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Maleo- and Fumaro-Pimaric Acids Synthesized from Indonesian *Pinus merkusii* Rosin and Their Sizing Properties

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Abstract: This research is directed at characterizing purified maleopimaric acid (MPA), looking at the amount of MPA and fumaropimaric acid (FPA) made from a large amount of rosin and maleic anhydride (MA) or fumaric acid (FA) with various molar ratios and sources of rosin and evaluating the properties of fortified rosin sizes made from both MPA and FPA. Results showed that identification of the Diels-Alder adduct of abietic acid and maleic anhydride using Mass spectrometry produced a mixture of endo-maleopimaric acid methyl ester with endo-maleopimaric acid tri methyl ester, as indicated by a fragment ion at $m/z = 146$ with a molecular weight of 414 and fragment ions at $m/z = 121, 187, 316$ and 386 , denoting an endo-maleopimaric acid methyl ester. A fragment ion at $m/z = 146$ with a molecular weight of 460 and other fragment ions at $m/z = 187, 121, 400$ and 428 indicated endo-maleopimaric tri methyl ester. Using a large amount of rosin as a raw material to produce MPA, the equation $Y = -0.8475 X^2 + 10.448X - 9.7125$, at a reaction temperature of 200°C is still relevant as it denoted that a molar ratio of 1:6.2 (rosin and MA) is the best. However, the equation $Y = -0.46X^2 + 5.268X - 4.47$ did not apply to FPA. Using a large amount of rosin, an increase in the molar ratio led to an increase in FPA products. In terms of free rosin and pH, the maleo- and fumaro-pimaric rosin sizes have met the requirement of Indonesian national standards for paste rosin size. In terms of free alkali property, the maleo- and fumaro-pimaric rosin sizes were better than the free alkali of the commercial forms.

Key words: Rosin, maleopimaric acid, fumaropimaric acid, molar ratio, size

INTRODUCTION

Rosin is produced from pine resin. It remains as an involatile residue after the distillation of turpentine. It is insoluble in water but soluble in many organic solvents and is graded and sold on the basis of color, those products with the palest shades of yellow-brown having the better quality. It contains predominantly a mixture of abietic- and pimaric-type acids. This intrinsic acidity enables it to be converted to a large number of derivatives which have a wide range of applications. The derivatives include salts, esters and maleic anhydride adducts and hydrogenated, disproportionated and polymerized rosins. The most important of their uses in the manufacture is for adhesives, paper sizing agents, printing inks, solders and fluxes, various surface coatings, insulating materials for the electronics industry, synthetic rubber, chewing gums, and soaps and detergents (Coppen and Hone, 1995). Zhaobang (1995) described that MPA, one of the derivatives of rosin, is primarily used as a sizing agent in pulp and paper industries. It is also utilized in painting, ink and other chemical industries. Other, commonly used

products made from rosin are glues, technical resins, synthetic rubbers and cosmetic and dental materials (Hong Li *et al.*, 2005). Indonesia, as the world's third biggest rosin-producing country after China and Portugal, uses unmodified rosin in small quantities. Almost all the rosin, about 55,000 tons in 2006, is exported.

Previous study showed that the main constituents of rosin from *Pinus merkusii* in Indonesia are abietic and palustric acids (Wiyono *et al.*, 2006) and these acids, including neoabietic acid, could be reacted with MA or FA to form fortified rosin (Sundqvist *et al.*, 2001). Moreover, Diels-Alder reactions of abietic acid (AA) and MA or FA studied and the adduct were identified by GC-MS using a Shimadzu QP 5050A. The reaction product of abietic acid and maleic anhydride produced endo-maleopimaric acid (MPA) and endo-maleopimaric acid tri carboxylic acid; while, the reaction product of abietic acid and fumaric acid produced fumaropimaric acid (FPA) and endo-MPA (Wiyono *et al.*, 2007a). Further study indicated that the relationship between molar ratio and the concentration of MPA or FPA could be expressed as a quadratic equation. From the equation, we predicted the

best molar ratio to produce the highest yield of MPA or FPA adducts. Using the equation $Y = -0.8475X^2 + 10.448X - 9.7125$, at a reaction temperature of 200°C, the greatest proportion of MPA (around 22.5%) was obtained with a molar ratio of rosin to MA of 1:6.2. Meanwhile, using the equation $Y = -0.46X^2 + 5.268X - 4.47$, at 200°C, the greatest proportion of FPA (around 10.6%) was obtained with a molar ratio of rosin to FA of 1:5.8.

