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Application of Natural Rubbers as Blend Component in Formulation of Flexographic Printing Photopolymer. Part I: Effect of Natural Rubber Types, Blend Ratios as well as Types and Quantities of Acrylate Monomer

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Flexographic printing photopolymer based on natural rubber (NR) was prepared by blending rubber with styrene-isoprene-styrene block copolymer (SIS) in solution state using toluene as a solvent. The effect of NR types i.e. *NR, epoxidised natural rubbers 25(ENR 25®), ENR 50® and acrylated epoxidised natural rubber (AENR) on the properties of photopolymer was studied at various rubber:SIS blend ratios. The influence of types and quantities of acrylate monomer on the properties of flexographic printing photopolymer was also investigated. The results show that tensile strength, elongation at break and tension set as well as abrasion resistance decreased with an increase of rubber content in the blends. Different types of rubber gave rubber/SIS photopolymers optimal properties at different blend ratios. The photopolymers which were prepared by blending NR/SIS, ENR 25®/SIS at 25/75 wt/wt and AENR/SIS at 10/90 wt/wt together with 10% of trimetylolpropane triacrylate monomer and 5% of Irgacure 819 photoinitiator provided properties,* i.e. *tensile properties, swelling resistance in ink and printability that were comparable to those of the commercial photopolymer. A relief printing plate from ultraviolet exposed photopolymer was later prepared. The imaging ability of NR based relief printing plates (NR/SIS and AENR/SIS) was comparable to relief printing plate from commercial photopolymer.*

Keywords: Flexographic printing; natural rubber; photopolymer; styrene-isoprene-styrene block copolymer; relief printing plate

Flexographic printing plates are well known for use in printing surfaces which range from soft and easy to deform to relatively hard, such as packaging materials, *e.g*. cardboard, plastic films, aluminum foils, *etc*. Flexographic printing plates can be prepared from photopolymerisable compositions or photopolymer that generally comprise of an elastomeric binder, at least one photopolymerisable monomer and a

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photoinitiator[1,2]. Photosensitive elements generally have a layer of photopolymer interposed between a support and a cover sheet or a multilayer cover element. Upon imaging exposure to actinic radiation, polymerisation and hence photocuring (insolubilisation) of the photopolymer occurs in the exposed areas. Conventionally, the element is treated with a suitable solution, *e.g*. solvent or aqueous-based washout, to remove the unexposed areas of the photopolymer, leaving a printing relief which can be used for flexographic printing[3,4].

As such, an elastomeric binder, the main composition in the photopolymer use, is made of polyurethane elastomer, urethane modified acrylate (obtained by introducing polyether or polyester into a compound having a polymerisable double bond), styrene-butadiene block copolymer, styrene-isoprene block copolymer and 1,2-polybutadiene. They satisfy the required hardness (40-80 Shore A hardness) but are insufficient in toughness, causing the printing plate and its relief to be easily broken as well as having shallow depth and narrow range of moldable hardness[4].

In order to improve the performance of these relief plates, widely usable rubbers such as chloroprene rubber, acrylonitrile-butadiene rubber, styrene-butadiene rubber and the like[4,5] have been recently developed. However, a printing plate with prior use of an elastomeric binder generally becomes very hard, lack of rubber elasticity, poor in transition against durability, solvent resistance, wear resistance and aqueous ink as compared with vulcanised rubber printing plate[5].

Natural rubber (NR) is a renewable material with excellent elastomeric properties. The presence of unsaturation at every repeating unit of the NR molecular structure provides good reactivity of the NR with active free radicals[6]. Therefore, NR can be reactively modified or photopolymerised (in the presence of monomer, photoinitiator and actinic radiation) *via* free radical mechanism. In this present work, a novel flexographic printing photopolymer was developed. NR and modified forms of NR were applied into flexographic printing photopolymer composition as part of elastomeric binder with styrene-isoprene-styrene (SIS) block copolymer. Various types and parts of NR and modified NR in blend composition of SIS based photopolymer were investigated. Furthermore, the influence of types and quantities of acrylate monomer on various properties of flexographic printing photopolymer was also studied.

EXPERIMENTAL

Materials

NR (air dried sheet, ADS) was purchased from Khuan Pun Tae Farmer Co-operation, Phattalung, Thailand. ENR 25® and ENR 50® were supplied by Muangmai Guthrie PCL, Phuket, Thailand. Acrylated epoxidised natural rubber (AENR) was prepared in-house on a lab scale at Prince of Songkla University, Pattani campus, Thailand[7]. SIS block copolymer (Kraton D1107C) was purchased from Kraton Polymer LLC, USA. Commercial flexographic printing photopolymer (Cyrel® DPC125) was supplied by Dupont Ltd., Germany. 1,6-Hexanediol diacrylate (HDDA) and trimetylolpropane triacrylate (TMPTA) used as acrylate monomer were received from Sartomer Arkema Group, USA. Bis-acylphosphine oxide (Irgacure 819) photoinitiator was supplied by Ciba Speciality Chemicals Inc., Switzerland. Dioctyl phthalate (DOP) plasticiser was received from Kaohiung Plant, Taiwan. Commercial grade toluene was supplied by Lab Scan Asia Co. Ltd., Thailand. Three types of commercial available inks *i.e*. Horse® (Nan Mee Industry Co. Ltd.,

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Thailand), Only One® (Smart One Distributor Co. Ltd., Thailand) and Sakura® (Sakura Color Products Corp., Japan) were used for test of ink resistance.

Preparation of Flexographic Printing Photopolymer

NR and SIS solutions in toluene were separately prepared at 40% dry rubber content by adding the rubber (small pieces of NR and SIS granules) into a glass container charged with toluene. Mixing continued for several hours at room temperature until the rubber was fully solubilised. The NR and SIS solutions as well as other chemicals were then mixed at desired blend composition. Mixing steps and times are shown in *Figure 1*. The mixture was then poured into a teflon coated container and kept at room temperature for 30 minutes. Solvent in the mixture was then evaporated in a vacuum oven at 40ºC for 72 hours. Received photopolymer with 3.15 mm thickness was subjected to photopolymerisation with UV-A irradiation for 5 min before being used for testing and characterisation. Mechanical properties, ink resistance and printability of selected photopolymers were also compared with those of commercial flexographic printing photopolymer in order to investigate the end use of the prepared photopolymer.

Part 1: Effect of NR Types and Blend Ratios

- Four types of rubber were investigated in a blend formulation of flexographic printing photopolymer. They were NR, ENR 25® , ENR 50® and AENR.
- Blend ratios of rubber/SIS composition were varied from 0-100 parts (based on 100 parts of rubber and SIS).

