



Evaluation of soft adhesives containing dual-curable melamine-based compounds



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ABSTRACT

Although pressure-sensitive adhesives can be used in a wide variety of applications, their durable temperature range is generally limited due to their weak cohesive power. In this study, melamine-based compounds bearing UV-curable *N*-methyl acrylate groups and thermal-curable *N*-methoxymethyl groups were evaluated as dual-curable materials for PSAs. The photo-curing abilities of MAOs are slightly inferior to those of TMP(EO)TA due to their rigid melamine core, but they could be improved by substituting acrylate groups onto the melamine core. In photo shrinkage, MAOs are less shrunk than TMP(EO)TA because of their greater size. Following the dual curing process, the storage modulus of MAO-containing PSA was maintained at approximately 3E6 dyne/cm², even at high temperature. In particular, MAOs are very tolerant to heat exposure and thus could afford highly cohesive cured materials with a sufficient thermal curing process.

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1. Introduction

Compared to conventional adhesives, pressure-sensitive adhesives (PSAs) offer many advantages allowing quick, easy, and automatic procedures and thus they can be used in a wide variety of applications. However, the durable temperature range of PSAs is limited because their internal cohesion is relatively weak. If the temperature is too high, the PSA can ooze out of the substrates and bubbles can form inside the adhesives. This problematic feature can cause serious damage to the end product [1–4]. To improve the internal cohesion of the adhesive, there are two major methods. The first method is to use a crosslinking agent that forms a chemical linkage between linear polymers, as shown in Fig. 1a. With a crosslinking agent simply added, the cohesion strength can be greatly enhanced. However, this method provides too short a pot-life for the application process, and the performance of the original material can be seriously degenerated. An alternative is the entanglement method. In this method, new polymer chains are created between the networks of existing polymers, resulting in semi-IPN (semi-interpenetrating polymer network) structures (Fig. 1b) [5–7]. This method is commonly processed by UV/EB

technology, and the pot-life and performance of the adhesives is relatively controllable. The dual-curing method, a combination of two separate curing methods, generally consists of UV-curing and thermal-curing. UV-curing is a rapid energy-saving process that can reduce the deterioration of the mechanical properties of substrates. On the other hand, the thermal-curing method does not have a shadow effect, and it is therefore useful to completely curing residual materials following UV curing. There are a variety of examples of the implementation of dual-curing methods. Park et al. synthesized a monomer bearing both a thermal-curing epoxy group and a UV-curing acrylate group. In this study, a synthetic monomer was applied in the LCD manufacturing process by the dual-curing method [8]. Cho et al. studied additives to optimize conversion in a dual-cure system [9]. Park et al. introduced self-curing at a high temperature using epoxy groups pended on a main chain [10].

In this paper, we wish to report on dual-curable compounds bearing UV-curable *N*-methyl acrylate groups and thermal-curable *N*-methoxymethyl groups on a rigid melamine core for highly cohesive PSAs. The UV-curing behaviors and mechanical properties of the dual-curable melamine-based compounds were evaluated as curable materials for PSAs and compared with a representatively common curable material for PSAs, trimethylolpropane-(EO)₉ triacrylate (TMP(EO)TA).

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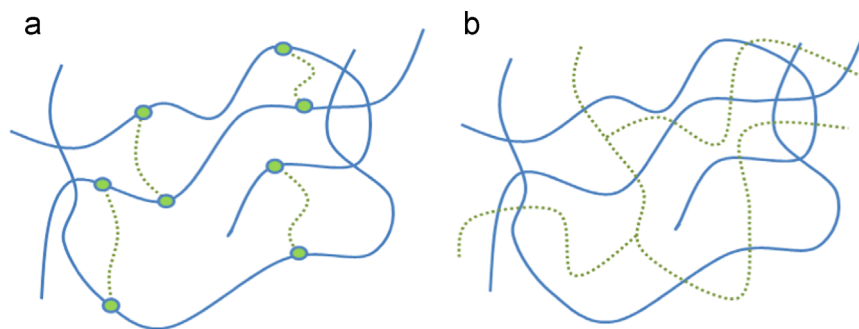


Fig. 1. Two types of crosslinking by (a) crosslinking agent and (b) entanglement.