Based on the above results, we obtained MPA and FPA by using a large amount of rosin as a raw material. Further, these rosins were used as raw materials for producing fortified rosin sizes. This research is directed at characterizing purified MPA and looking at the amount of MPA and FPA made with a large amount of rosin and MA or FA with various molar ratios and sources of rosin. The last aim is to look at the properties of fortified rosin sizes made from both MPA and FPA.

MATERIALS AND METHODS

Sources of chemicals: In this experiment, conducted in 2007, we used abietic acid (AA), maleic anhydride (MA) and fumaric acids (FA), purchased from Wako Pure Chemical Company Ltd., Japan. We also utilized commercial fortified rosin obtained from Indo Piceri Company and rosin from Forest Estate Company, Indonesia. Other chemicals, such as sodium hydroxide, potassium hydroxide, hydrochloric acid, etc. were procured from Merck Corporation.

Synthesis of maleopimaric acid (MPA): After purification of abietic acid by repeated crystallization from ethanol and water, mp 172-175°C (Anonymous, 2001), MPA was produced (Wiyono *et al.*, 2007a). After drying in a vacuum oven, 5 g of purified abietic acid and 10.06 g of maleic anhydride (molar ratio of AA to MA 1:6.2) were well mixed in a mortar. The powder was transferred to a small flask (25 mL) and heated at 200°C for an hour under a nitrogen atmosphere. The brownish-red reaction products were dissolved in toluene and extracted with water to remove the excess of MA; dried with MgSO₄, filtered and evaporated. Further purification was performed by column chromatography on silica gel eluted with hexane, hexane-ethyl acetate with increasing amounts of ethyl acetate and decreasing amounts of hexane, ethyl acetate and acetic acid and finally with methanol. The MPA product of the column chromatography was then purified by recrystallization from diethyl ether and hexane (Nilsson *et al.*, 2002). After methylation, the purified product was analyzed by GLC and MS.

Making MPA and FPA: The procedure to react the rosin from various regions (East Java, Central Java and West Java, Indonesia) with MA or FA follows a previous method (Wiyono *et al.*, 2006). Around 5 g of rosin and 10.06 g of MA with a ratio of 1:5.2, 1:6.2, or 1:7.2 were mixed in a mortar, then transferred to a round flask and heated at 200°C in an oil bath for one hour under a nitrogen stream. The brownish reaction products were dissolved in toluene and then washed with water. The remaining water was removed with anhydrous sodium sulphate, the toluene solution was concentrated under a nitrogen stream and the concentrate was dried in the vacuum oven.

The above procedure was also used to make FPA. Around 5 g of rosin and 11.14 g of FA with a ratio of 1:4.8, 1:5.8 or 1:6.8 were mixed in a mortar, then transferred to a round flask and heated at 200°C in an oil bath for 1 h under a nitrogen stream. The reaction products were dissolved in toluene and washed with water and the remaining water was removed with anhydrous sodium sulphate. The toluene solution was concentrated under a nitrogen stream and the concentrate was dried in the vacuum oven. After methylation, the methylated products, both MPA and FPA, were analyzed using GLC. The GLC-based analysis of reaction products was performed using a HITACHI 3000 Gas chromatograph, equipped with an electronic Chromato-integrator D-2500. The conditions followed those in a previous investigation (Wiyono *et al.*, 2007b).

The quantification of constituents was conducted with a GC-FID profile obtained on a capillary column according to the peak area percent method without response factor correction (Pteifhover, 2000).

