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Investigation of the thermal degradation of polyacrylate adhesives by evolved gas analysis–(gas chromatography)–mass spectrometry

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ABSTRACT

The thermal degradation behavior and the stability of polyacrylate adhesives were evaluated by evolved gas analysis–mass spectrometry (EGA–MS) and evolved gas analysis–gas chromatography/mass spectrometry (EGA–GC/MS). Thermal degradation processes of two steps for adhesives 1 and 2 were found from EGA–MS analysis, and the evolved gases from each thermal zone were analyzed by EGA–GC/MS. The degradation products and a residual monomer caused by isobornyl acrylate of adhesive 1 were evolved from 100 °C to 170 °C. These fumes are able to cause a failure of the optical transparency of double-sided ITO (Indium tin oxide) film throughout the ITO crystallization process. The thermal degradation of adhesive 2 occurred at a higher temperature of ca. 50 °C compared to adhesive 1. Consequently, adhesive 2 is more thermo-stable than adhesive 1.

1. Introduction

Pressure-sensitive adhesives (PSAs) are the primary materials used to attach surfaces between diverse substrates through the properties of adhesion and cohesion [1]. PSAs are distinguished from general-purpose adhesives as they can be attached or detached several times from the surfaces with a slight pressure while leaving no residue behind. Furthermore, they are characterized by their ability to wet a surface and adhere quickly (tack property), their resistance to removal by peeling from an attached surface (adhesion property) and the ability to hold in position when shearing forces are exerted (cohesion property) [2]. These adhesives can be generally classified into solvent-based, water-based, and solvent-free forms. PSAs have been widely used as important materials in the fields of electronics, automobiles, and optical devices owing to their unique properties [3–5]. Among them, PSAs play a key role in the manufacturing of electronic devices. These adhesives provide special properties in double-sided adhesive tapes and protective films associated with IT devices.

Indium tin oxide (ITO) is one of the most widely used transparent conducting materials because of its high electrical conductivity, wide electrochemical potential window, and good optical transparency, as well as the ease with which it can be deposited as a thin film [6]. For this reason, adhesives used for double-sided ITO films require the property of optical transparency. In some cases, fumes evolve from adhesives under the high temperature conditions of the ITO crystallization process. Due to these evolved fumes, the transparency of the ITO film decreases and a failure in the optical transparency occurs owing to the increased haze of the ITO film. Therefore, it is essential to understand the thermal degradation behavior of adhesives in various thermal environments.

Many analytical methods have been used to characterize the thermal degradation behavior of polyacrylates, such as thermogravimetric analysis [7–11], spectroscopic analysis [12] and pyrolytic analysis [13–16]. In previous studies, we reported the thermal degradation behavior of rigid and soft polyurethanes using EGA–MS (evolved gas analysis–mass spectrometry) and EGA–GC (gas chromatography)/MS [17]. In comparison with Pyrolysis GC/MS, the EGA–MS and EGA–GC/MS methods have the advantage of providing analytical results for polymer degradation according to the thermal zone. In this study, we applied the EGA–MS and EGA–GC/MS methods to investigate the thermal degradation behavior of PSAs used for double-sided ITO film. In addition, evolved fumes, such as the residual monomers, were analyzed using this technique.

2. Experimental

2.1. Sample preparations

All materials were technical grade and used without further purification. Adhesive 1 and adhesive 2 were synthesized from BA