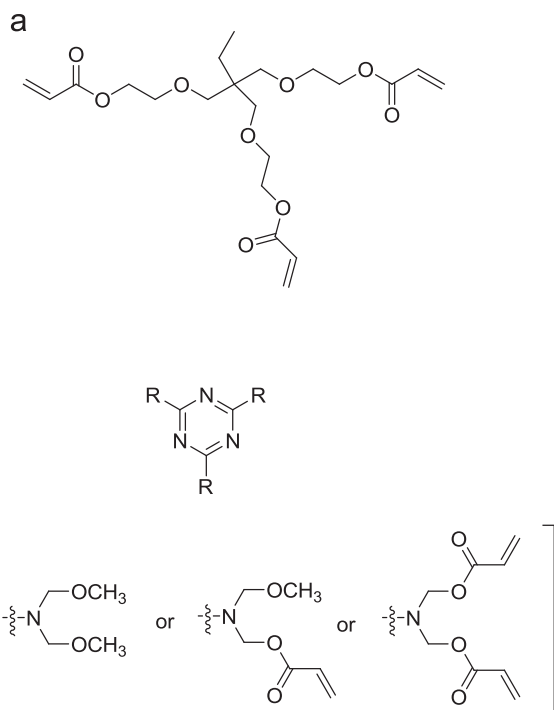


Fig. 2. Chemical structures of (a) TMP(EO)TA and (b) MAOs (sum of *N*-methylmethoxy groups and *N*-methyl acrylate groups on one melamine core is 6).

2. Experimental

2.1. Materials

2.1.1. Curable materials for PSAs

Two types of dual-curable melamine-based compounds (named MAO-1 and MAO-2) differing by the ratio of UV- and thermal-curable groups on one melamine core (for the average number of UV-curable acrylate groups on one melamine core, MAO-1=4 and MAO-2=5.5) and UV-curable trimethylolpropane-(EO)₉ triacrylate (TMP(EO)TA) for comparison were provided as a gift by Miwon Specialty Chemical (Korea) (for chemical structure, see Fig. 2). Hydroxycyclohexyl phenyl ketone (CP-4, Miwon Specialty Chemical, Korea) and hydroxydimethyl acetophenone (HP-8, Miwon Specialty Chemical, Korea) were used as photo-initiators. The chemical and physical properties of MAO-1 and MAO-2, including the average molecular weight, average number of acrylate groups on one melamine core, refractive index (RI), and viscosity, are summarized in Table 1.

2.1.2. Synthesis of base pre-polymer

The base pre-polymers for the PSA by the entanglement method were prepared by solution polymerization (50% solid

Table 1
Chemical and physical properties of dual-curable melamine-based compounds MAO-1 and MAO-2.

	MAO-1	MAO-2
Average molecular weight	1500	1500
Number of acrylate groups on one melamine core	4	5.5
Refractive index	1.51	1.51
Viscosity (25 °C)	1000~4000 cps	3000~7000 cps

content). The typical procedure was as follows: 135 g of 2-EHA (2-ethylhexyl acrylate), 15 g of acrylic acid, 0.3 g of AIBN (azobisisobutyronitrile) and 125 g of ethyl acetate (EtOAc) were mixed in a 500-ml four-neck flask equipped with an overhead stirrer, a dropping funnel and a thermometer. The mixture was heated to 70 °C with stirring. After the exothermic reaction was completed, the temperature was maintained for 30 min. Then, AIBN (0.3 g) in EtOAc (50 g) was added, and the reaction mixture was stirred for 3 h. Afterwards, more AIBN (0.3 g) in EtOAc (50 g) was added, and the reaction continued for 2 h to give the base pre-polymer for PSA. M_n of pre-polymer was approximately 100 K, and PDI is 4.2–4.5 that depends on the each test.

2.1.3. Preparation of curable PSA sample

For the investigation of the UV-curing behaviors, samples were prepared by adding 2.5 parts per hundred resin (phr) of each photo initiator (CP-4 and HP-8) to TMP(EO)TA, MAO-1, and MAO-2. For the evaluation of dual-curable PSAs, samples were prepared by mixing the curable compounds (TMP(EO)TA, MAO-1, and MAO-2) with the synthesized base pre-polymer in the presence of 2.5 phr of photo initiator (CP-4- or HP-8). Then, the prepared samples were coated to a 40 μm coating thickness and heated at 70 °C in an oven for 20 min. A conveyor belt type UV irradiator equipped with a mercury lamp light source was used for UV curing with irradiation with 200, 600, 1000, and 2000 mJ/cm² light intensity. Subsequently, further thermal curing was carried out at 120 °C in an oven. The heat exposure times were 30 min and 24 h.

2.2. Analysis

2.2.1. Photo-DSC

Photo-DSC experiments were conducted using a TA Instruments Q-1000 DSC equipped with a photo-calorimetric accessory, using light from a 100 W middle-pressure mercury lamp. The light intensity was determined by placing an empty DSC pan on the sample cell. The UV light intensity on the sample was 40 mW/cm² over a wavelength range of 300–545 nm. The weight of the sample was approximately 3 mg, and the sample was placed in an open aluminum DSC pan. Measurements were carried out at 25 °C.