Making and analyzing fortified rosin size properties: The procedure to prepare fortified rosin size was the method of Leffler (Patent No. 4219382). A small quantity of MPA or FPA was heated at 95°C and then added to 10 mL of water containing 10 g of NaOH and 15 g of Na₂CO₃ to maintain the liquid moderately alkaline. The aqueous soap was filtered off, leaving the insoluble polymeric rosinate and the insoluble product was washed with alkaline water, heated to the point of melting and cooled. It was a brown glassy solid. The fortified rosin sizes were then analyzed as to their properties, covering free rosin, total rosin, combined rosin and free alkali by using TAPPI standard (T628 cm-01).

RESULTS AND DISCUSSION

Reaction product of AA and MA: Abietic acid is the major component of colophony and used as a starting

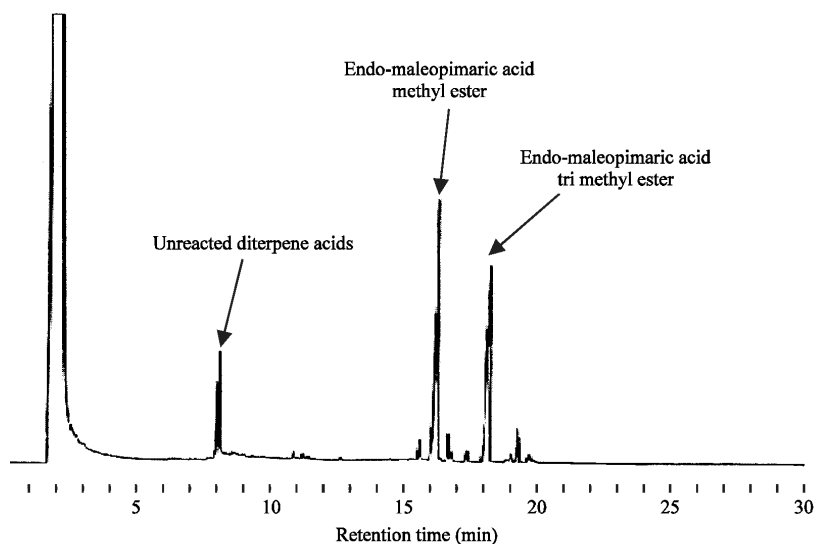


Fig. 1: A chromatographic profile of the crude MPA reaction product (before purification)

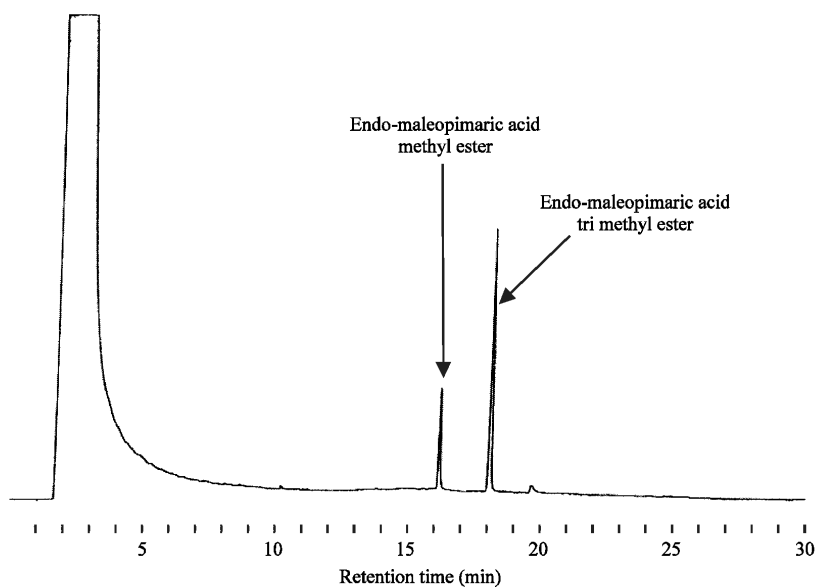


Fig. 2: A chromatographic profile of the purified MPA reaction product (after purification)

material and useful synthetic intermediate. Numerous common products can be obtained from abietic acid and they could be utilized in paper size, printing ink, glue (Zhaobang, 1995).

