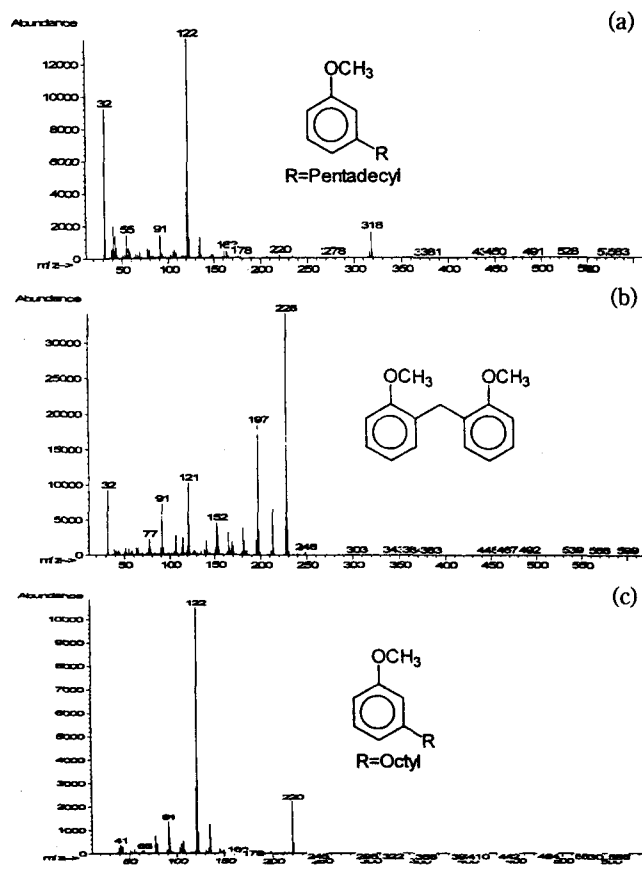**Pyrolytic behaviors and characteristic mass spec-**

tra of cashew resin (SPMRT 3). Cashew resin from cashew nut shell liquid (CNSL) is an important resource of phenolic resin in rubber compounding, which is used for reinforcing resins with hexamethylenetetramine as a hardener. The main components of CNSL are cardanol and cardol. PR-YR-45® is one of the cashew resins.

Several characteristic pyrolyzates of cashew resin have been identified by molecular ion at m/z 94 for phenol, at m/z 108 for 3-methylphenol, at m/z 122 for 3,5-dimethyl phenol, at m/z 206 for 3-octylphenol, at m/z 200 for 2,2'-methylene bisphenol, and at m/z 304 for 3-pentadecylphenol. Some major mass spectra were shown in Figure 7.

Characteristic ether forms of vulcanized rubber containing cashew resin (SPMRT 3) by SPM have been identified as follow: molecular ions at m/z 318 for 1-methoxy-3-phentadecyl benzene, at m/z 228 for methoxy methylene bisphenol, at m/z 220 for 1-methoxy-3-octylbenzene, and at m/z 122 for 1-methoxy-3-methyl benzene. Their mass spectra were shown in Figure 8. The molecular ion at m/z 318 for 1-methoxy-3-pentadecyl benzene is an ether form formed from molecular ion at m/z 304 of 3-pentadecylphenol by SPM in vulcanized rubber. Another ether form of m/z 228 and 220 in Figure 8b and Figure 8c were resulted from m/z 200 of 2,2'-methylene bisphenol of Figure 7b and from m/z 206 of 3-octylphenol of Figure 7c respectively by SPM. Stearic acid in vulcanized rubber was also reacted with

TMAH. However, the major methylated phenolic pyrolyzates of vulcanized rubber containing cashew resin have been identified without any interference from other additives in vulcanizate.

Conclusion

Simultaneous pyrolysis methylation (SPM) effect were studied to characterize commercially available three kinds of tackifying resins such as wood rosin modified with terpene (Hi-Rosin™), *t*-octylphenol formaldehyde resin, and cashew resin by means of direct analysis in vulcanized rubber containing these resins. Methyl dehydroabietate (molecular ion at m/z 314) and methylabietate (molecular ion m/z 316) were identified as characteristic esters formed from this resin by SPM of the Hi-rosin vulcanizate. The molecular ion at m/z 220 for methyl ether of *t*-octylphenol was the characteristic pyrolysate formed after SPM in the *t*-octylphenol formaldehyde vulcanizate. The ion at m/z 318 of 1-methoxy-3-pentadecylbenzene was identified as the characteristic pyrolysate in vulcanized rubber containing cashew resin. Although stearic acid has a reactive polar site, it did not interfere with the reaction of polar site of the resins by TMAH. SPM of tackifying resins led to enhance the peak intensity of the oligomeric components having hydroxyl and carboxylic sites in vulcanized rubber. In this study, we have shown that SPM of oligomeric tackifying resins produces characteristic pyrolyzates suitable for identification of these resins in rubber vulcanizates.

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