2.2.2. Shrinkage meter

The shrinkage ratio was measured by a linometer (RB Model 308, R&B, South Korea). First, the designated amount of the sample was loaded onto a stainless steel plate and covered with a glass slide. They were placed on an LVDT (linear variable differential transformer) transducer, and the glass slide on the top was fixed [11,12]. When the shrinkage of the sample occurred in the process of UV irradiation, the stainless steel plate moved up by a distance that was recorded with time. This linear shrinkage in the vertical direction was transformed to volumetric data, and the shrinkage ratio was calculated [13].

2.2.3. ARES rheometer

The viscoelastic properties including the storage modulus, loss modulus and tangent delta of the PSAs were measured by an ARES rheometer. The PSAs were set between a pair of parallel 8 mm diameter plates. The plate pair was twisted under a temperature range from -50 to 120 °C with various strains (0.05–40%) at a frequency of 1 Hz and a heating rate of 5 °C /min.

2.2.4. Peel test

The specimen was cut to widths of 25 mm, attached to a stainless steel substrate and pressed 2 times (2.7 km/in) using a rubber roller (2 kg). The measurements were carried out at an angle of 180° with a crosshead speed of 300 mm/min at 20 °C based on ASTM D3330. The force was recorded in g during seven different runs, and the average value was reported in g/25 mm.

3. Result

3.1. Photo-curing behaviors of curable materials

3.1.1. Curing rate and conversion

The curing rate and conversion were determined by photo-DSC (Fig. 3a). As a sample starts to cure in photo-DSC, an exothermic reaction progresses because the heat flow is generated by a chain reaction of the acrylate C=C double bond. First, the general UV-curing material TMP(EO)TA was analyzed for comparison, showing a time to reach maximum heat flow of approximately 32 s and a maximum heat flow of 65 W/g. The time to reach maximum heat flow for MAO-1 was 37 s, and the maximum heat flow was 23 W/g. For MAO-2, the maximum heat flow was 43 W/g, which was reached in 33 s. The results indicate that the photo-curing rates of both MAO-1 and MAO-2 were slower than that of TMP(EO)TA, which means that the MAOs are less reactive in this photo-curing condition. This could be explained by the rigidity of their core melamine structure compared with TMP(EO)TA, which makes the reactive end groups move less freely. Nevertheless, the reactivity of the MAOs is still high enough for them to be utilized as photo-curable compounds. All results are summarized in Table 3. The total conversion of curable material is also a crucial factor. To prevent unexpected reactions across the double bond of unreacted acrylates, complete conversion is of importance. In this experiment, the total conversion of each curable material was estimated by the integral of the heat flow produced during the exothermic polymerization of the acrylates. MAO-2, showing the slowest curing rate, afforded the highest conversion (Fig. 3b). It is believed that the higher number of reactive groups in MAO-2 molecules (5.5 per molecule) provides a greater chance to interact [14–16].

3.1.2. Shrinkage ratio and rate

The shrinkage rate was measured in real-time using an LVDT transducer. In most cases, low shrinkage is desirable because shrinkage creates tension within the material, which might cause flaws such as internal destruction, loss of attachment and, detachment from