Previously, using a small amount of AA (0.520 mg) and MA (0.380 mg), we have investigated the reaction product of both chemicals (Wiyono *et al.*, 2007a). The Diels-Alder product, MPA, was purified by column chromatography on a silica gel eluted with ethyl acetate with increasing amounts of acetic acid, without any further purification after the isolation of MPA. Even though identification by comparing mass spectra for

the injected samples to mass spectra studied by Mayr *et al.* (1984) gave similar results, this MPA product was not a white solid as mentioned in several references. In a recent study using much more AA (5 g) and MA (10.06 g) to produce MPA, after purification of the product by column chromatography on a silica gel eluted with a combination of hexane-ethyl acetate followed by further purification and by recrystallization with diethyl ether-hexane, a white crystal was produced by Nilsson *et al.* (2002). Then, the products were analyzed by GLC before and after purification. Two peaks appeared in both chromatograms (Fig. 1, 2). However,

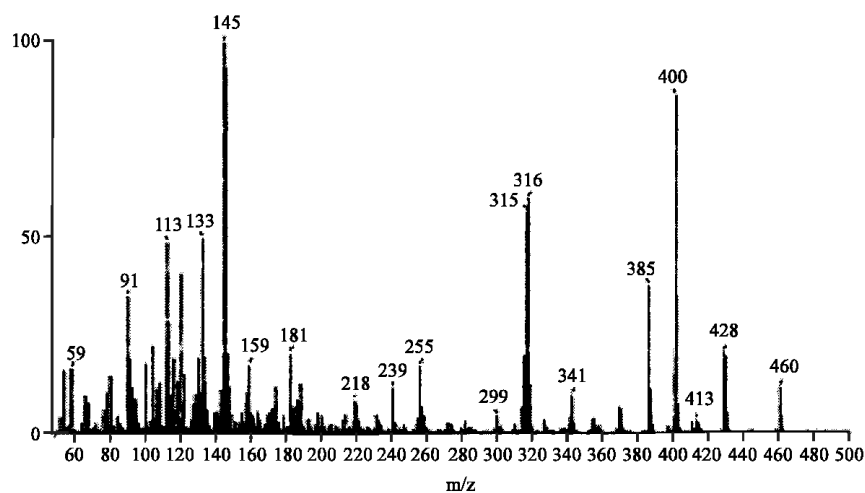


Fig. 3: A mass spectrum of Endo-maleopimaric acid methyl ester mixed with Endo-maleopimaric acid tri methyl ester

some unreacted diterpene acids were also found in the chromatogram (Fig. 1). During the purification process, almost all unreacted diterpene acids were removed from the reaction product and pure MPA remained. After purification, two peaks still appeared in the chromatogram (Fig. 2). By comparing to a previous report (Wiyono *et al.*, 2006), both peaks could be identified, one as endo-maleopimaric acid methyl ester, the other as endo-maleopimaric tri methyl ester. Further analyses with MS indicated that the spectra contained not one compound but two. If we look at a profile of spectra studied by Mayr *et al.* (1984), there was a peak with a base peak at $m/z = 146$ with a molecular weight of 460 with a prominent ion at $m/z = 187$, another small ion at $m/z = 121$ and a significant ion at $m/z = 400$ and 428. Figure 3 indicated endo-maleopimaric tri methyl ester. Further, there was also a base peak at $m/z = 146$ with a molecular weight of 414 and ions at $m/z = 316$ and 386, which indicated an endo-maleopimaric acid methyl ester. During this recent research, when a sample of MPA was subjected to Mass Spectrometry using DIEI, all these ions were found in the spectra of DIEI results, even though the base peak and mass spectra were not as high as in the reference, as shown in Fig. 3.

Reaction products of rosin and MA or FA: The modification of rosin achieved by heating it with maleic anhydride is important in its industrial utilization. The most important reaction to occur during this treatment is the formation of maleopimaric acid from the abietic type acids, covering palustric, neoabietic and abietic acids. By heating a mixture of rosin and MA, a very small proportion of levopimaric acid reacts with the maleic anhydride to give the Diels-Alder product, MPA (Gafvert, 1994).

