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A Study of Thermal Behaviour and Functional Group Exist in the New Formulation of Natural Organic Surface Finish Based on Natural Rubber (SMR L) for PCB Coating

[1]Ainmardiana A. Basri, [1]Athirah Eleyas, [1]Sharifah Shahnaz Syed Bakar, [1]Norainiza Saud, [1]Mohd Salleh M.A.A., [2]Mustafa Albakri

[1]School of Materials Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, 02600 Arau, Perlis, Malaysia
[2]Center of Excellence Geopolymer & Green Technology (CEGeoTech), School of Material Engineering, Universiti Malaysia Perlis (UniMAP), P.O. Box 77, D/A Pejabat Pos Besar, Kangar,Perlis 01000, Malaysia

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ABSTRACT

The presence of functional groups and thermal properties of Natural Rubber (SMRL) and its formulations, NOSF1 and NOSF2 were investigated as a function of different composition of the active ingredient of phenylimidizole. The reaction of Natural Rubber (SMRL) with composition of Organic Solderability Preservatives (OSP) has been investigated with the transmission FTIR spectroscopy. The highest peak detected for NOSF1was 728.06cm^{-1} and NOSF2 was 727.96cm^{-1} represent the existing of functional group of aromatic functional group with C-H bond. The difference of the NOSF1 compared to the NOSF2 was the existence of the peak at absorbance 2919cm^{-1} assignment the alkanes functional group with C-H stretch. Thermogravimetric analysis plot confirms the better thermal stability for NOSF1 and NOSF2 as well when mixed with the OSP ingredient with different composition. The Natural Rubber (SMRL) shows the decomposition temperature around 345^{o}C. The NOSF1 which consists of phenylimidizole shows the decomposition temperature approximately around 300^{o}C while the NOSF2 without the phenylimidizole shows the decomposition temperature around 350^{o}C which is slightly lower compared to the last generation of the active ingredient Aryl Phenylimidazole that decomposed at 354.7^{o}C.

Keywords: PCB, surface finish, natural rubber, TGA, FTIR

INTRODUCTION

All the Printed Circuit Boards (PCB) have copper finishes on their surface. The copper is easy to oxidise and deteriorate if left unprotected. The PCBs need surface finish to protect the copper on the surface. Apart from functioning as protect the copper finish from oxidation; it also must meet functional criteria such as solderability, environmental, electrical, and physical and durability demands. In July 2006, the Restriction of Hazardous Substances (RoHS) stated that all the PCB assembly need to eliminate all lead from technology process make the PCB industry adopted lead free solder [7]. In addition, this trend will cause the current surface finish cannot withstand modern environmental element which can lead to the corrosion failures and end up with solderability issues. Besides that, the assembly nowadays had to have final finished quality that has ability to be used with the development of lead free solder.

The only organic coating adopted by the PCB assembly is Organic Solderability Preservative (OSP) which consists of azole group as the active ingredient to create a bonding between the Cu on the copper pad which can protect the copper. Besides that, the OSP itself will prevent the oxygen and humidity which can affect the solderability issue [2]. In order to formulate the new formulation of surface finish, certain component need to be add such as vehicles, activators, surfactant, solvent and also thickening agent to ensure that the formulation fully function . The example of the activator which is the most important in the order to protect PCB from oxidation is carboxylic acid such as acetic acid. The ingredient of the ordinary OSP formulation consist of 89.05, 0.6, 10, 0.15 and 0.2 (%w/w) for water, phenylimidazole, acetic acid, chloride copper and zinc acetate respectively [1].

The Fourier Transform Infrared Spectroscopy (FTIR) is done to detect various functional groups available in the formulation or material. The basic principle of this FTIR method analysis is certain material will absorb infrared light at different frequency which can produce a unique "spectral pattern" based on the frequency of the material absorbs infrared light and the intensity of the absorption. The functional group of the Natural Rubber (SMRL) consist of natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene). Natural

Corresponding Author: Ainmardiana A. Basri, School of Materials Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, 02600 Arau, Perlis, Malaysia.
Ph: +04-979 8154. E-mail: ainmardiana89@gmail.com

rubber has the cis configuration for the methyl groups.

The thermal behaviour of the surface finish itself plays important role in overall process. Thermal behaviour of the natural organic surface finish formulation was studied by using the Thermogravimetric Analysis (TGA Pyris 1 TGA). The basic principle of the TGA analysis is to determine the changes in the weight to a temperature program in a controlled atmosphere. The degradation of the SMRL starts at the earlier temperature of 296^{o}C [4]. The current OSP adapted by PCB industry show the evolution of the decomposition temperature range from 250^{o}C up to 354.7^{o}C [2]. The decomposition temperature of the material used in the surface finish formulation must be in accordance with range of the peak temperature of reflow for typical lead free soldering process [2].