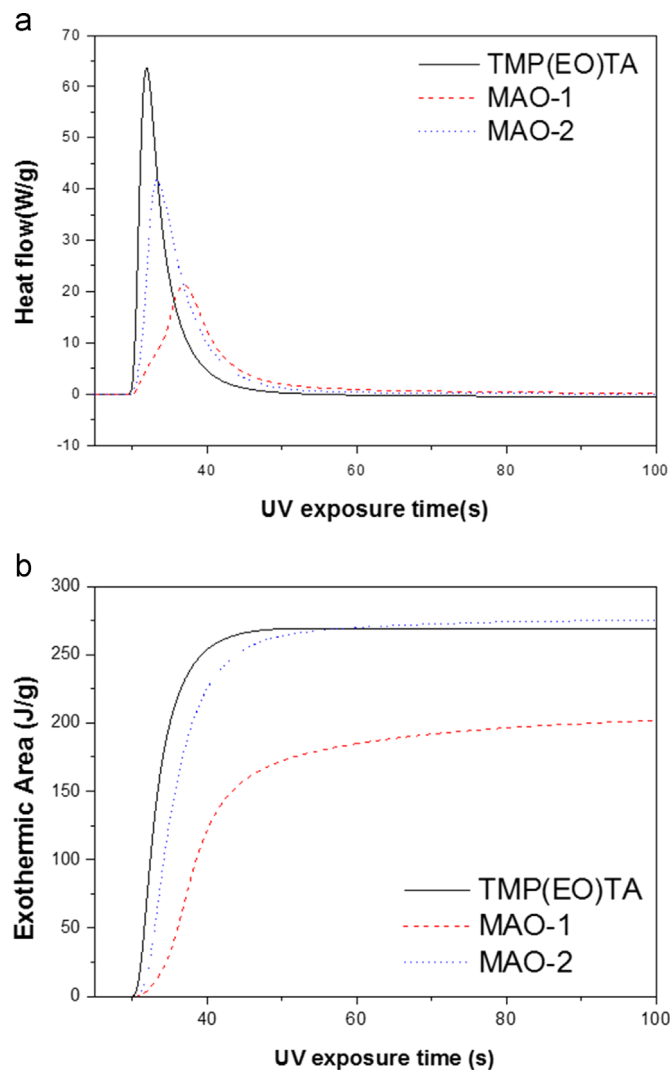


Fig. 3. (a) Heat-flow profiles and (b) exothermic areas (integrated heat flow) of TMP(EO)TA (black line), MAO-1 (red dotted line), and MAO-2 (blue dotted line), measured and calculated by photo-DSC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

basement. Shrinkage occurs due to the removal of spaces between single molecules by polymerization, and it can be correlated with the size of the molecule and the number of reactive groups because a larger molecule gives a smaller change in molecular size after curing and the higher number of reactive groups leads to a more packed structure in the final product. Therefore, the shrinkage can be suggested to be correlated per

$$\text{Shrinkage} \propto \frac{\text{Number of Reactive Groups}}{\text{Size of Molecule}}$$

MAO-2 showed a higher shrinkage and MAO-1 showed a lower shrinkage, compared with TMP(EO)TA (Fig. 4a). Although MAO-1 has higher number more functional groups than TMP(EO)TA (4 for MAO-1 versus 3 for TMP(EO)TA), it showed a lower shrinkage due to its larger molecular size. Meanwhile, although the molecular size of MAO-2 is similar to that of MAO-1, it had a higher shrinkage than TMP(EO)TA because of its greater number of reactive sites (5.5 for MAO-2 versus 3 for TMP(EO)TA). When the shrinkage rates are derived from the differentiation of shrinkage over time and compared with the results of curing rates obtained by photo-DSC, it was confirmed that the shrinkage rates are correlated with the curing rates (Fig. 4b).

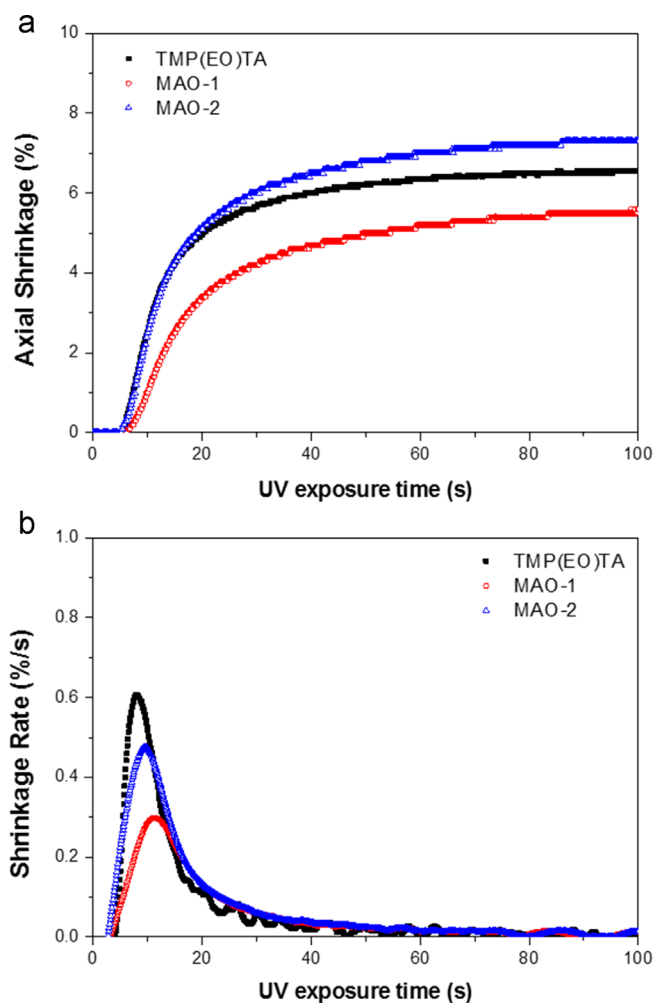


Fig. 4. (a) Shrinkage ratios and (b) shrinkage rates of TMP(EO)TA (black line), MAO-1 (red dotted line), and MAO-2 (blue dotted line), measured and calculated by LVDT transducer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Mechanical properties of PSA