The formulation of flexographic printing photopolymer used in this study is shown in *Table 1*.

Part 2: Effect of Types and Quantities of Acrylate Monomer

- *Tables 2* and *3* show blend formulations of this part. The experiment was divided into two parts. In part 2.1, the influence of two types of acrylate monomer *i.e*. HDDA and TMPTA, on properties of photopolymers was investigated at 10 p.h.r. The acrylate monomer which gave better properties of photopolymers was selected and used in the second part thereafter. In part 2.2, the effect of various quantities of the chosen acrylate monomer on properties of photopolymers was studied at 10, 15 and 20%.

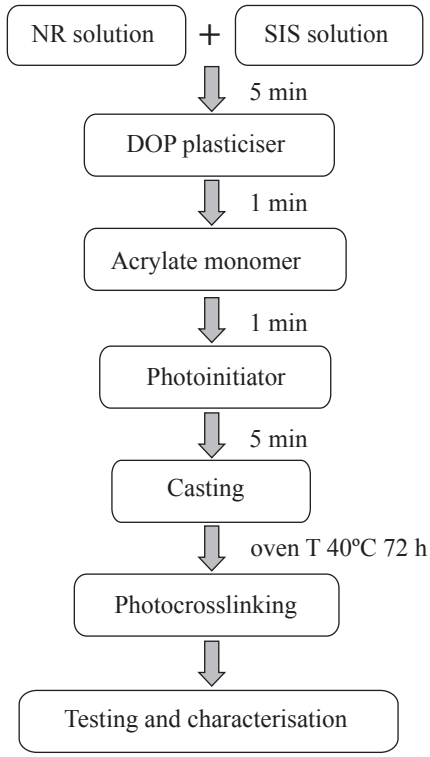


Figure 1. Mixing step and mixing time for preparation of flexographic printing photopolymer.

TABLE 1. BLEND FORMULATIONS OF FLEXOGRAPHIC PRINTING PHOTOPOLYMER: NR TYPES AND RUBBER/SIS BLEND RATIOS

Ingredients	Quantity (%)				
	0/100	10/90	25/75	50/50	75/25
Rubber (NR, ENR®s or AENR) (part)	0	10	25	50	75
SIS (part)	100	90	75	50	25
HDDA	10	10	10	10	10
Irgacure 819	5	5	5	5	5
DOP	10	10	10	10	10

TABLE 2. BLEND FORMULATIONS OF FLEXOGRAPHIC PRINTING PHOTOPOLYMER: TYPES OF ACRYLATE MONOMER

Ingredients	Quantity (%)							
	HDDA				TMPTA			
	NR	ENR 25®	ENR 50®	AENR	NR	ENR 25®	ENR 50®	AENR
Rubber (part)	25	25	25	10	25	25	25	10
SIS (part)	75	75	75	90	75	75	75	90
HDDA	10	10	10	10	-	-	-	-
TMPTA	-	-	-	-	10	10	10	10
Irgacure 819	5	5	5	5	5	5	5	5
DOP	10	10	10	10	10	10	10	10

TABLE 3. BLEND FORMULATIONS OF FLEXOGRAPHIC PRINTING PHOTOPOLYMER: QUANTITIES OF ACRYLATE MONOMER

Ingredients	Quantity (%)								
	NR			ENR 25®			AENR		
Rubber (part)	25	25	25	25	25	25	10	10	10
SIS (part)	75	75	75	75	75	75	90	90	90
TMPTA	10	15	20	10	15	20	10	15	20
Irgacure 819	5	5	5	5	5	5	5	5	5
DOP	10	10	10	10	10	10	10	10	10

Testing and Characterisation

Tensile Test. Tensile properties of prepared photopolymers were tested according to *ASTM D412* at a crosshead speed of 500 mm/min by using a Hounsfield tensile tester (H10KS, Hounsfield Test Equipment, England). Tensile strength, elongation at break and tension set were reported.

Abrasion Resistance. Abrasion resistance of prepared flexographic printing photopolymer was performed using a Taber abrader in accordance to *ISO 5470*. An abrasion roller

no. H18 was used for testing with contact force of 100 g for 2000 cycles. Weights of the test samples, both before (M_0) and after (M_1) testing were measured and Taber abrasion loss (mg/cycle) was calculated using *Equation 1*. The average of Taber abrasion loss of three specimens was reported.

$$\text{Taber abrasion loss} = \frac{M_0 - M_1}{2000} \times 1000 \quad \ldots 1$$

Ink Resistance. The swelling resistance in ink medium of prepared photopolymers was tested. The three types of ink used in this study were of commercial grade. They were Hourse® (water based ink), Only One® and Sakura® (solvent based ink). Samples with a dimension of 10.0 mm × 10.0 mm × 3.15 mm were immersed in ink at room temperature for 72 hours. Tested samples were then taken out from the ink and excess ink on sample surface was removed with blotting paper. The swelling of samples percentage was then calculated according to *Equation 2*.

$$\text{Swelling (\%)} = \frac{M_1 - M_0}{M_0} \times 100 \quad \ldots 2$$

Where, M_0 is the initial weight of test sample and M_1 is the weight of test sample after ink immersion.

Test of Printability. End use of prepared flexographic printing photopolymer was studied in terms of printability on A4 office paper and on kraft paper. A relief printing plate was prepared and compared with that of commercial photopolymer. Preparation of the relief printing plate started by exposing the photopolymer with negative black film on the top surface to actinic radiation and polymerisation, hence, photocrosslinking of the photopolymer occurred in the exposed areas. The element was then treated with toluene to remove the unexposed areas of the photopolymer, leaving the printing relief which was used for stamping.

