

CHAPTER IV

RESULTS AND DISCUSSION

In this study, the temporary solder masks were prepared from vinylic-compound using the radical polymerization of concentrated vinyl monomer. The property was adjusted by additives, for example, the viscosity was adjusted by a thickening agent.

The goals of this research were to obtain the appropriate condition for the preparation of the temporary solder mask by varying the concentration of vinyl monomer, initiator, releasing agent, pigment, and thickening agents which have sufficiently cured cohesive strength for substantially all of the cured materials to be peeled off in one piece. Secondly, the physical and mechanical properties of the solder masks would be investigated.

4.1 Preparation of the temporary solder mask

The temporary solder masks of this study were prepared from the thermal polymerization of vinyl monomer which was carried out in order to evaluate the effect of temperature vinyl monomer, initiator, polymer, thickening agent, releasing agent, inhibitor, pigment, ammonium hydroxide concentrations. The N-vinyl

(NVP) and hydroxypropyl methacrylate (HPMA) were polymerized by radical initiator (2,2'-azo-(bis)-isobutyronitrile (AIBN)), *in situ*. The physical properties of film were adjusted by thickening agent (carbopol T-45), pigment (TiO₂), polymer (acrylic polymer UT-50) and releasing agent (silicone oil 350s).

4.2 The properties of commercial temporary solder mask

The purpose of this investigation is to measure the mechanical and physical properties of commercial temporary solder mask. They will be used as a guideline in the development of the temporary solder mask in this study.

Table 4.1 The properties of commercial temporary solder mask

Property Product	Viscosity (cps.)	Tensile Strength (Mpa)	%Elongation	Hardness (shore A)	Thermal Resistance (°C)	Price/ 1 L (\$)
A*	40,000	28	>20	-	345	85.50
B*	90,000	3	≈ 25	75	268	47.50
C*	10,000	1	≈ 30	65	265	38.75

* remark : A, B and C are solder masks currently available in the market.

Preparation of the temporary solder mask A

4.3 The effect of NVP:HPMA monomer concentration

The effect of NVP:HPMA ratio was studied by varying the concentrations of 80:20, 70:30, 60:40, 50:50, 40:60, 30:70 and 20:80 phr. The thermal initiating system was used in this experiment. The details are shown in appendix A and Figure 4.1.

The parameters of thermal polymerization were obtained as follows:

- Initiator (AIBN) : 0.3 phr
- Inhibitor (hydroquinone) : 1 phr
- Reaction temperature : 100 °C
- Reaction time : 15 min.

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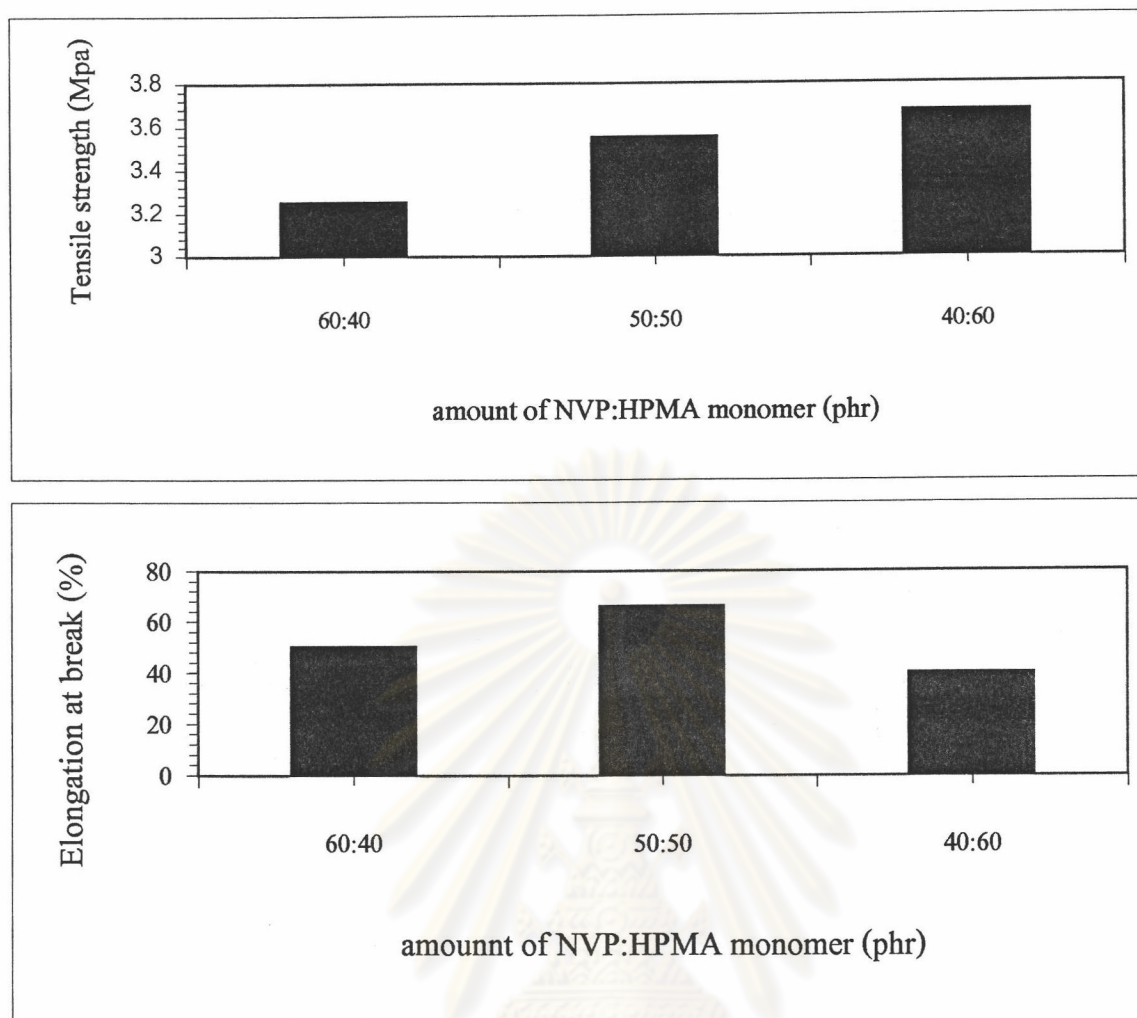