3.2.1. Dynamic mechanical properties

The dynamic mechanical properties of dual curable PSA were investigated at each curing step. A PSA sample was prepared by formulation with a base pre-polymer and the dual curable material MAO-1, and the storage modulus (G') and damping coefficient ($\tan D$) were measured as a function of temperature using ARES after no curing, UV curing, and dual curing (UV then thermal curing). The storage modulus of all samples gradually reduced as the temperature rose in a low-temperature range (-50°C to 30°C), which is a typical pattern of thermoplastic polymers. This clearly shows that a semi-IPN structure was formed by the polymerization of MAO-1 during the curing process. This property is essential to its utilization as a PSA. On the other hand, the storage modulus of the dual-cured sample showed a different pattern from that of the uncured and solely UV-cured samples in the high-temperature range over 30°C . The storage modulus of the dual-cured sample (empty triangles, crosshairs in Fig. 5a) stayed at approximately 3×10^6 dyne/cm² over 30°C , which shows a sufficient cohesive strength to be utilized as an adhesive. On the other hand, the storage modulus of the non-heat-cured samples continued to decrease until 80°C , at which point it dramatically increased. This indicates that both samples were thermally cured over 80°C during the analysis.

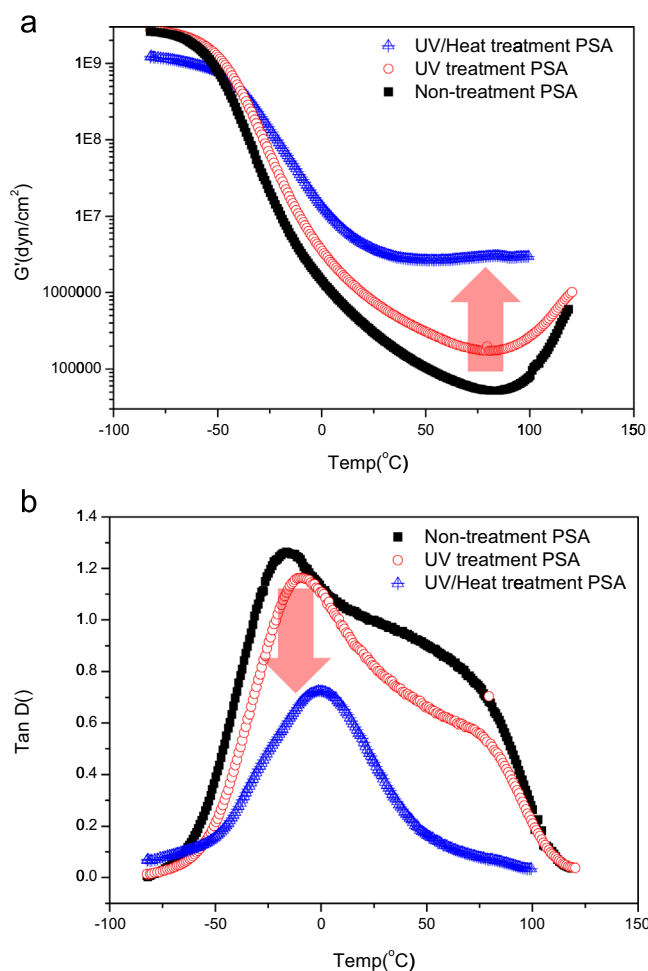


Fig. 5. (a) Storage moduli and (b) damping coefficients according to temperature of MAO-1 (2.5 phr of CP-4 and HP-8) after non-curing (black filled squares), UV-curing (red empty circles), and dual-curing (blue triangles, crosshairs) processes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Sample preparation of curable PSAs for peel test (unit: g).

	Sample name					
	TMP (20)	TMP (40)	MAO-1 (20)	MAO-1 (40)	MAO-2 (20)	MAO-2 (40)
Base pre-polymer	25	25	25	25	25	25
TMP(EO)TA	5	10	–	–	–	–
MAO-1	–	–	5	10	–	–
MAO-2	–	–	–	–	5	10
Photo initiator	0.25	0.5	0.25	0.5	0.25	0.5

The damping ratio (integral value of $\tan D$ by temperature) and T_g (peak point of $\tan D$ graph) were calculated with $\tan D$ measured as a function of temperature. T_g increased as the curing progressed [T_g (uncured) = -20°C , T_g (UV-cured) = -10°C , T_g (dual-cured) = 5°C], but the damping ratio decreased. It was confirmed that the PSA containing MAO-1 became hard by the formation of an entangled structure (Fig. 5b).

3.2.2. Peel strength

To evaluate the performance of the PSAs in the curing process, the peel strength of the cured PSAs was measured using a texture

Table 3

Peak time and total heat flow of TMP(EO)TA, MAO-1, MAO-2.