The investigation reported in this article focused on the formulated of the surface finish namely NOSF1, of which the formulation is filled with the active ingredient from the OSP while NOSF2 is formulated without it. The functional group and thermal analysis of the NOSF1 and NOSF2 were studied. Analysis of the functional group exist were carried out to determine the bond exist on the formulation itself while decomposition temperature of the NOSF1 and NOSF2 formulation were analyze to determine whether it is suitable for lead free solder processing.

Experimental:

Preparation of the formulation of NOSF 1 and NOSF 2:

The ingredient compositions of the ordinary OSP were weight and mixed using the magnetic stirrer for 2 hours. 5 g of SMR L were dissolved with the 30ml of toluene to break the bond. The mixture of the OSP and SMR L were mixed with the magnetic stirrer for about 2 hours at room temperature on sealed beaker. The only difference between NOSF1 and NOSF2 was the existing of the active ingredient which is phenylimidazole. Table 1 shows the compositions of NOSF1 and NOSF2 surface finish based on SMRL formulation.

Table 1: Composition of the NOSF1 and NOSF2 surface finish based on Natural Rubber (SMR L) formulation.

NOSF 1	NOSF 2
5g (SMR L)	5g (SMR L)
100ml toluene	100ml toluene
10.00ml acetic acid	10ml acetic acid
0.2g zinc acetate	0.2g zinc acetate
0.15g chloride copper	0.15g chloride copper
0.6g phenylimidazole	0.0g phenylimidazole

Functional group in the formulation of NOSF1 and NOSF2:

The sample preparation for Fourier Transform Infrared Spectroscopy (FTIR) was done according to ASTM E168E1252. The FTIR was set in the region between 400 until 4000cm with a resolution of 2cm^{-1}. 0.3 g of NOSF 1 in liquid form was put on the ATR crystal. Then the sample was excited by using 785nm diode laser. After that, spectral pattern image was performed on the computer screen. Spectral pattern image was analyzed and interpreted. The step was repeated for NOSF 2 sample which also in the liquid form.

Thermal analysis of the formulation of NOSF1 and NOSF2:

Sample preparation of NOSF 1 and NOSF 2 undergo Thermogravimetric analysis is done according to the ASTM E1131, ISO 11358. The SMR L was weighted for about 10miligrams. The TGA machine was set to the inert (N2) and oxidative (O_2) gas flow rates. 10miligrams of the NOSF1 placed in the specimen holder and the furnace was raise. The initial weight reading was set to 100% followed by the initiating heating program. For TGA analysis, the scan temperature set from 30° to 600°C and the heating rate of 20°C /min. These steps ware repeated for NOSF 2.

Results and Discussion

Functional group of NOSF1 and NOSF2:

Figure 1 shows the infrared spectra for the SMRL sample. The highest intensity functional group of the pure SMRL was detected at 2339cm^{-1} presented as aldehydes in H–C=O: C–H stretch bond. The formulation of NOSF 1 consists of the active ingredient of phenylimidizole. In the C-H "oop" stretch region, the highest functional group of the NOSF1 detected at 728.06cm^{-1} presented as aromatic compound similarly to the NOSF2 formulation detected amount at 727.96cm^{-1}. There were a lot of changes of the functional group detected between SMRL and its formulations, while only slight differences were observed of the infrared spectra for NOSF1 and NOSF2.

The spectrum of NOSF1 shown in Figure 2 displays the peak at 3026.3cm^{-1} attributed to the present of carboxylic groups corresponds to the O-H stretch. Frequency observed at 2919cm^{-1} attributes to the C-H stretch alkanes vibration. The peak absorption at 1713.41cm^{-1} shows the C=O bond with carboxylic acid group. The absorption peaks observed at 1611.8cm^{-1} correspond to the 1* amines group with N-H bend. The other peak at 1454 cm^{-1} consists of alkanes with C-C stretch bond represent aromatic functional group. The peak displays for aliphatic amines group detected at wavelength

1034.1 cm^{-1} with C-N stretch. The other peak at 1034.2cm^{-1} consists of aliphatic amines with C-N stretch bond. The peak displays for aromatic group detected at wavelength 694.17cm^{-1} and 727.96cm^{-1}. The spectrum of NOSF2 displays the peak at 3023.3cm^{-1} attributed to the present of carboxylic acid groups corresponds to the O-H stretch (Figure 3). Frequency observed at 1713.51cm^{-1} with assignment of C=O stretch represent of carboxylic acid. The wavelength detected at 1600cm^{-1} represent the 1*amines group with N-H bend and 1495.58 cm^{-1} attributes to the C-C stretch (in ring) aromatic vibration. The absorption peaks observed at 1460 cm^{-1} correspond to the aromatic group with C-C bend. The alkyl halides detected at peak 1292.52 cm^{-1} with C-H wag (-CH_2X). The other peak at 1034.2cm^{-1} consists of aliphatic amines with C-N stretch bond. The peak displays for aromatic group detected at wavelength 694.17cm^{-1} and 727.96cm^{-1}. The only different between NOSF1 and NOSF2 was the detection of alkanes group at spectrum length 2919cm^{-1} detected at NOSF1.