Figure 4.1 The effect of NVP:HPMA ratio on the physical properties of solder mask A

In this study, the effect of NVP: HPMA content on tensile properties of the temporary solder mask is shown in Figure 4.1. The tensile strength increases with increasing of HPMA contents. It can be seen that the HPMA is a naturally rigid, glassy thermoplastic; therefore the HPMA composite improves the tensile strength of this product. However, the %elongation at break is too low, thus make it broken easily.

The NVP:HPMA monomer concentrations as high as 80:20 and 70:30 phr can not be tested because it causes cracking and unpeelable. The concentrations at 30:70 and 20:80 make the solder mask look like adhesives. This study chooses the ratio of NVP:HPMA at 50:50 because it gives workable solder mask.

4.4 The effect of acrylic polymer

The effect of acrylic polymer was studied by varying the amount at 80, 100, 120, and 140 phr. This experiment used UT-50 acrylic polymer with the glass transition temperature at 7 °C. This acrylic polymer affected on the flexibility of temporary solder mask. The details are shown in appendix A and Figure 4.2.

The parameters for thermal polymerization were obtained as follows:

- NVP: HPMA monomer : 50:50 phr
- Initiator (AIBN) : 0.3 phr
- Inhibitor (hydroquinone) : 1 phr
- Reaction temperature : 100 °C
- Reaction time : 15 min.