Earlier studies have investigated the relationship between the molar ratio and the concentration of MPA or FPA by using a regression analysis (Wiyono *et al.*, 2007b), the regression analysis showed that there was a relationship between the molar ratio and the concentration of MPA or FPA expressed as quadratic equations for both adducts. MPA and the molar ratio at a reaction temperature of 200°C could be expressed as $Y = -0.8475 X^2 + 10.448X - 9.7125$ with a coefficient determination (R^2) = 0.999. At a similar reaction temperature, the relationship between the molar ratio and the concentration of FPA was expressed as a quadratic equation, $Y = -0.46X^2 + 5.268X - 4.47$ with a coefficient determination (R^2) = 0.97. Based on these equations, there could be predicted the best molar ratio to produce the highest MPA or FPA adducts. Using the equation $Y = -0.8475 X^2 + 10.448X - 9.7125$, at a reaction temperature of 200°C, the highest proportion of MPA (around 22.5%) could be achieved by using a molar ratio of rosin to MA of 1:6.2. Using the equation $Y = -0.46X^2 + 5.268X - 4.47$, at a similar reaction temperature, the highest proportion of FPA (around 10.6%) could be achieved by using a molar ratio of rosin to MA of 1:5.8. With these molar ratios we made MPA or FPA using much more rosin as a raw material compared to previously, with not only rosin obtained from East and Central Java but also rosin from West Java as a raw material. We applied three molar ratios and one reaction temperatures, 200°C, for one hour in making MPA and FPA.

Using rosin obtained from one of the enterprises in East Java-Indonesia, the increase in molar ratio at the reaction temperature of 200°C initially gave a higher yield of endo-maleopimaric acid, then, it decreased with further increase in the molar ratio (Table 1). The amount of reaction product, endo-maleopimaric acid, was in the

Table 1: MPA and FPA content at various molar ratios (rosin and MA)

Source	Molar ratio											
	1:5.2		1:6.2		1:7.2		1:4.8		1:5.8		1:6.8	
	MPA	Unreacted resin	MPA	Unreacted resin	MPA	Unreacted resin	FPA	Unreacted resin	FPA	Unreacted resin	FPA	Unreacted resin
East Java	43.6	23.6	55.8	33.5	42.3	1.1	24.3	40.1	29.3	36.0	37.3	35.8
Central Java	56.7	19.8	65.5	18.1	43.8	11.2	33.6	37.2	34.0	40.1	38.6	32.5
West Java	26.3	28.5	39.2	21.2	37.7	30.8	24.0	28.5	31.4	37.9	34.5	39.1

range of 42-56%. The highest proportion of this product was obtained at a molar ratio of 1:6.2 (55.8%). This study confirmed that using a molar ratio of 1:6.2 was best for making MPA as mentioned previously (Wiyono *et al.*, 2007b). In terms of the yield of the reaction product, this recent research almost tripled previous findings that were 8-20% (Nilsson *et al.*, 2002). Wiyono *et al.* (2007b) found 12-23%. The difference in the yield of MPA in this study was probably due to the use of a large amount of rosin (almost seventeen times higher amount used compared to earlier studies) in the making of MPA.

Besides using rosin from East Java, another source of rosin as a raw material for producing MPA is Central Java (Table 1). The result indicated that the increase in molar ratio from 1:5.2 to 1:7.2 with a similar reaction temperature a higher yield of endo-maleopimaric acid was first obtained. Then, with the increase in the molar ratio, the reaction product was decreased. The product was in a range of 43-66%. The highest proportion of this product was obtained at a molar ratio of 1:6.2 (65.5%). This study also confirmed that using a molar ratio of 1:6.2 was best for making MPA. Relating to the amount of the reaction product, this recent research provided more than three times that were obtained in a previous study (Nilsson *et al.*, 2002; Wiyono *et al.*, 2007b).

Another source of rosin as a raw material for producing MPA is that from West Java (Table 1). The result was similar to that above, where the increase in molar ratio from 1:5.2 to 1:7.2 initially increased the amount of reaction product and then decreased it. The product was in a range of 26-40%. The highest proportion of this product was obtained at a molar ratio of 1:6.2 (39.2%). Again, this study confirmed that a molar ratio of 1:6.2 produced the most MPA. Relating to the amount of the reaction product, this recent research provided more than three times previous amounts (Nilsson *et al.*, 2002; Wiyono *et al.*, 2007b).