	Peak time (s)	Total heat flow (J/g)
TMP(EO)TA	31.87	272.1
MAO-1	36.87	192.8
MAO-2	33.27	275.4

analyzer. Each sample was prepared as shown in Table 2 and cured by UV and then heat. The peel test of the cured PSAs was carried out immediately after coating onto stainless steel. Because the performance of the adhesives is dependent on the field of application, it is important to set criteria for a possible application. For our purpose, the acceptable peel strength was set to 1000 g per 25 mm.

The peel strengths of PSAs containing curable material corresponding to TMP(EO)TA, MAO-1, or MAO-2 were examined according to the amount of curable material contained and the UV dose (Fig. 6). In general, the heat tolerances of cured materials are improved but the peel strengths deteriorate due to the lower flexibility and wetting ability. As expected, the adhesive powers of all prepared PSAs decreased after UV-curing. The higher the amounts of curable material and the dose of UV that were used, the lower the peel strength was in all cases. The degradation of the peel strengths of the MAO-containing PSAs were greater than that of the TMP(EO)TA-containing PSAs, for a value of less than 1000 g per 25 mm. This was considered to be due to the more rigid core structure of the MAOs (Fig. 6). After UV curing then thermally curing for 30 min at 120 °C, the peel strengths of all PSA samples were enhanced regardless of the amounts of curable material and the dose of UV (Fig. 7). It was believed that further thermally curing the materials allowed a higher cohesive power to form. When the heat exposure was extended to 24 h, the peel strengths of the TMP(EO)TA-containing PSAs were lessened, particularly in the cases using a low UV dose. Prolonged heat exposure could cause undesired decomposition to diminish the cohesive power of ready-cured materials, which is a typical phenomenon in common PSA materials, the so-called aging effect. However, interestingly, the peel strengths of the MAO-containing PSAs were enhanced after thermally curing for 24 h at 120 °C (Fig. 8). In particular, PSAs containing MAO-2 afforded dramatically improved peel strengths over the measurement limit when 40 wt% MAO-2 was used and the UV curing was 2000 mJ/cm². It may be concluded that MAO-2 is a very heat-tolerant compound, and thus it could be utilized as a curable material for a highly cohesive PSA after sufficient thermal curing.

4. Conclusions

In conclusion, melamine-based compounds bearing reactive groups (MAOs) allowing both UV and thermal curing were evaluated as dual-curable materials for PSAs. The photo-curing abilities of MAOs were slightly less than those of TMP(EO)TA due to the rigid melamine core, but they could be controlled by varying the number of acrylate groups substituted onto the melamine core. In photo-shrinkage, the MAOs were shrunk less than the TMP(EO)TA because of their large sizes. Following the dual-curing process, the storage modulus of the MAO-containing PSA was maintained at approximately 3E6 dyne/cm², even at high temperature. In particular, the MAOs were excellently tolerant to heat exposure and could thus afford highly cohesive cured materials after sufficient thermal curing.