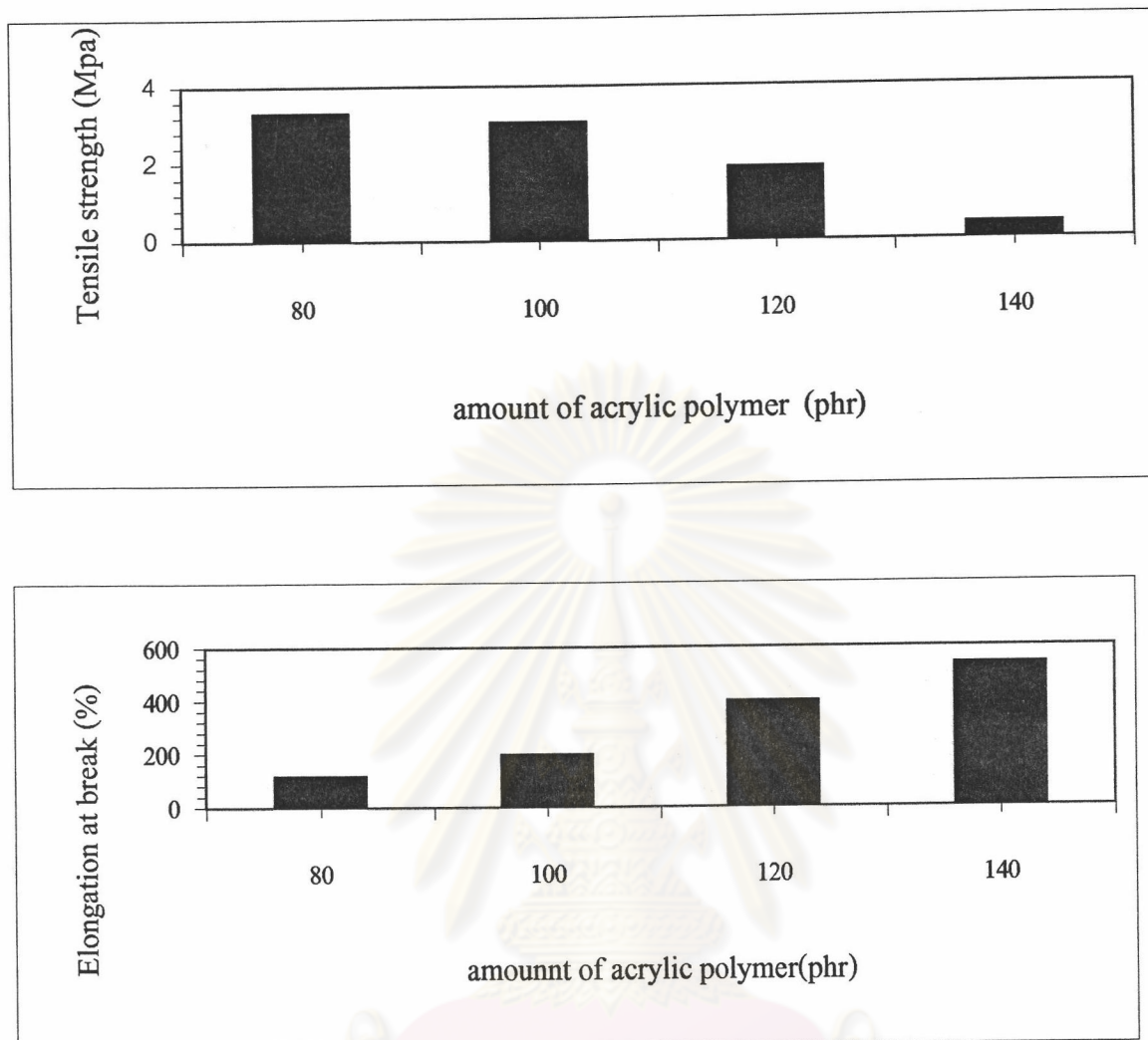


Figure 4.2 The effect of UT-50 acrylic polymer on physical properties of solder mask A

In this study, the effect of UT-50 acrylic polymer on tensile properties of the temporary solder mask is shown in Figure 4.1. The tensile strength decreases with increasing of UT-50 acrylic polymer contents. Since the UT-50 Acrylic polymer is flexible and has more elasticity than HPMA and NVP, thus resulted in an increased number of %elongation at break. Therefore, the UT-50 acrylic polymer improves the elastic property of this product.

The suitable flexibility occurred when 100 phr of UT-50 acrylic polymer was used. The 120 and 140 phr of UT-50 acrylic polymer have more flexibility than that of 100 phr of UT-50 acrylic polymer but are not tensile resistance. The film were broken when they were removed.

The physical properties of solder mask A at various NVP:HPMA ratios were not significant different but at the 60:50 ratio of NVP: HPMA the mask is easily peelable. Therefore, this formula is chosen and the appropriate amount is calculated as the following :

$$\begin{aligned}
 \text{NVP} &= \frac{\text{the used amount NVP}}{\text{total ingredient (NVP+HPMA+UT-50)}} \\
 &= \frac{60}{210} = 28.57 \text{ part} \\
 \text{HPMA} &= 23.81 \text{ part} \\
 \text{UT-50 acrylic polymer} &= 47.62 \text{ part}
 \end{aligned}$$

4.5 The effect of releasing agent

The effect of the amount of releasing agent was studied by varying the amount to 2, 5, 10, and 15 phr.. The releasing agent is 350s silicone oil, which is non-toxic and thermal resistance. This amount of releasing agent caused some affected on the peelable of temporary solder mask. The details are shown in Figure 4.3.

The parameters of thermal polymerization were obtained as follows:

- NVP monomer : 28.57 phr
- HPMA monomer : 23.81 phr
- Acrylic polymer (UT-45) : 47.62 phr
- Initiator (AIBN) : 0.3 phr
- Inhibitor (hydroquinone) : 1 phr

- Reaction temperature : 100 °C
- Reaction time : 15 min.

