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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*-methoxylmethyl 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/cm^2, 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.

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*-methoxylmethyl 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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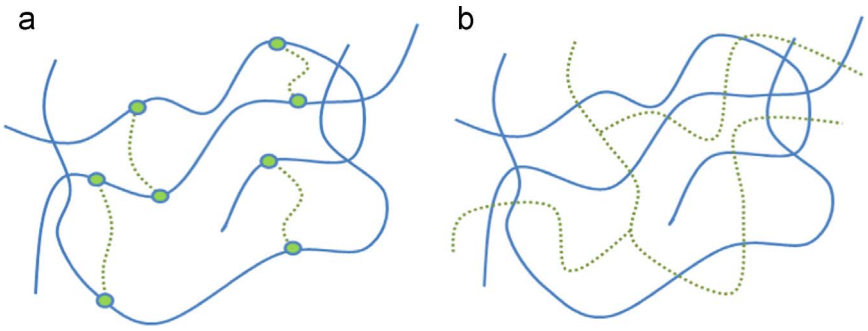

Fig. 1. Two types of crosslinking by (a) crosslinking agent and (b) entanglement.

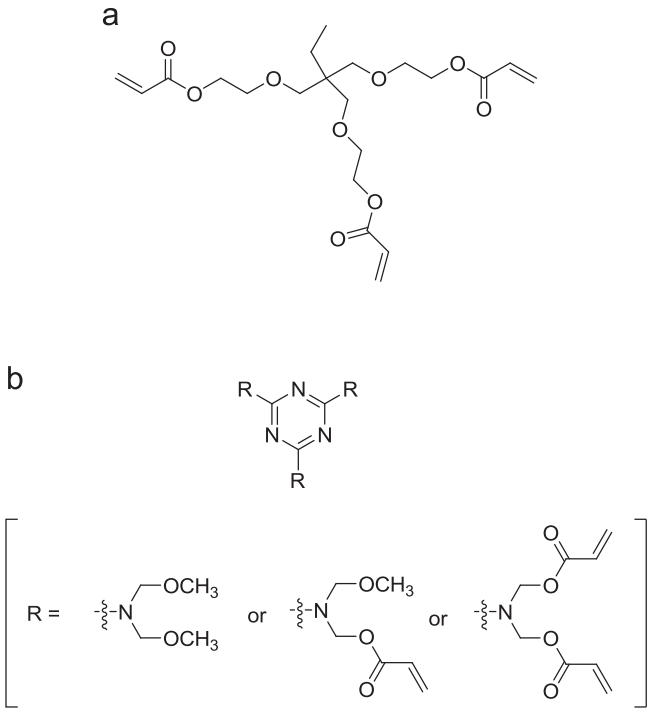

Fig. 2. Chemical structures of (a)TMP(EO)TA and (b) MAOs (sum of *N*-methylmethoxy groups and *N*-methyl acrylate groups on one melamine core is 6).

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 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.

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

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 (CP4- 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 conveyer 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/cm^2 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/cm^2 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.