RESULTS AND DISCUSSION

Effect of NR Types and Blend Ratios on Properties of Flexographic Printing Photopolymer

Figures 2 and *3* show tensile strength and elongation at break of flexographic printing photopolymers as a function of NR types and blend ratios. It can be noticed that mechanical properties of NR/SIS at blend ratio of 75/25 disappear due to the opaque test sample, thus, full photopolymerisation cannot be performed. Irrespective of the blend ratios, results in *Figures 2* and *3* show that tensile strength and elongation at break of the photopolymers increase slightly with the addition of NR and modified NRs into SIS until they reach maximum values around 10% of rubber, after which, the blend ratios decrease. This might be attributed to the chemical structure of NR, ENR® and AENR. Presence of polar functional groups like epoxide rings and acrylate functions in the ENR® and AENR molecules can generate some interactions with functionalities of acrylate monomer during photopolymerisation[7,8] and provide good compatibility with SIS. Therefore, improvement in tensile strength and elongation at break of blended photopolymers is observed. However, each type of rubber gives different maximum values of tensile strength and elongation at break at different blend ratios. With a higher degree of modification, rapid decrease of these two properties was observed at blend ratios of rubber/SIS with lower parts of rubber. For example, the turning points are 75 parts of ENR 25® for the ENR 25®/SIS blend and 50 parts of ENR 50® and AENR for the ENR 50®/SIS and the AENR/SIS blends, respectively. The observation of a decrease in tensile strength and elongation at break at high quantity of rubber parts is due to the possibility of the rubber molecules with higher polar functional groups to form phase separation from the SIS phase[9]. Surprisingly,

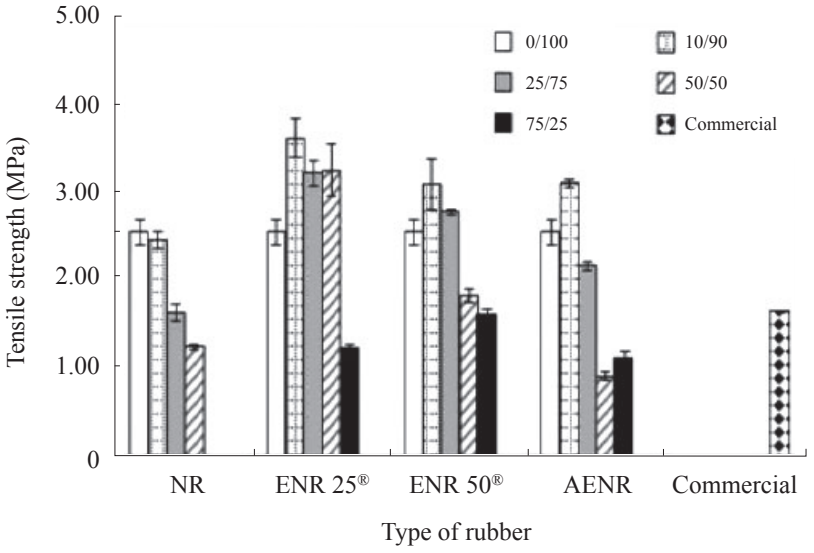


Figure 2. Tensile strength of flexographic printing photopolymer as a function of NR types and Rubber/SIS blend ratios.

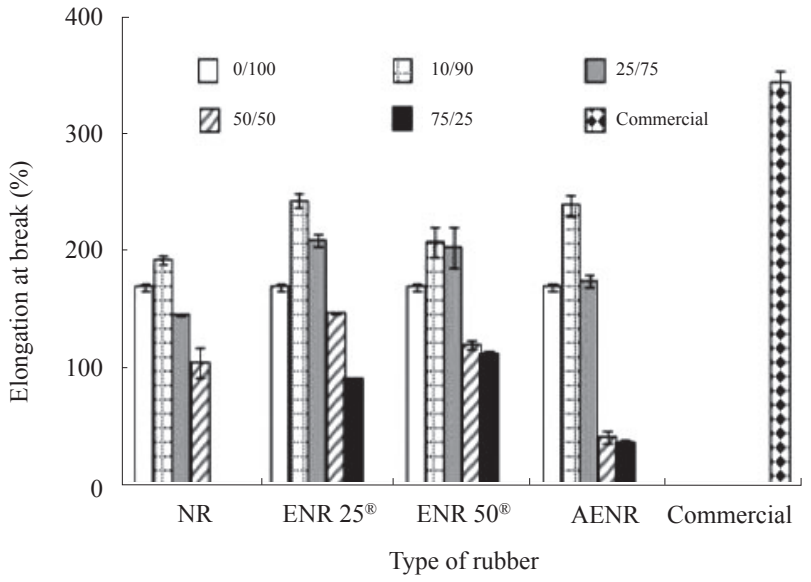


Figure 3. Elongation at break of flexographic printing photopolymer as a function of NR types and Rubber/SIS blend ratios.

in the case of NR/SIS photopolymers, NR is non polar and should provide good compatibility with SIS. However, in this study we found that increasing the NR content in the blend ratio leads to a decrease in tensile strength and elongation at break. This might be due to the fact that NR has very high molecular weight and molecular entanglement compared to other modified NRs. Therefore, the nature of viscosity contrast induces phase incompatibility. Furthermore, interactions between polar functional groups of NR and monomer cannot be promoted. Hence, there is a reduction of tensile strength and elongation at break with increasing NR content in the photopolymer composition.

The elastomeric property of prepared flexographic printing photopolymers was also investigated by focusing on tension set values. A lower percentage of tension set means that a material has good ability to recover back to its original shape. The rubber/SIS blends with elongation at break lower than 100%, as shown in *Figure 3*, could not be tested for tension set. As seen in *Figure 4*, tension sets of all photopolymers are similar except in the case of AENR. AENR having the highest polar functionality from the epoxide rings and acrylate functions exhibited the worst tension set property of AENR/SIS photopolymer comparably.

Figure 5 illustrates abrasion resistance of flexographic printing photopolymer as a function of NR types and blend ratios. Flexographic printing polymers with high contents of rubber in blend composition and with a high degree of modification resulted in high amounts of material loss during testing. This is due to phase separation in the photopolymer. For ENR 25® and ENR 50® based photopolymers with proportion of the rubber is lower than 50%, it can be seen in *Figure 5* that their abrasion losses are small and quite close to the NR based photopolymers, even though the ENR® is polar and stiffer than the NR. However, interaction between polar

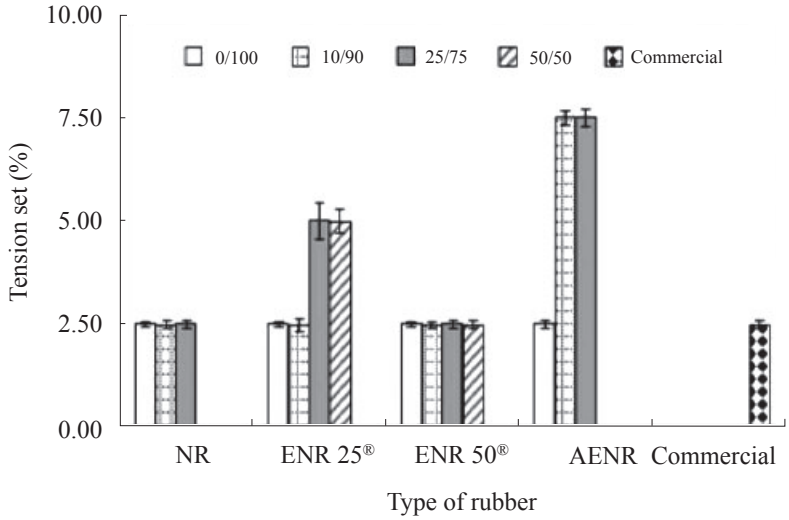


Figure 4. Tension set of flexographic printing photopolymer as a function of NR types and Rubber/SIS blend ratios.