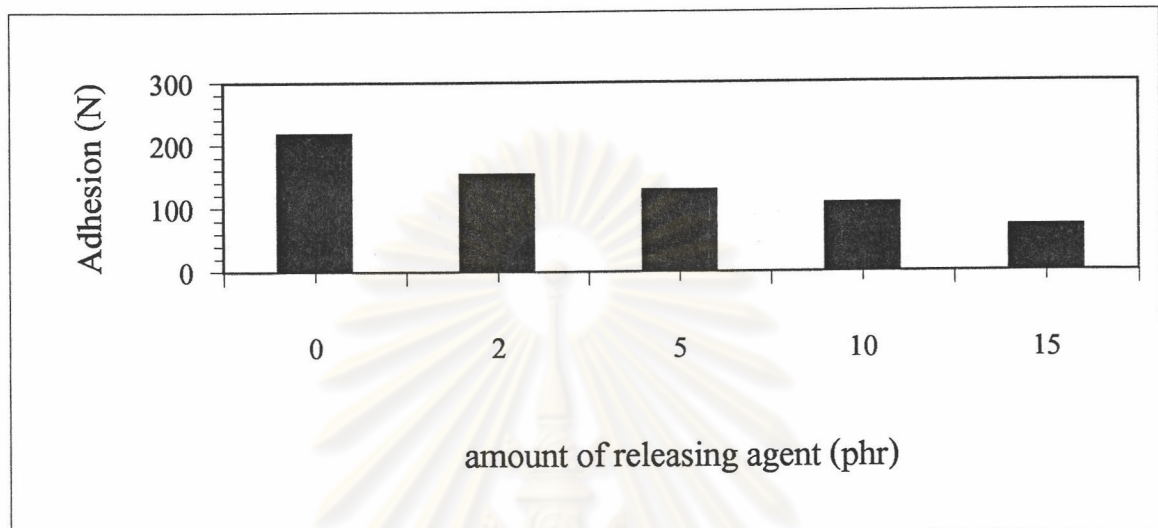


Figure 4.3 The effect of releasing agent on the adhesion of solder mask A

From Figure 4.3, the amount of releasing agent could decrease adhesion of the temporary solder mask. At higher amount of releasing agent, it is easier to peel off than at lower amount of releasing agent because releasing agent helps to decrease adhesion between surfaces of the temporary solder mask with material's surface.

As can be seen in Figure 4.3 the temporary solder mask can be removed easily when the amounts of releasing agent was increased. However, the increasing amount of releasing agent prolonged drying time, therefore the appropriate amount of releasing agent at 5 phr was selected.

4.6 The effect of thickening agent

The effect of the amount of thickening agent was studied by varying the amount to 2, 5, 10, 15, 20, and 25 phr. The thickening agent is T-45 acrylic polymer. The viscosity is measured at 10-rpm machine rate and spin No. 4. The amount of thickening agent affects on the viscosity of temporary solder mask. The details are shown in Appendix A and Figure 4.4.

The parameters of thermal polymerization were obtained as follows:

- NVP monomer : 28.57 phr
- HPMA monomer : 23.81 phr
- Acrylic polymer (UT-45) : 47.62 phr
- Ammonium hydroxide : 1 %wt of thickening agent
- Releasing agent : 5 phr.
- Initiator (AIBN) : 0.3 phr
- Inhibitor (hydroquinone) : 1 phr
- Reaction temperature : 100 °C
- Reaction time : 15 min.

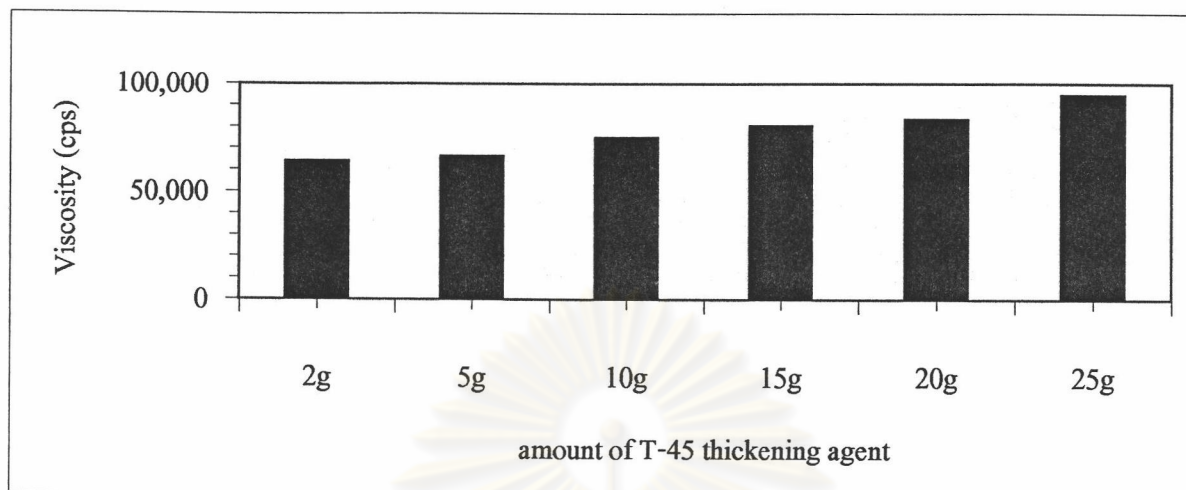


Figure 4.4 The effect of T-45 on the viscosity of temporary solder mask A

From Figure 4.4, thickening agent influences the viscosity of temporary solder masks. When the thickening agent increases, the viscosity increases.

The viscosity of solder masks increases with the increasing amount of T-45. If the viscosity was too low, thus the control of flow became difficult. The appropriate amount of the thickener used was 5-10 g, preferably 5 g per 100 g of the NVP monomer, HPMA monomer and acrylic polymer. If the viscosity is too low or too high, the coating workability are inferior. The appropriate amount of the thickener used in this study is 5 phr.