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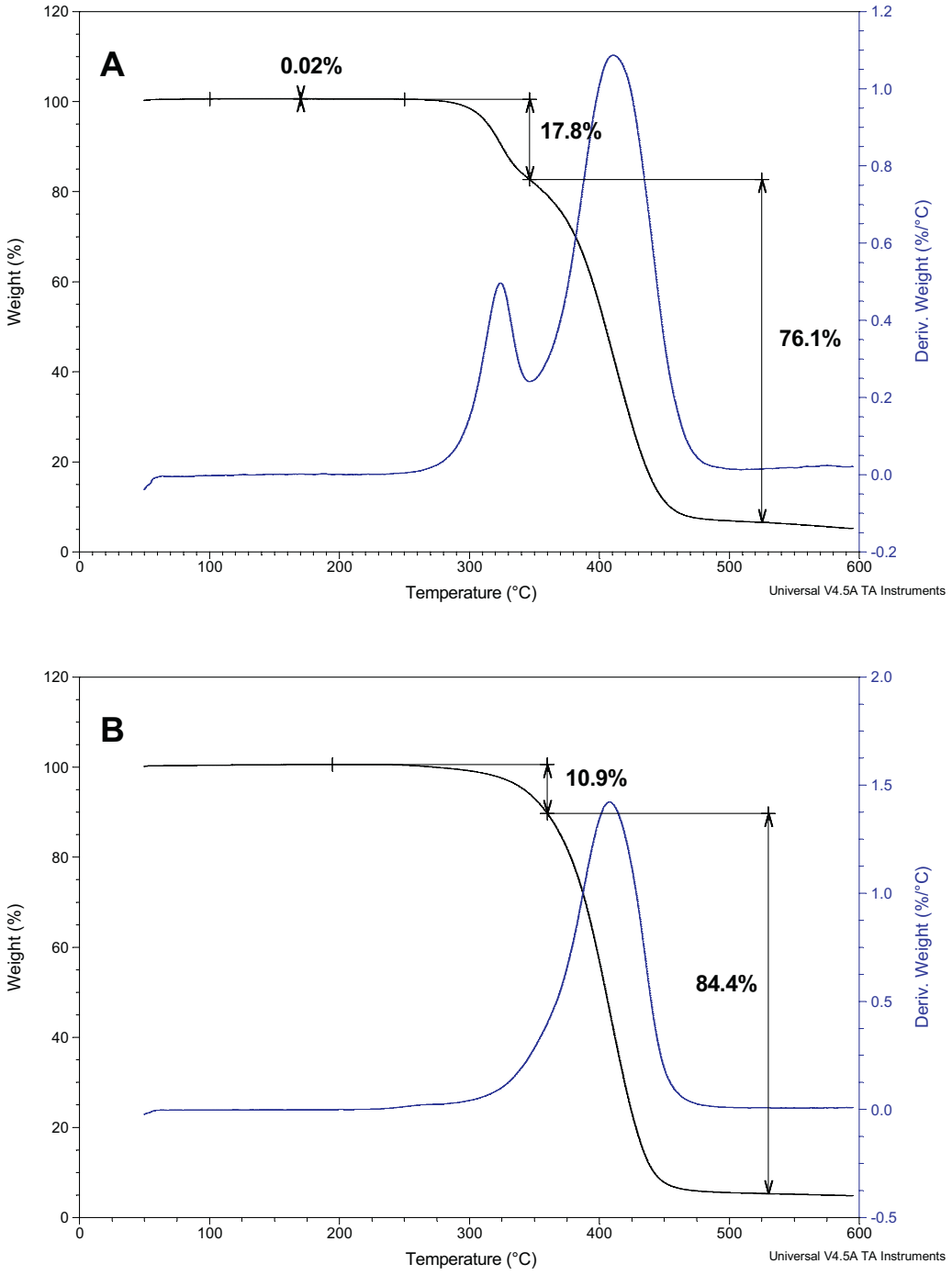

Fig. 1. TG and DTG curves of adhesive 1 (A) and adhesive 2 (B) from 50 °C to 600 °C at a heating rate of 10 °C/min.

(butyl acrylate), MTA (2-methoxyethyl acrylate), IBOA (Isobornyl acrylate), MA (methyl acrylate), and HEA (2-hydroxyethyl acrylate) (15/40/20/15/10, w/w (%)), and EHA (2-ethylhexyl acrylate), MA, and HEA (50/40/10, w/w (%)) using ethyl acetate as the solvent. Polymerization was performed at 65 °C for 8 h under N_2 atmosphere. In addition, 500 ppm of AIBN (2,2′-azo-bis-diisobutyronitrile) was used as the thermal initiator in radical polymerization. After solvent dried, total solid contents of adhesive 1 and adhesive 2 were about 25%.

Gel permeation chromatography (Alliance 2695 equipped with 2414 refractive index detector, Waters, MA, USA) was used to analyze the weight-average molecular weight (M_w) and polydispesity index (M_w/M_n) of polyacrylate adhesives. The analysis results show that the weight-average molecular weight is 7.0×10^5 g/mol for adhesive 1 and 1.4×10^6 g/mol for adhesive 2, the polydispersity index is 5.0 for adhesive 1 and 4.0 for adhesive 2.

The prepared acrylate polymers were coated on PET (polyethylene terephthalate) film without further purification, and dried at 120 °C for 30 min. Approximately 500 μg of adhesive sample taken from these adhesive films was used in each of the EGA–MS and EGA–GC/MS analysis.

2.2. Instrument conditions of EGA–MS, EGA–GC/MS, and TGA

Py–GC/MS was employed in the EGA–MS and EGA–GC/MS analysis. Py–GC/MS consists of a PY-2020iD double-shot pyrolyzer