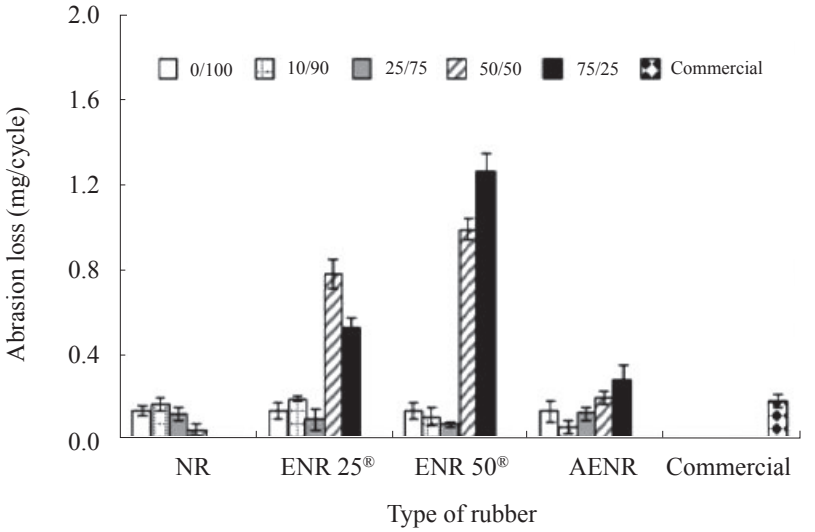


Figure 5. Abrasion resistance of flexographic printing photopolymer as a function of NR types and Rubber/SIS blend ratios.

functional groups promotes good adhesion between interphases. Therefore, good abrasion resistance is observed and is comparable to that of the NR/SIS blends.

Surprisingly, AENR/SIS photopolymer had very low amounts of abrasion loss compared to ENR 25®/SIS and ENR 50®/SIS photopolymers due to its very sticky surface. Therefore, the excess material from the abrasion (small dust) agglomerated and remained on the specimen surface resulting in almost similar weights of before and after.

From this part of the experiments, it can be concluded from *Figures 2* to *5* that proper blend ratios of rubber/SIS were 25/75 wt/wt for photopolymers with NR and ENR®s and 10/90 wt/wt with AENR. This was concluded by comparing all results with those of commercial flexographic photopolymer. These blend ratios were chosen for further study.

Effect of Types and Quantities of Acrylate Monomer on Properties of Flexographic Printing Photopolymer

The properties of flexographic printing photopolymer do not only depend on rubber types and blend ratios of elastomeric binder but also on acrylate monomer and photoinitiator used[1,2]. In this part of the experiment, the influence of types and quantities of acrylate monomer on properties of flexographic printing photopolymer was investigated. *Figures 6* to *9* show the properties of the photopolymers as a function of types of acrylate monomer. At a fixed concentration of acrylate monomer (10%) HDDA mixed photopolymers tend to slightly increase tensile strength with decreasing of elongation at break, tension set and abrasion loss in comparison with TMPTA mixed photopolymers. However, differences of desired values (tensile strength, tension set and abrasion loss) as affected by types of acrylate monomer were not much, unlike

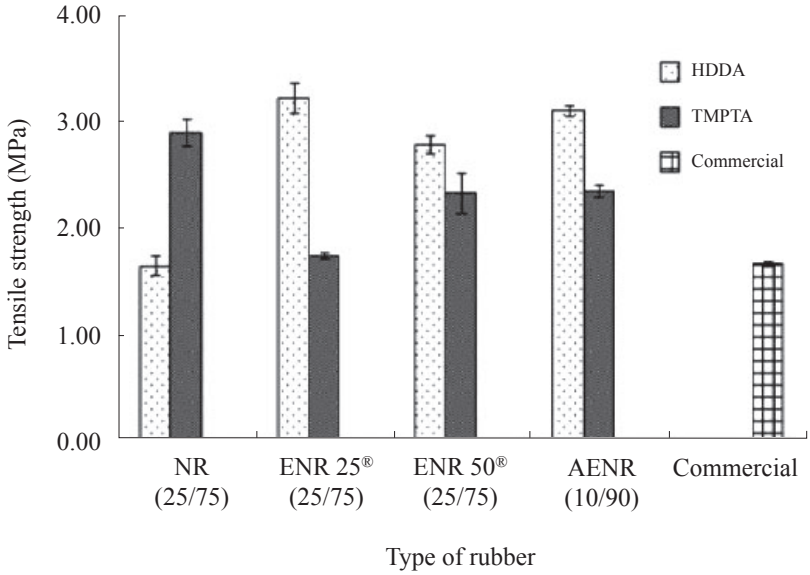


Figure 6. Tensile strength of flexographic printing photopolymer as a function of types of acrylate monomer at 10% addition.

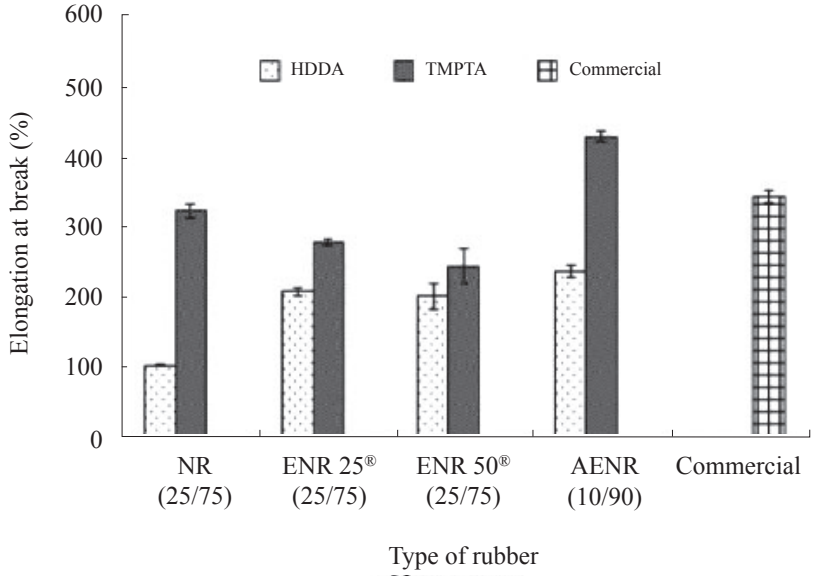


Figure 7. Elongation at break of flexographic printing photopolymer as a function of types of acrylate monomer at 10% addition.

