



Effect of the interfacial structures of alkyl-side-chain polymer films on the peel force



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ABSTRACT

Poly(ethylene-co-vinyl-*n*-octadecyl carbamate) (PEVODC) belongs to the general class of long alkyl side chain polymers, which are widely used as release coatings for pressure-sensitive adhesive (PSA) tapes. The physical and structural properties of PEVODC films and the mechanisms of the adhesion/abhesion processes were investigated using surface sensitive techniques. The surface free energies and the surface roughnesses of two films with different peel forces did not differ significantly. This suggests that surface free energy and surface roughness has little effect on the peel force. In contrast, sum frequency generation spectroscopy and X-ray diffraction analysis results showed that the orientation and crystallinity of the polymer that had the lower peel force were superior to those of the polymer with the higher peel force. This indicates that polymer orientation and crystallinity has a major effect on the peel force developed at the PEVODC/adhesive interface. The formation of highly ordered crystalline domains on the PEVODC surface effectively decreases the peel force. Finally, the intercalation of the polymer chains of both adhesives and release agents as well as the entanglement of polymers play critical roles in determining the adhesion/abhesion characteristics of the PEVODC coating.

1. Introduction

Pressure-sensitive adhesives (PSAs) are widely used in everyday and industrial applications, such as packaging, masking, and protecting tapes. PSAs simply form a bond with the adherend on application, with no chemical reactions taking place. For ease of use, one side of the adhesive is coated with a release agent in order to reduce the force required for peeling [1]. The release agents used can be broadly classified into two types: a) silicones and b) non-silicones. Highly cross-linked silicones provide good thermal stability. Although polydimethylsiloxane is a commonly used silicone, polycondensation on the base resin sheet is a complicated process. Non-silicone agents include polyolefin waxes and long-alkyl-chain polymers. For example, poly(vinyl carbamate), composed of poly(vinyl alcohol) and alkyl isocyanates, is widely used in PSA tapes.

To manufacture PSA tapes, base resin sheets are coated with a release agent solution in an organic solvent, followed by drying. It is well

established that drying conditions such as the temperature, time, solvent, and release agent concentration determine the release characteristics of the PSA. The peel force is a particularly critical property because it directly affects both the required release energy and the peel-off sensation. Drying usually takes place at temperatures as high as 100 °C. This annealing process is not only important for drying polymer films but also for minimizing the peel force. Nevertheless, thorough investigations of the drying mechanism of PSA films are limited.

On the other hand, many studies have investigated the adhesion/abhesion mechanisms of PSAs. Surface roughness is another influential factor because it is related to the contact surface area [2,3]. The correlation between surface free energy (γ) and peel force has been the focus of previous studies [4–6]. In particular, the surface free energy of long-unbranched-side-chain polymers, including poly(vinyl carbamate), has been thoroughly studied [7]. Reported free energy values ranged from 20 to 29 mJ m⁻², which are comparable to those of methyl groups (19–20 mJ m⁻²) and methylene groups (32–34 mJ m⁻²). This

Abbreviations: PEVODC, Poly(ethylene-co-vinyl-*n*-octadecyl carbamate); PSA, pressure-sensitive adhesive

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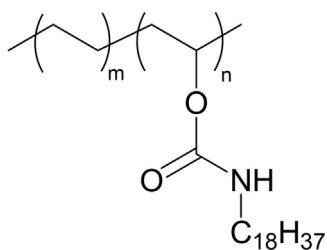


Fig. 1. Chemical structure of PEVODC, where m and n denote the relative mole fractions.

suggests the emergence of alkyl groups on the surface. Although the aforementioned parameters have been recognized as major factors affecting adhesion, they cannot sufficiently explain the adhesion/abhesion phenomenon. The role of connector molecules, i.e., polymer chains bound to the interface, has also attracted researchers' attentions [6,8–12]. In this case, the entanglement of polymers or the intercalation of polymer chains of both adhesives and release agents occurs followed by an increase in the peel force. However, a detailed analysis of the phenomenon has not been performed.