4.7 The effect of pigment (Titanium dioxide)

The effect of the amount of titanium dioxide was studied by varying the amount to 1, 2, 3, and 4 phr. The amount of titanium dioxide affected on the optical and physical properties of temporary solder mask. The details are shown in Appendix A and Figure 4.5.

The parameters for thermal polymerization were obtained as follows:

- NVP monomer : 28.57 phr
- HPMA monomer : 23.81 phr
- Acrylic polymer (UT-45) : 47.62 phr
- Ammonium hydroxide : 1 %wt of thickening agent
- Releasing agent : 5 phr
- Thickening agent (T-45) : 5 phr
- Initiator (AIBN) : 0.3 phr
- Inhibitor (hydroquinone) : 1 phr
- Reaction temperature : 100 °C
- Reaction time : 15 min.

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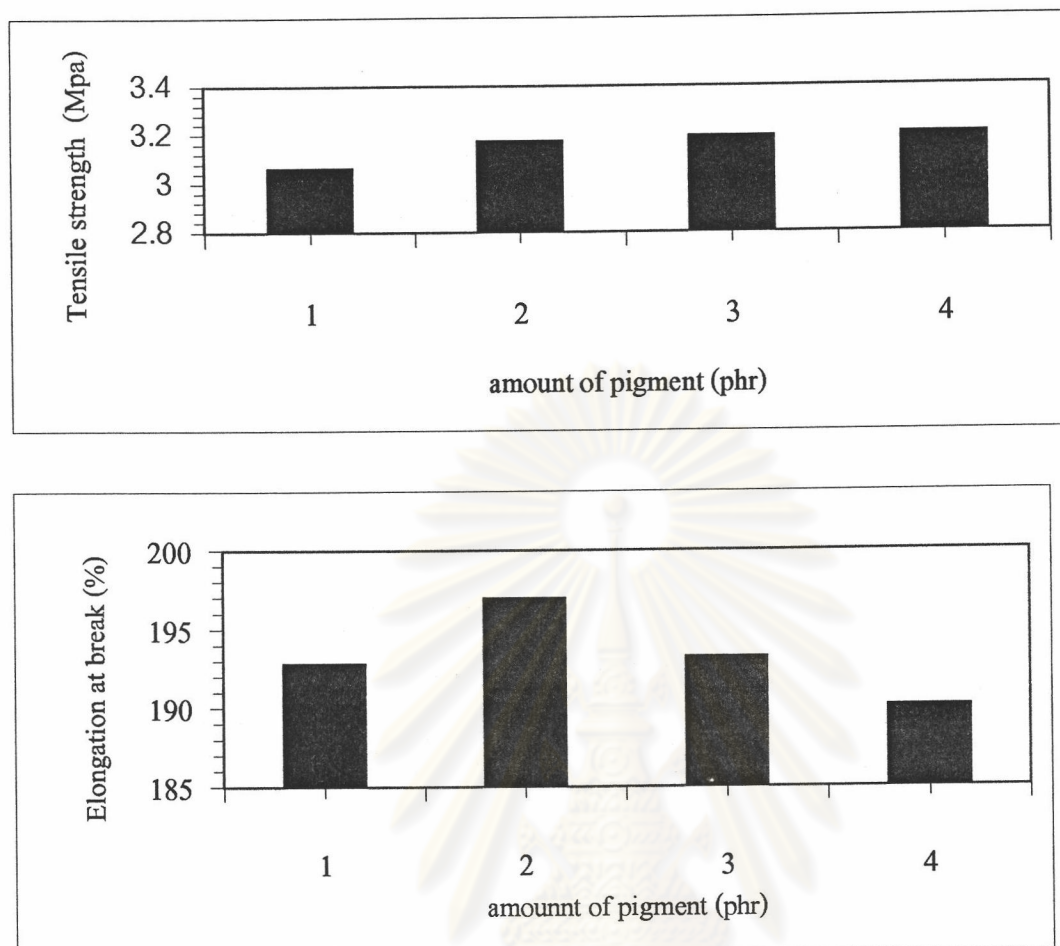


Figure 4.5 The effect of titanium dioxide on the physical properties of solder mask A

From Figure 4.5, the increase in titanium dioxide content decreased the %elongation at break of the temporary solder mask. It is generally acceptable that the titanium dioxide content increases, more titanium dioxide inserts in the monomer phase, which resulted in the decrease of the %elongation at break.

The tensile strength and % elongation of temporary solder mask under various phr of pigment seem to be different. At 2 phr of pigment the temporary solder mask become opaque and pigment was used on the basis of cost saving.

4.8 The characterization of the surface of temporary solder mask by

Scanning Electron Microscopy (SEM)

The scanning electron microscope was employed to investigate the smooth surface and phase distribution of specimen. In Figures D.1, D.2, D.3, D.4 and D.5 at appendix D, the phase distribution of various formula are shown in Table 4.2 .