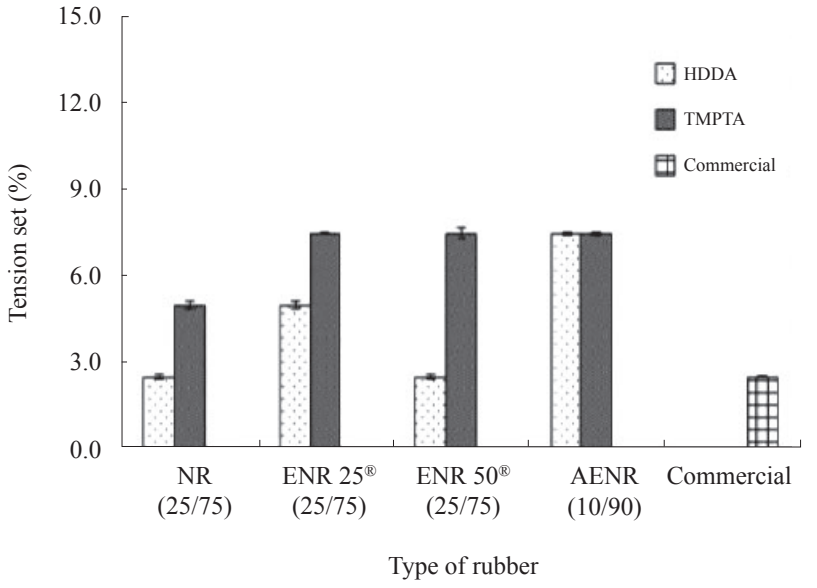


Figure 8. Tension set of flexographic printing photopolymer as a function of types of acrylate monomer at 10% addition.

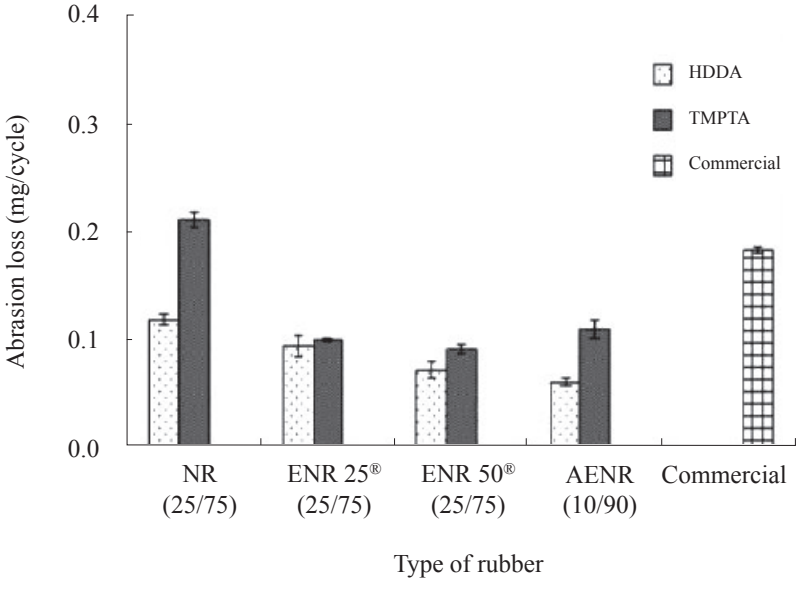


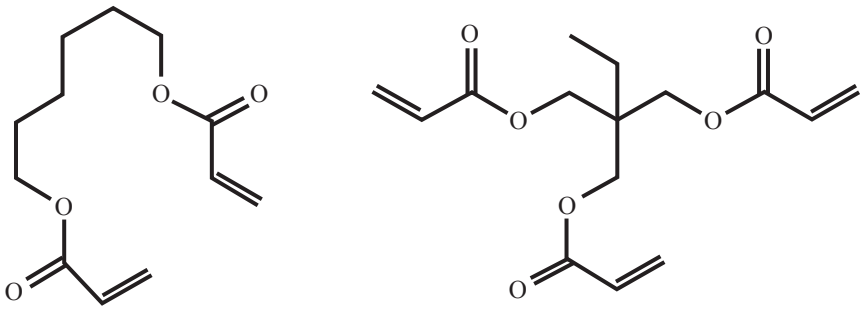
Figure 9. Abrasion resistance of flexographic printing photopolymer as a function of types of acrylate monomer at 10% addition.

elongation at break. This can be explained by the chemical structure of the monomers as shown in *Figure 10*. TMPTA is a triacrylate monomer having three vinyl chain ends. It can promote complex photocrosslinking in elastomeric binder molecules and provides higher crosslinking than HDDA which is a diacrylate monomer[10]. Furthermore, TMPTA is stiffer than HDDA. TMPTA has a glass transition temperature (Tg) of 62ºC which is higher than that of HDDA (43ºC). Therefore, using TMPTA as acrylate monomer produces a photopolymer with better overall balance of properties than HDDA and is comparable to the properties of commercial flexographic printing photopolymer.

Further observations from this part of the experiment that are not discussed in this study were the appearance of prepared photo-polymer. Authors found phase separation in photopolymer of 25/75 ENR 50®/SIS blend, probably due to the fact that during evaporation of the toluene from the photopolymer mixture, ENR® and SIS phases formed self combination by their structure and polarity. Two layers of ENR® and SIS phases were therefore observed.

The effect of quantities of TMPTA acrylate monomer on properties of flexographic printing photopolymer was later studied at 10, 15 and 20%. Results are shown in *Figures 11* to *14*. It was found that the quantity of TMPTA monomer did not affect the tensile strength of the photopolymers. However, it had an effect on the alteration of elongation at break, tension set and abrasion resistance of the photopolymers. Elongation at break and abrasion loss seemed to decrease with increasing quantity of TMPTA in the blend formulation, whilst tension set increased. A higher degree of complex crosslinking was observed with the increase quantity of TPMTA. Furthermore, the production of excess acrylate monomer to homopolymerise might occur. There is a report that acrylate homopolymer can form clusters and act like hard and brittle fillers in the matrix of a polymer blend[11,12].