The rosin from Central Java produced the best reaction product, MPA. At the best molar ratio, 1:6.2, the modification of rosin by heating with maleic anhydride for one hour 200°C produced the highest yield of MPA, around 66%. Second was the rosin from East Java, followed by the rosin from West java. If we looked at

the previous results, rosin from Central Java contained more resin acids (abietic, palustric and neoabietic acids) which could react with MA. Central Java rosin contained around 66% resin acids. Resin acids in East Java rosin were about 50%; while, West Java rosin had around 31% (Wiyono *et al.*, 2007b).

The result of the recent study in modifying rosin to FPA showed that for all sources of rosin (East, Central and West Java) the increase in molar ratio at a reaction temperature of 200°C for one hour gave an increase in yield of the reaction product, fumaropimaric acid (FPA). The reaction product was in a range of 24-39%. The highest yield of this product was not obtained at a molar ratio of 1:5.8 as we predicted from the equation. The best molar ratio to produce FPA should be found. In terms of the yield of the reaction product, this recent research gave more FPA than previous results (Wiyono *et al.*, 2007b). The difference in the yield of FPA was probably because the rosin still contained more resin acids (abietic, palustric and neoabietic acids) which could react with FA. This means that to obtain the highest yield of the reaction product of FPA, we need more FA.

MPA or FPA contained unreacted diterpene acids and the reacted form (Fig. 4, 5, Table 1). Unreacted diterpene acid contained pimaric acid, dehydroabietic acid (DHA), etc. As described earlier, Wiyono *et al.* (2007b), one compound is formed during the reaction, i.e., pimaric acid and the amount of one compound in the unreacted product, dehydroabietic acid (DHA), increases. Some resin acids were isomerized into pimaric acid during the process. Moreover, the increase in the concentration of DHA, which does not react with MA or FA, was due to the fact that abietic type resin acids easily isomerize upon the action of heat or mineral acids. Thermal isomerization of some resin acids is actually catalyzed by the carboxyl group (Takeda *et al.*, 1969). The heating of levopimaric acid yielded DHA, besides the abietic type isomers plus. These side reactions were found to be enhanced by trace amounts of oxygen. Furthermore, owing to oxidation, palustric acid was converted into DHA, while abietic and neoabietic acids were not (Enoki, 1976). All these factors led to the increase in the DHA concentration in the reaction product.