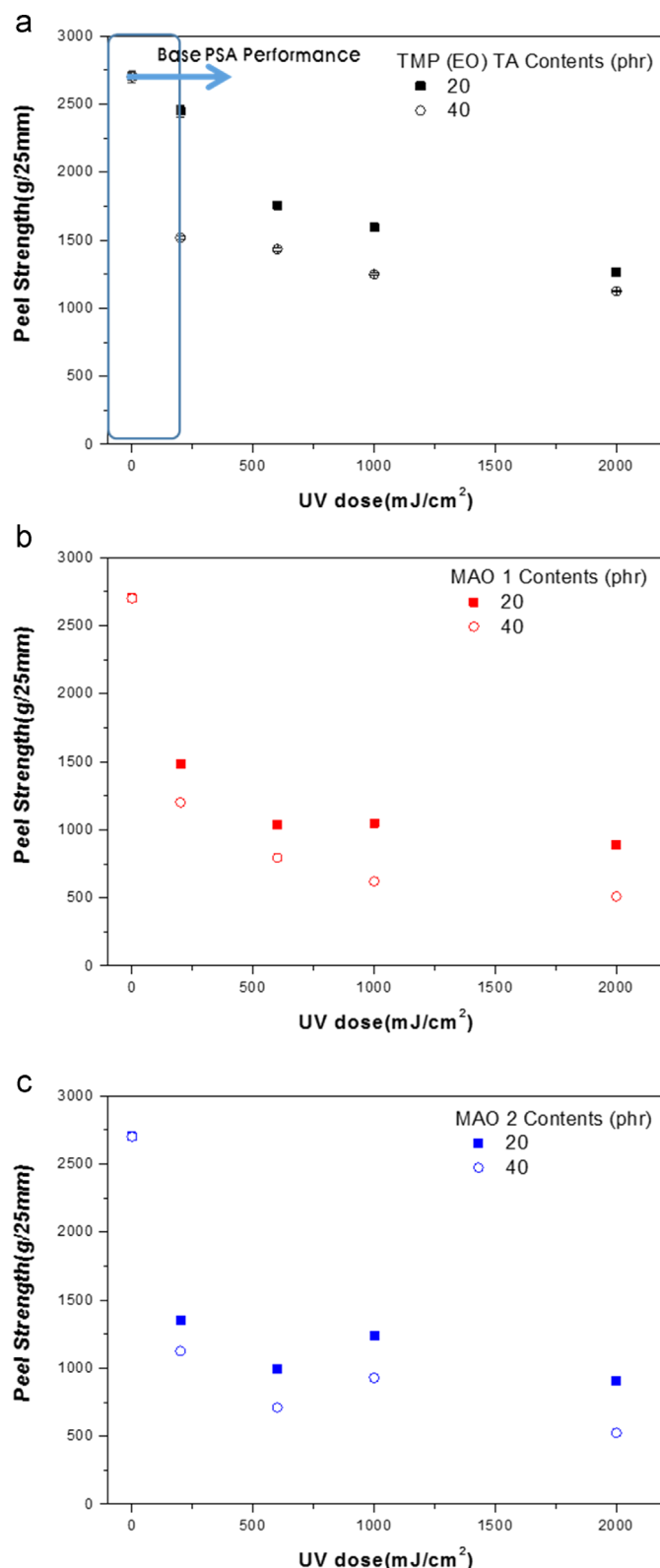


Fig. 6. Peel strengths according to UV dose of curable PSAs consisting of synthesized base pre-polymer and (a) TMP(EO)TA, (b) MAO-1, or (c) MAO-2 in the presence of 2.5 phr of each photo initiator (CP-4 and HP-8) after UV-curing process (squares: 20 wt% curable material; circles: 40% curable material).