The general mechanism of photocrosslinking of polymer *via* a free radical mechanism is shown in *Figure 15*. It is a desirable pathway for positive photocrosslinking in rubber molecules. However, due to the very high reactivity of free radicals generated in the system, sometimes side reactions also happen at the same state of photocrosslinking. Possible side reactions shown in *Scheme 1* where an increasing concentration of acrylate monomer leads to the possibility of excess acrylate monomer to homopolymerise (MM



HDDA TMPTA

Figure 10. Chemical structure of acrylate monomers.

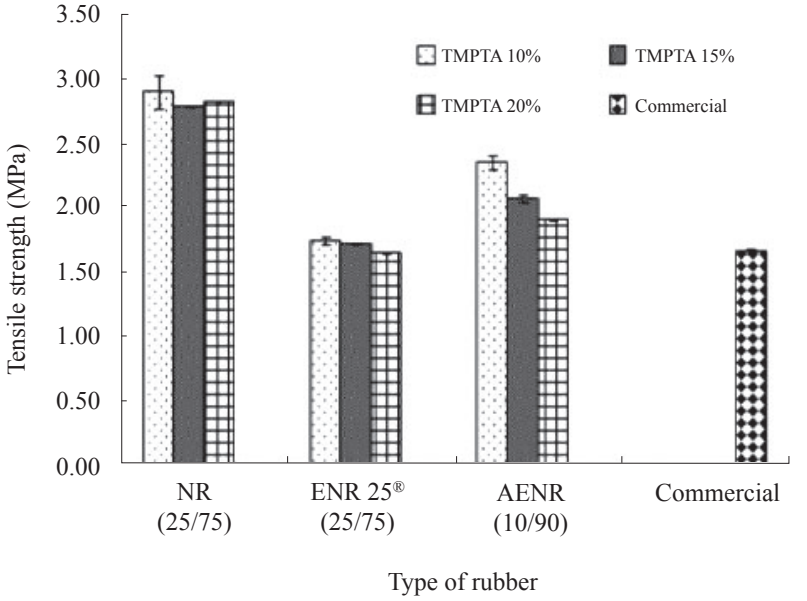


Figure 11. Tensile strength of flexographic printing photopolymer as a function of quantities of TMPTA.

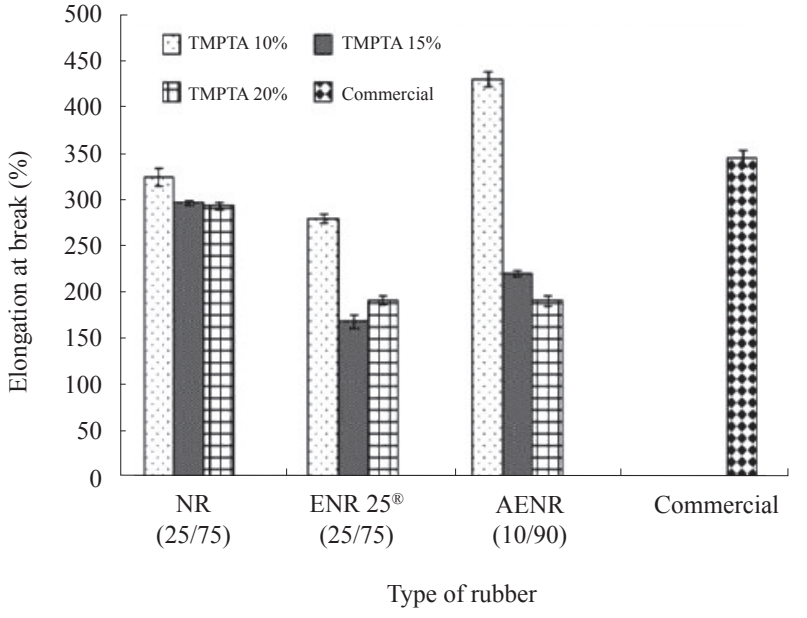


Figure 12. Elongation at break of flexographic printing photopolymer as a function of quantities of TMPTA.

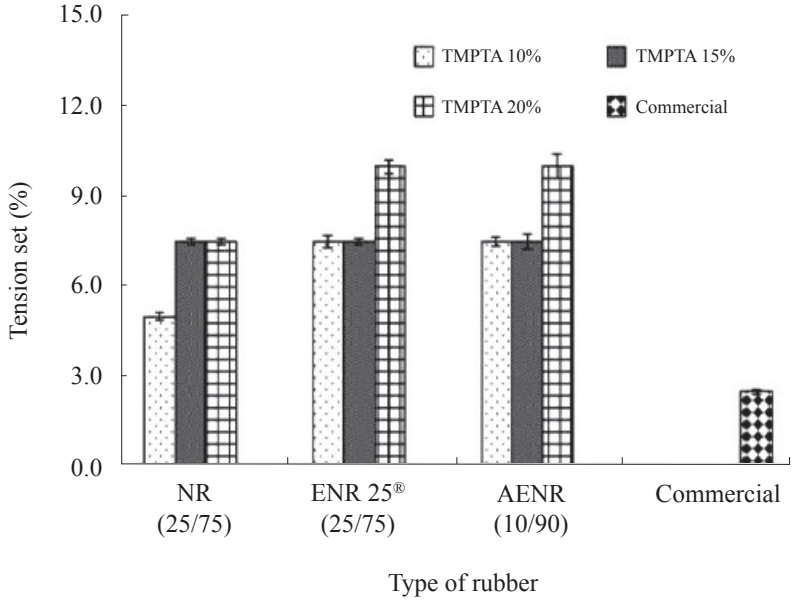


Figure 13. Tension set of flexographic printing photopolymer as a function of quantities of TMPTA.

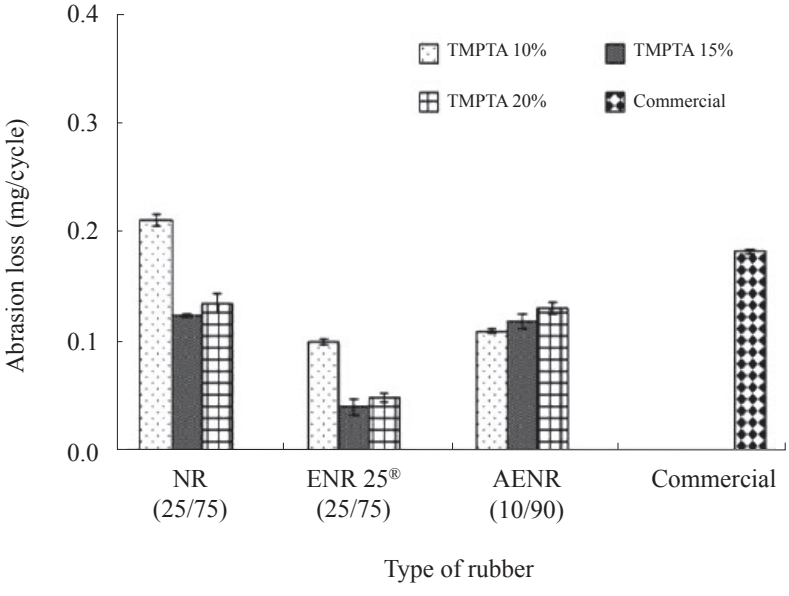
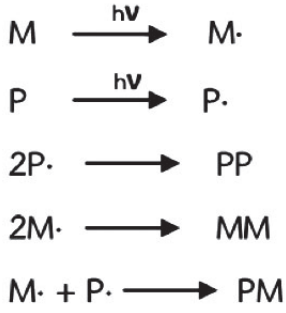