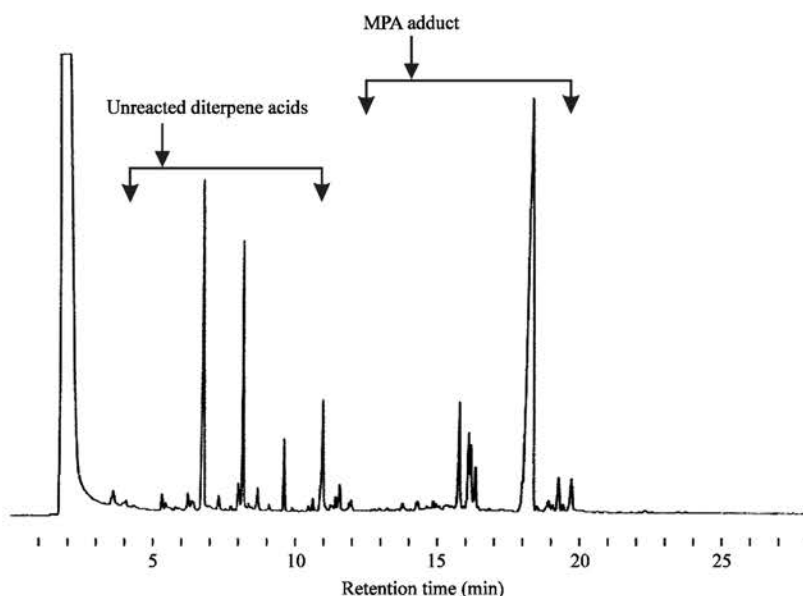


Fig. 4: An example of chromatograms of crude MPA

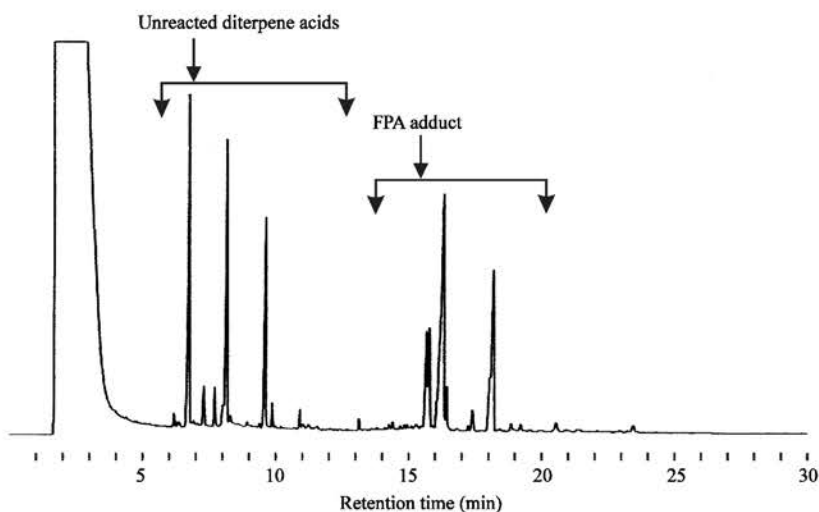


Fig. 5: An example of chromatograms of crude FPA

Fortified rosin size: Internal sizing is a process of providing paper and paperboard with resistance to liquid wetting, penetration and absorption by using a sizing agent during paper production (Zou *et al.*, 2005; Casey, 1981). The common objective of paper sizing is to inhibit aqueous liquid penetration to give the cellulose product some desirable end-use characteristics, such as control of water and ink penetration. The use of a sizing agents could contribute to the grade of paper produced (Casey, 1981). One of the most important sizing agents in use is rosin, used for internal and external sizing. The carboxyl group and the hydrophobic bulk of the chemical

compound in rosin play a critical role in sizing. It is considered that fortified rosin size is more efficient than unfortified rosin sizes, where a given sizing result can be obtained with less sizing agent. The economics offered to the paper maker by fortification are such that almost all the rosin size currently used is fortified form (Casey, 1981; Wang *et al.*, 1998).

In this investigation, maleopimaric acid and fumaropimaric acid obtained by reacting MA or FA with rosin were then saponified to make fortified rosin size. The results are shown in Table 2. Using rosin from East Java, the solid content of fortified rosin size was in a range of

Table 2: Maleo- and fumaro-pimaric rosin sizes properties at various molar ratios (rosin and MA or FA)

Region	Molar ratio	Properties					
		Solid content (%)	Total rosin (%)	Free alkali as NaOH (%)	Free rosin (%)	Volatile content (%)	pH
East Java	MPA						
	1:5.2	80.6	33.2	4.8	0	19.4	9-10
	1:6.2	81.0	34.6	4.9	0	19.1	9-10
	1:7.2	75.9	30.5	6.5	0	24.1	9-10
	FPA						
	1:4.8	74.3	39.8	5.3	0	25.7	9-10
Central Java	1:5.8	70.4	33.6	5.3	0	30.0	9-10
	1:6.8	69.4	33.5	4.7	0	30.6	9-10
	MPA						
	1:5.2	84.8	34.1	7.4	0	15.2	9-10
	1:6.2	83.9	34.4	5.0	0	16.1	9-10
	1:7.2	80.2	35.1	4.7	0	19.8	9-10
West Java	FPA						
	1:4.8	60.1	32.8	5.4	0	39.1	9-10
	1:5.8	62.3	34.6	5.8	0	37.7	9-10
	1:6.8	59.9	32.3	5.7	0	40.1	9-10
	MPA						
	1:5.2	77.3	37.4	4.5	0	22.7	9-10
Sizing made from commercial fortified rosin	1:6.2	71.3	34.4	4.7	0	28.7	9-10
	1:7.2	78.9	34.5	6.0	0	21.1	9-10
	FPA						
	1:4.8	66.7	37.4	5.0	0	33.3	9-10
	1:5.8	63.9	34.3	6.0	0	36.1	9-10
	1:6.8	69.9	38.9	4.2	0	30.1	9-10
		73.4	37.0	7.1	0	26.6	9-10