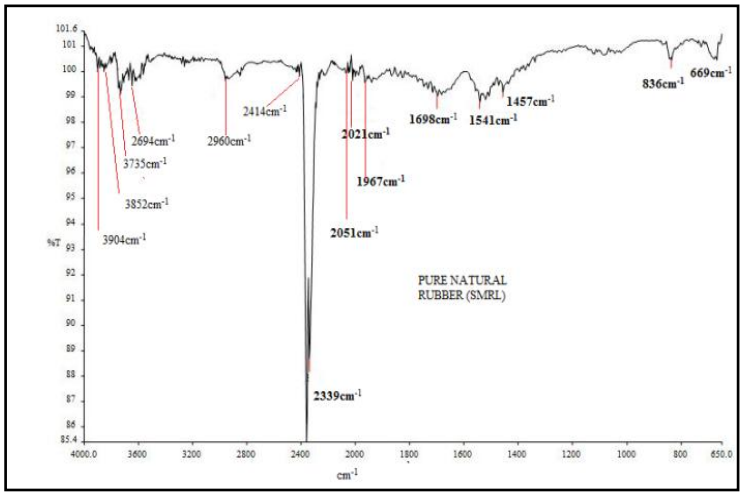

Table 2: FTIR spectrum for SMRL.

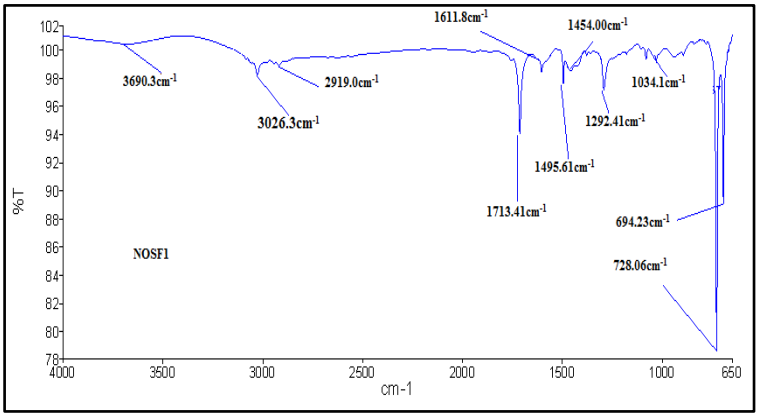

Table 3: FTIR spectrum for NOSF1.

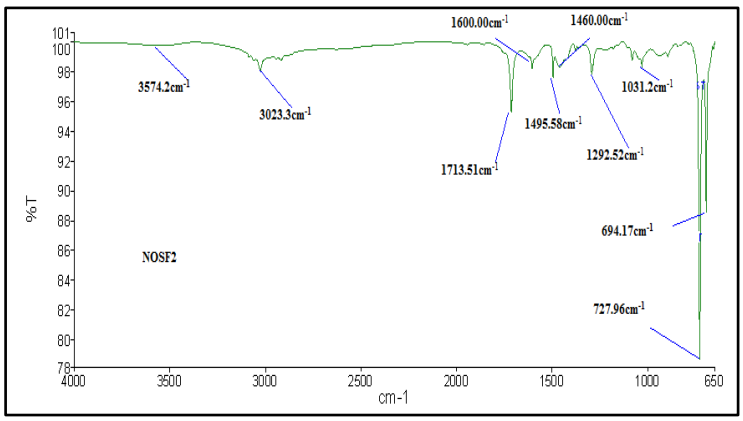

Table 3: FTIR spectrum for NOSF2.

Table 2: Characteristic bands of the infrared spectra NOSF1 and NOSF2.

NOSF1	Assignment	NOSF2	Assignment
3026.3	O-H stretch carboxylic acid	3023.3	O-H stretch carboxylic acid
2919	C-H stretch alkanes	1713.51	C=O stretch carboxylic acid
1713.41	C=O stretch carboxylic acids	1600	N-H bend 1* amines
1611.8	N-H bend 1* amines	1495.58	C-C stretch(in ring) aromatic
1495.61	C-C stretch(in ring) aromatic	1460	C-C stretch(in ring) aromatic
1454	C-C stretch(in ring) aromatic	1292.52	C-H wag(-CH2X) alkyl halides
1292.41	C-H wag(-CH2X) alkyl halides	1034.2	C-N stretch aliphatic amines
1034.1	C-N stretch aliphatic amines	727.96	C-H"oop" aromatics
728.06	C-H"oop" aromatics	694.17	C-H"oop" aromatics
694.23	C-H"oop" aromatics		