At 1,500 x magnification, the SEM electron micrographs of the surface and distribution of the components of temporary solder mask can be seen.

Table 4.2 The formulation of temporary solder mask used in SEM study

Chemicals No.	NVP:HPMA (phr)	Acrylic Polymer (UT- 50)(phr)	Thickening Agent %wt	Releasing Agent %wt	Titanium Dioxide %wt
1	25:25	50	5	5	2
2	30:20	50	5	5	2
3	35:15	50	5	5	2
4	25:25	50	5	10	2
5	25:25	50	5	5	4

From the scanning electron microscope, the cracking is evidence from the increasing of NVP (fig. D.1, D.2 and D.3) which is glassy thermoplastic ($T_g = 175^\circ\text{C}$) and it increases the glass condition of this product. Figure 4.9 shows that the high level of releasing agent will give oil droplet on the surface of temporary solder mask. In Figure 4.10, the 4 % phr of titanium dioxide will cause poor dispersion and rough surface due to insoluble pigment. These information from SEM helps to confirm the result in choosing the appropriate ratio of the temporary solder mask.

Preparation of the temporary solder mask B

4.9 The effect of poly(vinyl alcohol) on physical properties of solder mask B

The effect of the amount of PVA(GH-17):PVA(GL-05) was studied by varying the amount to 5:5, 5:10, 5:15, 5:20, 10:5, 15:5 and 20:5 phr. This poly(vinyl alcohol) polymer improve on the flexibility and film formation of temporary solder mask. The details are shown in Figure 4.6.

The parameters of thermal polymerization were obtained as follows:

- Water (deionized) : balanced
- Reaction temperature : 100°C
- Reaction time : 15 min.

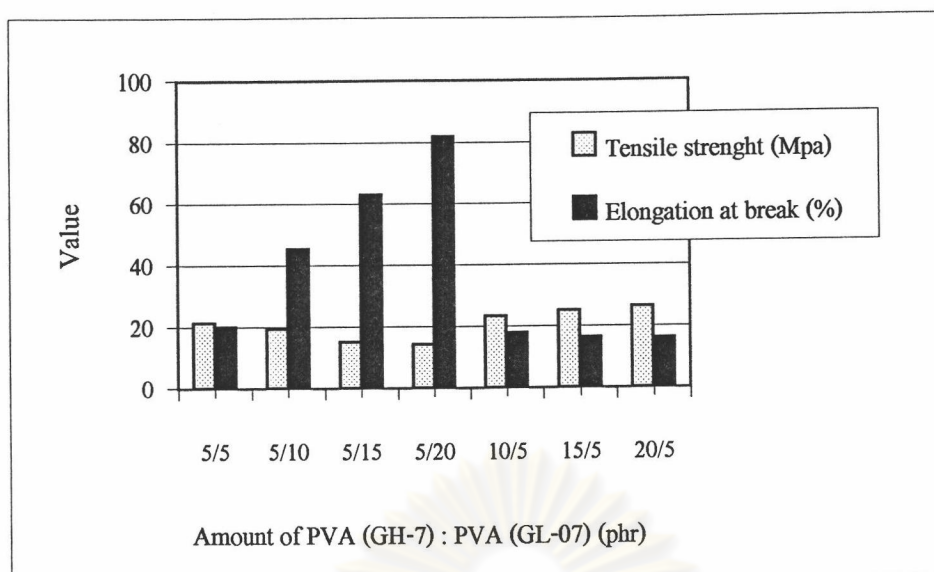


Figure 4.6 The effect of poly(vinyl alcohol)

In this study, the increasing of PVA (GH-17) content increased tensile properties of the temporary solder mask but the elongation at break decreased. It can be seen from figure 4.6 that the suitable flexible occurred when 5:10 phr of PVA (GH-17): PVA(GL-05) was used. It has the average value (tensile strength and elongation at break %) between 5:5 to 20:5 g and has the elongation at break, which is more suitable than at 5:5 phr.

4.10 The effect of reactive monomer

The effect of the amount of HPMA: NVP monomer was studied by varying the amount to 1:1, 1:2, 1:3, 2:2, 2:1 and 3:1 phr. This HPMA: NVP monomer improved the flexibility and tensile strength of temporary solder mask. The details are shown in Figure 4.7.

The parameters of thermal polymerization were obtained as follows:

- Water (deionized) : balanced
- PVA(GH-17):PVA(GL-05) : 10:5 phr
- Reaction temperature : 100 °C
- Reaction time : 15 min.