75-81% for maleopimaric rosin size (MPRS) and around 69-75% for fumaropimaric rosin size (FPRS)(Gafvert *et al.*, 1995). A solid content of around 50-80% is categorized as a paste fortified rosin size (TAPPI Standards). Based on solid content, there are three types of rosin size, i.e., dry rosin size with solid content at a maximum of 12%, emulsified rosin size and paste rosin size with a solid content 50-80%. So, the fortified rosin sizes that we made were categorized as paste rosin size. Further, using rosin from Central and West Java, it seems that the solid content of fortified rosin sizes was around 71-85% for MPRS and around 59-70% for FPRS. Moreover, among sources of rosin, MPRS made of rosin from Central Java was the highest, followed by MPRS from East Java, then from West Java. In addition, if we looked at the effect of molar ratio on the solid content of fortified rosin size, the molar ratio did not affect the solid content of fortified rosin size, as can be shown in Table 2. The solid content of fortified rosin size varied along with an increase in the molar ratio. Further, based on total solid of the sizing, these fortified sizes still met with the requirement of solid content for size being produced by New Tech-Polymer Ltd-India, which divide into two classes, minimal total solid at 50% and at 70% with a pH of around 9-12. Meanwhile, the pH of the fortified rosin sizes that we made was around 9-10, as can be seen in Table 2, which also met the standard requirement, including the Indonesian National Standard (1990).

Total rosin is the amount of rosin in fortified rosin size, both free and combined. In this research, total rosin was equal with combined rosin. During the analysis of free rosin, to the rosin solution was added the phenolphthalein indicator. If the solution turned red, it did not contain free rosin. This means that all rosin acids in the sizing have been saponified during the making of rosin sizes. Based on this property, the fortified rosin sizes that we made were in a good quality. The National Indonesian standard for rosin size gives a requirement of free rosin a maximum of 6%. Relating to the free alkali property, even though fortified rosins have been fully saponified, there was remaining alkali in the sizing in a range 4-6%. Moreover, the increase in a molar ratio, free alkali in the size was also varied. Among sources of rosin, free alkali in the rosin size made of West Java rosin was smaller than other sources of rosins (Central and East Java). Unfortunately, compared to the requirement of free alkali in the Indonesian National Standard, these sizings did not meet the requirement, a maximum of only 0.25%. Further, compared to the commercial fortified rosin size, a free alkali property of maleo- and fumaro-pimaric rosin sizes was still better as it indicated that their free alkali property was lower than that of the commercial one (Table 2).

Drawn back from the above discussion, identification of the Diels-Alder adduct of abietic acid and maleic anhydride using an DIEI (Mass spectrometry) revealed

that the reaction of abietic acid with maleic anhydride produced endo-maleopimaric acid methyl ester with endo-maleopimaric acid tri methyl ester, as indicated by a fragment ion at $m/z = 146$ with a molecular weight of 414 and fragment ions at $m/z = 121, 187, 316$ and 386 , which indicated an endo-maleopimaric acid methyl ester. A fragment ion at $m/z = 146$ with a molecular weight of 460 was also found in the spectrum, along with other fragment ions at $m/z = 400$ and 428 , which indicated endo-maleopimaric tri methyl ester. Using a large amount of rosin as a raw material to produce MPA, the equation $Y = -0.8475 X^2 + 10.448X - 9.7125$, at a reaction temperature of 200°C is still relevant as it denoted that a molar ratio of 1:6.2 (rosin and MA) is the best to produce MPA. However, the equation $Y = -0.46X^2 + 5.268X - 4.47$ did not apply for FPA. Using a large amount of rosin, the increase in molar ratio led to an increase in FPA products. In terms of free rosin and pH, the maleo- and fumaro-pimaric rosin sizes have met the requirement of the Indonesian national standards for paste rosin size. In terms of the free alkali property, the size of made maleo- and fumaro-pimaric rosin sizes was better compared to the free alkali of the commercial form.

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