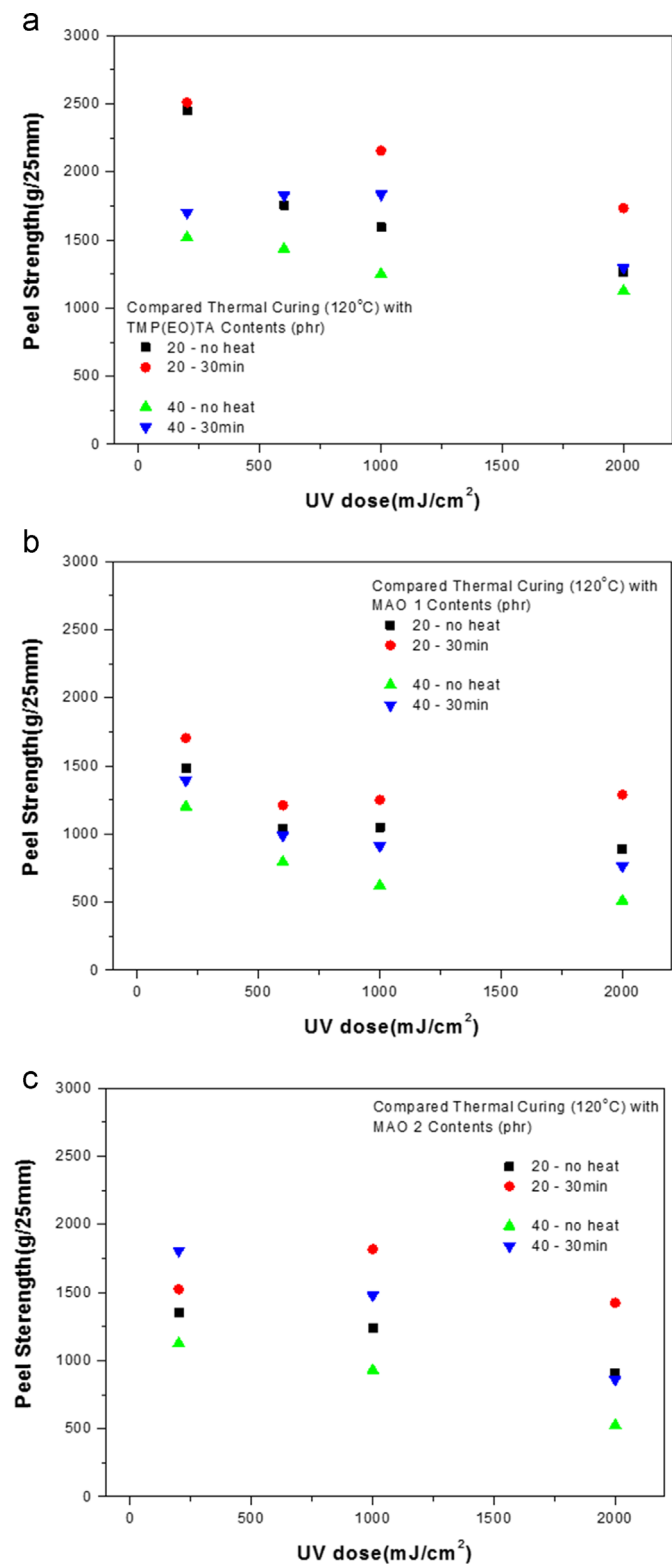


Fig. 7. Peel strengths according to UV dose of curable PSAs consisting of synthesized base pre-polymer and (a) TMP(EO)TA, (b) MAO-1, or (c) MAO-2 in the presence of 2.5 phr of each photo initiator (CP-4 and HP-8) after UV curing (black squares: 20 wt% curable material; green triangles: 40% curable material) and subsequent thermal-curing at 120 °C for 30 min (red circles: 20 wt% curable material 30 min thermal treatment; blue inverted triangle: 40% curable material 30 min thermal treatment). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

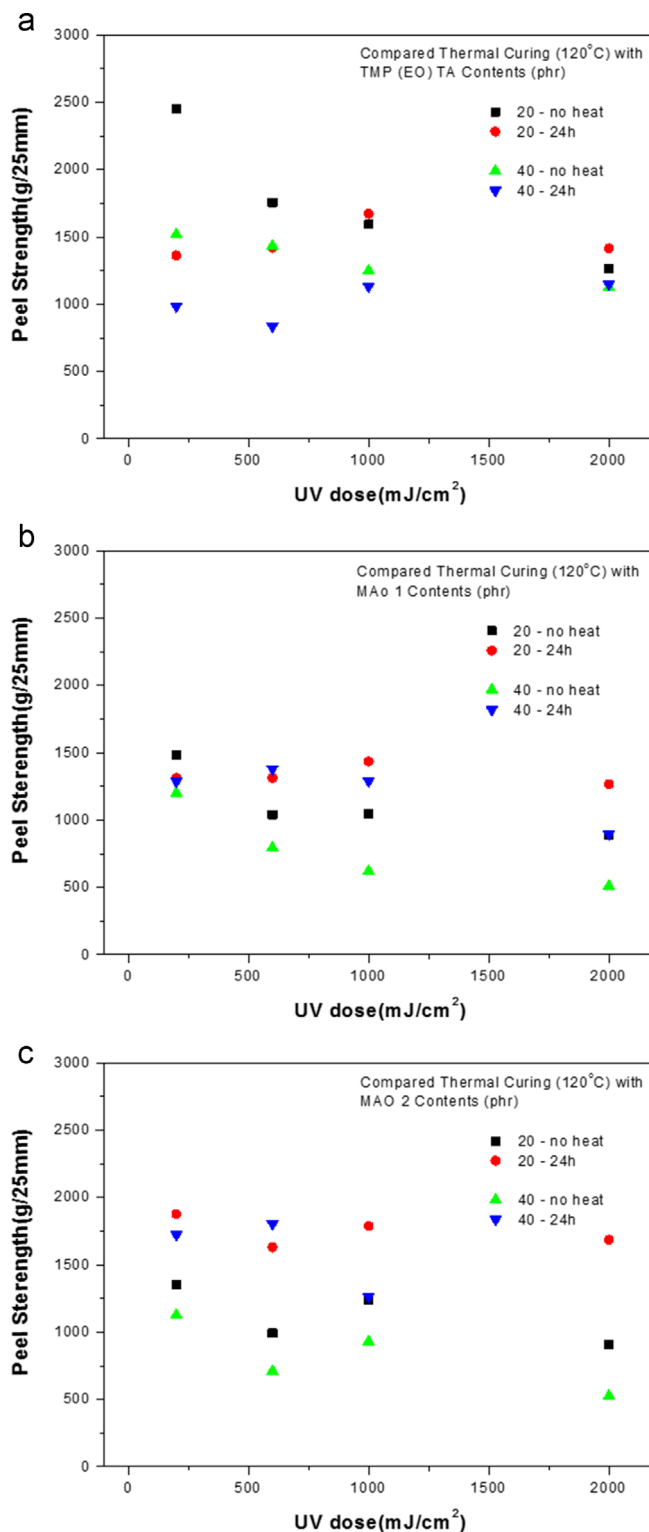


Fig. 8. Peel strengths according to UV dose of curable PSAs consisting of synthesized base pre-polymer and (a) TMP(EO)TA, (b) MAO-1, or (c) MAO-2 in the presence of 2.5 phr of each photo initiator (CP-4 and HP-8) after UV curing (black squares: 20 wt% curable material; green triangles: 40% curable material) and subsequent thermal-curing at 120 °C for 24 h (red circles: 20 wt% curable material; blue inverted triangles: 40% curable material). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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