Figure 14. Abrasion resistance of flexographic printing photopolymer as a function of quantities of TMPTA.

and/or PM structures in *Scheme 1*). The mechanism of acrylate monomer to form acrylate homopolymer by photo induced polymerisation as shown in *Figure 16*. Reduction of elongation at break and abrasion loss, together with increasing tension set (*Figures 12* to *14*) and TMPTA monomer is due to stress concentration of the applied force on specimen during mechanical tests. In addition, dissipation of energy at the interfaces was poor. Filler-like domains of acrylate homopolymer were the weak points in test specimens. Thus, photopolymers with poor mechanical properties *i.e.* high modulus and brittle in nature are acquired.

Swelling resistance in inks of flexographic printing photopolymer was also performed, as shown in *Table 4*. The prepared photopolymers showed the highest swelling % in Sakura® due to its toluene based ink solubility parameter's closeness to that of photopolymer unlike Only One® which is an acetone based ink. Furthermore, the blending of NR and modified



Scheme I. Possible side reactions occurring during photocrosslinking.

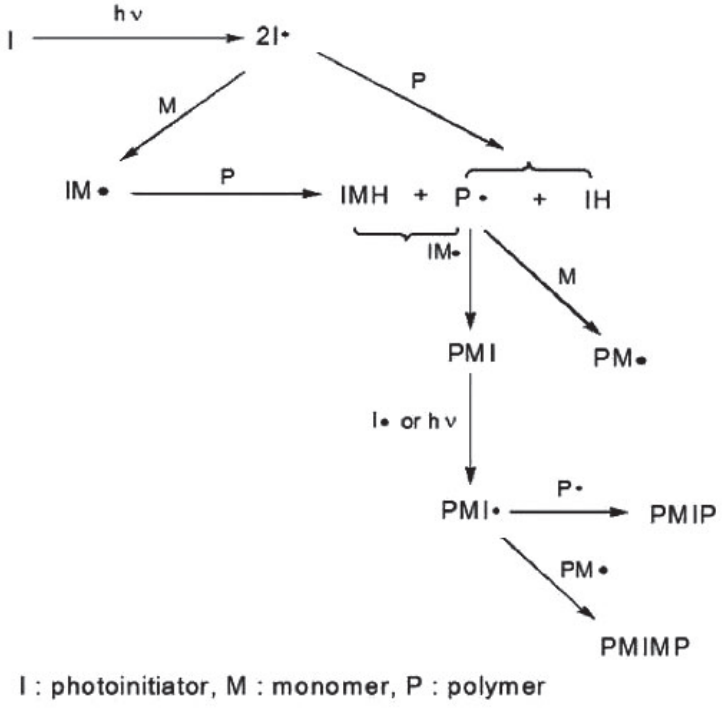


Figure 15. Mechanism of photocrosslinking of polymer via *free radical mechanism*[12].

TABLE 4. SWELLING RESISTANCE IN INK OF FLEXOGRAPHIC PRINTING PHOTOPOLYMER

Type of ink	Swelling (%)			
	NR/SIS (25/75)	ENR 25®/SIS (25/75)	AENR/SIS (10/90)	Commercial
Horse® (water based)	0.6±0.1	0.6±0.1	0.5±0.1	0.6±0.1
Only One® (acetone based)	2.2±0.2	1.8±0.1	1.6±0.2	2.2±0.4
Sakura® (toluene based)	88.7±5.1	98.5±2.7	114.1±13.3	113.5±20.3