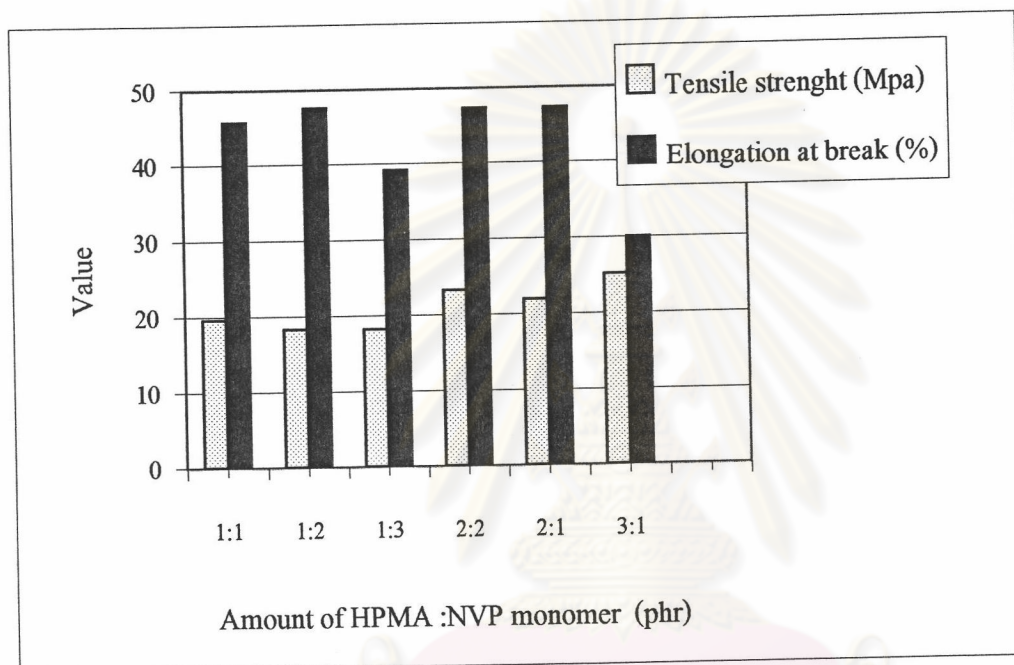


Figure 4.7 The effect of HPMA: NVP monomer

In this study, the increasing of HPMA content has a tendency to increase the properties of the temporary solder mask but the elongation at break is decreased. When consider the fix amount of NVP, the tensile strength is increased and specificity at different of HPMA: NVP between 1:1 with 3:1 can be seen clearly. The suitable value is 2:2 of HPMA: NVP monomer. Although 3:1 of HPMA: NVP has tensile

strength value more than but it occurred separation of composition phase. The obtain composition is not stable at long time.

4.11 The effect of xanthan gum

The effect of the amount of xanthan gum was studied by varying the amount to 0.1, 0.2, 0.3, 0.4 and 0.5 phr. This xanthan gum adjusted the viscosity and made the temporary solder mask easy to use. The condition in measuring is spindle No.2 and spin rate at 6 rpm. The details are shown in Figure 4.8.

The parameters of thermal polymerization were obtained as follows:

- Water (deionized) : balanced
- PVA (GH-17): PVA (GL-05) : 10:5 phr
- NVP: HPMA monomer : 2:2 phr
- Reaction temperature : 100 °C
- Reaction time : 15 min

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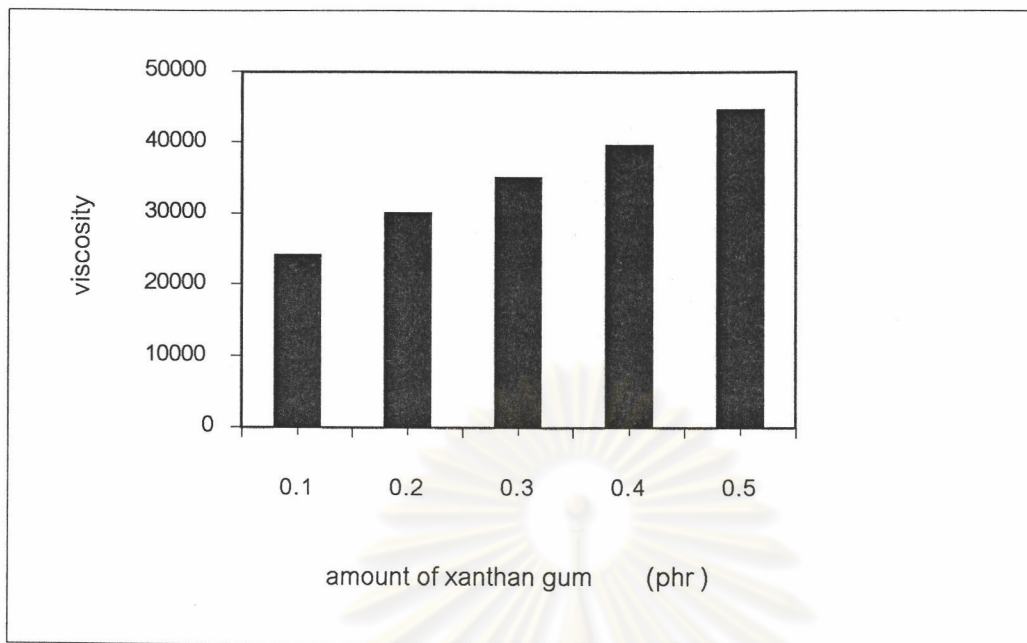