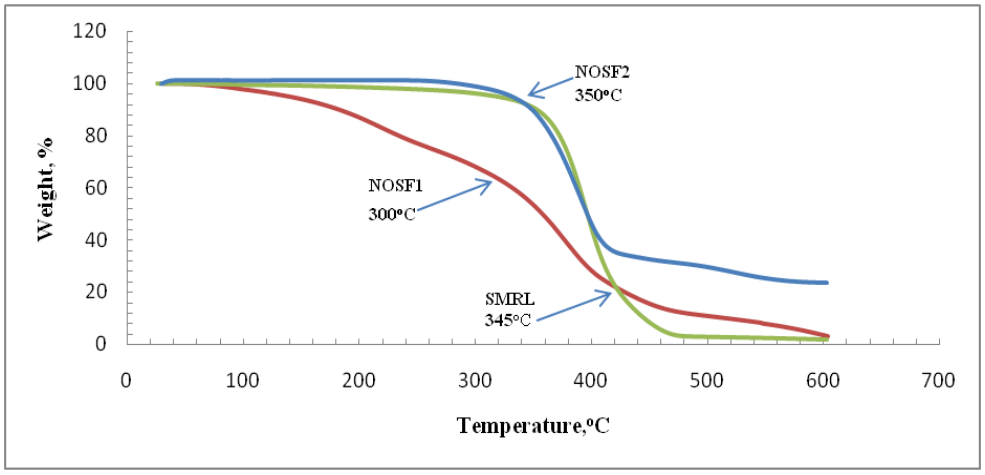

Table 3: Thermal decomposition temperature of pure Natural Rubber (SMRL), NOSF1 and NOSF2 formulation.

Thermal analysis of NOSF1 and NOSF2:

The thermal behaviour of the NOSF1 and NOSF 2 at heating rate of 20°C /min and scan temperature between 30-600°C is shown in Figure 5 as TGA plot. The decomposition temperature for SMRL is approximately 345°C. The decomposition temperature that results from the formulation of NOSF 1 and NOSF2 observed by significant weight loss were approximately started from 300°C and 350°C respectively, which indicates that the formulation have good thermal stability and able to stand temperature on the reflow soldering process. Other study showed the degradation of the natural rubber starts at earlier temperature of 296°C [4]. The formulations had a first weight loss at 100°C for NOSF1 and 150°C for NOSF2. The graph shows complete loss of weight at 604°C for NOSF1 and 602.7°C for NOSF 2. It can be seen from the graph that the slope values of the NOSF2 is much lower than NOSF1.

The examples of the lead free solder used by the PCB assembly industry such as Sn/Ag/Cu have the melting point range from 220 to 240°C. The evolution of the azole group from standard azole to alkyl benzimidazole and the latest generation of the Organic Solderability Preservative (OSP) is aryl-phenylimidazole also shows that the increasing of thermal stability and it can withstand the peak temperature of reflow for typical lead free soldering process which is 250°C. Second generation of alkyl benzimidazole starts to decompose at 250°C. The latest azole group which is aryl-phenylimizole shows much higher decomposition temperature up to around 350°C.

The formulation of the standard M-Coat select HT acetic acid based bath containing pure benzimidazole (BZIM) which the metal is not a copper and consists of organic additives shows the decomposition temperature completed around 221°C at heating rate 10°C/ min, which liquefied on surface before the peak temperature of 265°C [6]. Due to the addition of the acetic acid and organic additives on the BZIM which cause the melting point was much lower than 221°C. The studies also investigate the

decomposition temperature of the BZIM with and without metal compound. As the BZIM with metal compound such as Cu, Fe and ZN the decomposition temperature range was observed at the range of 220°C to 320°C similarly to pure BZIM [6]. For the second BZIM with another metal weight losses shifted about 50^{o}C to the higher temperature around 275-375^{o}C. The addition of the metal compound will delay the volatilisation [6].

4. Conclusion:

A new formulation of surface finish for PCB industry based on SMR L which enhanced in thermal behaviour was successful formulates. Based on the result obtained, the following conclusion can be drawn

1. The FTIR analysis reveals the various functional groups present in NOSF1 and NOSF2 shows that the reaction occurred between pure Natural Rubber (SMRL) with the Organic Solderability Preservative (OSP).
2. The formulation of the ordinary OSP with SMRL with and without active ingredient showed the shifting decomposition temperature from 300°C to 350^{o}C which indicates the enhancement in thermal stability and it can be used in the temperature range for lead free soldering process.
3. The addition of the active ingredient phenylimidazole will change the decomposition temperature of the pure Natural Rubber (SMRL).

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