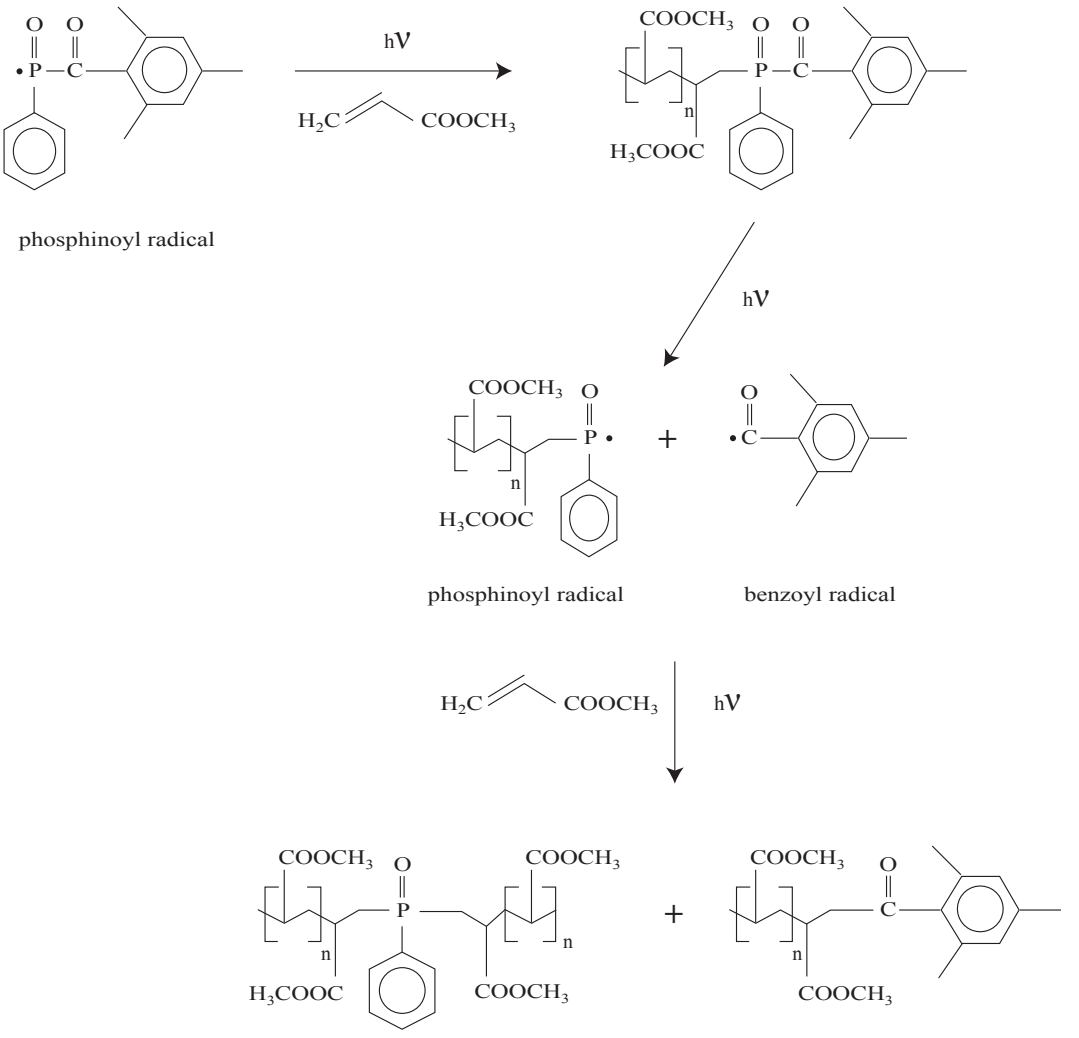


Figure 16. Mechanism of photo induced acrylate homopolymerisation[13].

NRs with SIS provides photopolymers with better solvent based ink resistance (low % swelling) than that of commercial photopolymer. This implies that the prepared printing photopolymers has good dimensional stability when the surface comes into contact with ink.

Printing and imaging abilities of prepared photopolymer were studied in order to evaluate the end use properties. Results of printing ability are shown in *Figures 17* to *18*. It was found that the prepared photopolymers (NR/SIS and AENR/SIS) show good wettability to water and solvent based inks, comparable to that of commercial photopolymer. Sharp borders of stamped images on paper are clearly seen. This implies that the prepared photopolymers can be used to print on real substrate *i.e*. as stamping for office work (A4 paper) and printing plate for carton box (kraft paper). Imaging ability of prepared photopolymer was tested with the words "PSU" and "RUBBER". Results in *Figure 19* concluded that good relief image with stable dimension can be produced from prepared rubber based photopolymer, similar to the commercial photopolymer.

CONCLUSION

Types of rubber and blend ratios had significant effects on properties of photopolymers. Tensile strength, elongation at break and tension set as well as abrasion resistance decreased with increasing rubber content in the blends. Different types of rubber gave rubber/SIS photopolymers with optimal properties at different blend ratios. The photopolymers prepared by blending NR/SIS, ENR 25®/SIS at 25/75 wt/wt and AENR/SIS at 10/90 wt/wt

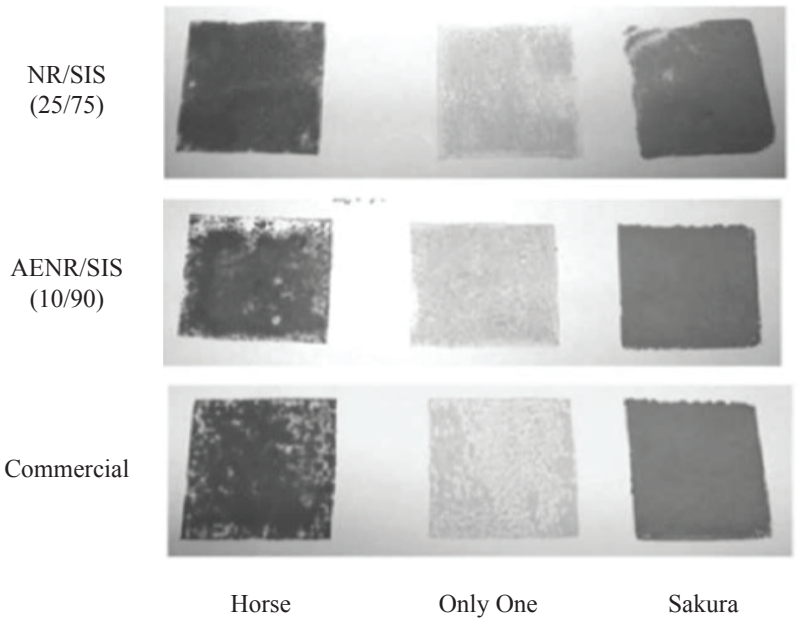


Figure 17. Stamping on A4 office paper.

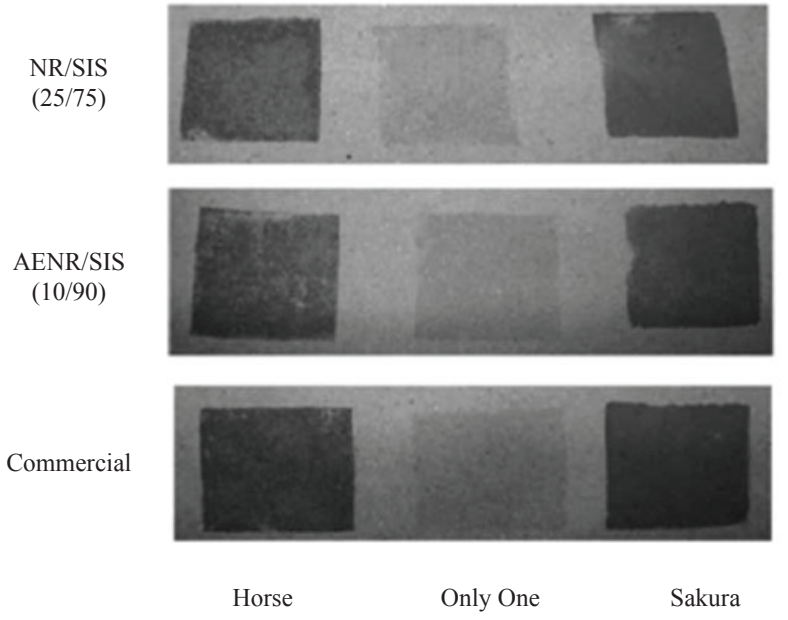


Figure 18. Stamping on kraft 125 paper.

Figure 19. Relief printing plate.

together with 10% of TMPTA monomer and 5% of Irgacure 819 provided tensile properties, abrasion resistance, swelling resistance in ink, printability and imaging ability that were comparable to those of the commercial photopolymer.

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