Figure 4.8 The effect of the amount of xanthan gum on the viscosity of temporary solder mask

From Figure 4.8, the viscosity of solder masks increased with the increasing amount of xanthan gum. If the viscosity was too low; thus, the control of flow became difficult. The appropriate amount of the thickener used was 0.2-0.5 phr or more, but in this research 0.2 phr of xanthan gum was chosen.

4.12 The effect of PEG-150

The effect of PEG-150 was studied by varying the amount at 0.1, 0.2, 0.3, 0.4 and 0.5 %wt. This PEG-150 prevented the texture of temporary solder mask from breaking apart. The parameters for thermal polymerization were obtained as follows:

Note that methylparaben was used to prevent fungi in this formulation.

- Water (deionized) : balanced
- PVA (GH-17): PVA (GL-05) : 10:5 phr
- NVP: HPMA monomer : 2:2 phr
- Xanthum gum : 0.2 phr
- Reaction temperature : 100°C
- Reaction time : 15 min

4.13 Thermal properties of solder mask

In this study, a Thermogravimetric Analyzer (TGA) was used to obtain the degradation temperature. The TG/DTG thermogram of temporary solder mask that was prepared from suitable formulae of temporary solder mask is shown in Appendix C. TG/DTG curves showed a continuous weight loss over 0-900° C temperature ranges. The TGA measurements showed that the degradation temperature of temporary solder mask A was 382.00°C and temporary solder mask B was 317.8 °C.

The liquidus and minimum reflow temperature of some common solders are shown in table 4.3. From this table, it could be concluded that both temporary solder mask A and B can with stand the temperature in normal solder bath quite well.

Table 4.3 Liquidus and minimum reflow temperature for some common solders

Solder	Liquid's temperature	Minimum reflow temperature	
		Copper	Alloy 42
63Sn/37Pb	183°C	203°C	218°C
60Sn/40Pb	188°C	208°C	223°C
62Sn/36Pb/2Ag	189°C	209°C	224°C

4.14 The stability of temporary solder mask A and B

The properties of temporary solder mask were determined after 1 month which were shown in Table 4.4.

Table 4.4 The properties of temporary solder mask after 1 month

Properties	Standard	Value (A)	Value (B)
Tensile strength (Mpa)	ASTM D638-99	3.16	23.21
% Elongation	ASTM D638-99	195.89	47.32
Adhesion (N)	ASTM D816-82	153.12	-
Adhesion	ASTM D3359-97	1B	1B
Viscosity	ISO 1652-1985(E)	66,900	30,000
pH value	-	6.56	6.13

As can be seen in Table 4.4, the viscosity of temporary solder mask is stable for 1 month. Therefore, The temporary solder masks of this study have good stability and are possible to be used in soldering process.

4.15 The characterize of N-vinyl pyrrolidone and hydroxypropyl methacrylate Copolymer

4.15.1 Differential Scanning Calorimetry

In the absence of miscibility, a composite of two polymers exhibits two distinct glass transitions of the pure components. Two comprehensive studies concerning the glass transition temperature of NVP and HPMA are reported at 175°C and 73°C respectively. The composition and the glass transition temperatures of composite NVP:HPMA are shown in Table 4.5. DSC thermograms of these composite products are shown in Appendix B.

Table 4.5 Glass transition temperature (T_g) of composite NVP:HPMA

Component NVP:HPMA	T _g (°C)
0:1	73
1:1	107.1
1.5:1	126.4

From DSC thermogram, increasing the amount of the secondary polymers in the N-vinyl pyrrolidone improved the resolution of the DSC measurements. The

determined value of glass transition temperatures of NVP (175°C) closely coincides with pure NVP. [6]

4.15.2 ATR FT-IR Spectroscopy

IR (film) of poly(N-vinylpyrrolidone) :

-OH stretch	3470	cm ⁻¹
C-H stretch (broad)	3420(w)	cm ⁻¹
C-H bend (CH ₂ gr.)	1450	cm ⁻¹
-C-N-	1280-1180	cm ⁻¹
C=O	1662	cm ⁻¹

The maximum of carbonyl stretching band in poly(hydroxypropyl methacrylate) lies at 1710 cm⁻¹, poly(N-vinylpyrrolidone) at 1662 cm⁻¹. In this case, poly(N-vinylpyrrolidone) copolymer with poly(hydroxypropyl methacrylate) can cause the shift of C=O band to 1547 cm⁻¹. The ATR FT-IR of these composite products are shown in Appendix E.