In this study, poly(ethylene-co-vinyl-*n*-octadecyl carbamate) (PEVODC, Fig. 1) [13] was used as the conventional release agent for the development of PSA tapes. For a series of poly(ethylene-co-vinyl-*n*-alkyl-chain carbamate) compounds, alkyl side chains with less than 12 carbon atoms lead to a disordered surface structure, while long unbranched side chains are more appropriate for obtaining highly ordered structures with low-surface-free-energy methyl groups on their surfaces [7]. The fact that PEVODC consists of such octadecyl side chains and is readily available and appropriately priced makes it a promising release agent candidate. Further, PEVODC is well known for its resistance at high temperatures, a feature that has been attributed to the ethylene units in the main chain. It is available as a white powder and can be easily dissolved in organic solvents, such as toluene and ethyl acetate, to form easy-to-apply solutions.

The present study aims to provide insight into the effect of thermal treatment on the interfacial structures of PEVODC films and its subsequent correlation with the peel force. As already recognized, the peel force can be optimized by modifying the curing temperature during the coating of the release agent on the base substrate. Furthermore, the peel force is affected by the thermal history following contact of the adhesive with the release agent. Therefore, the structure and physical properties of coating films cured at different temperatures have been assessed by employing several surface analytical techniques.

2. Materials and methods

2.1. Materials

PEVODC was supplied by Lion Specialty Chemicals Co Ltd. and used as received. Its molecular weight was 279 kg/mol, polydispersity was 2.99 and the mole fraction of *n*-octadecyl carbamate units was 0.68.

2.2. Sample preparation

Thin PEVODC films were developed on both polyethylene terephthalate (PET) substrates and silicon wafers by the cast-coating and spin-coating method, respectively. A 2-wt% solution of PEVODC in toluene was used to prepare coatings under ambient conditions. A volume of 1.5 mL of the aforementioned solution was placed on the top edge of a 25- μ m-thick 15 \times 40 cm² PET substrate and immediately spread evenly to the bottom edge of the substrate using a glass bar coater. The thickness of the final film was approximately 25 nm as measured by the light interference method using an FE-3000 thickness monitor (Otsuka Electronics Co., Ltd.). In the latter method, 200 μ L of the PEVODC solution was applied to the center of a 1.5 \times 1.5 cm²

silicon wafer attached to the sample holder of a 1H-D7 spincoater (MIKASA Co., Ltd.) at 4000 rpm for 30 s. The PEVODC films were dried under two distinct sets of conditions. A set of films was dried at room temperature (RT) (i.e., as cast films) under ambient conditions, while a separate set was thermally annealed at a constant temperature of 100 °C for 1 min in a standard drying oven (DK400T, Yamato Scientific Co., Ltd.). The selected annealing temperature of 100 °C is higher than the temperature at which the second transition of PEVODC is anticipated to occur, according to the differential scanning calorimetry (DSC) data obtained in this study.

Self-supporting PEVODC films were also prepared by placing ca. 10 g of the 2-wt% solution of PEVODC in toluene in a box composed of the release liner. This was followed by the removal of toluene under ambient conditions. The films were subsequently cured under both ambient conditions and elevated temperature (100 °C) for 1 min in an annealing oven. The thickness of the final film was approximately 0.5 mm as measured using a caliper.

2.3. Peel test

A thin film of polymer prepared on flat PET film was placed on a No. 31B adhesive tape (Nitto Denko Corporation). After 2 h, the 180° peel force was measured using an AGS-J autograph (SHIMADZU Corporation). The test conditions were as follows: peel speed = 300 mm/min, tape width = 25 mm, temperature = 23 °C.

2.4. Sample characterization

Bulk polymer powders were analyzed by differential scanning calorimetry (DSC) using a Diamond DSC (Perkin Elmer, Inc.). Samples were held at 20 °C for 5 min, after which they were heated to 120 °C at 10 °C/min.

The surface morphologies of PEVODC films on PET substrates were assessed using an atomic force microscope (AFM, SPM9500J3, SHIMADZU Corporation) in tapping mode. Micrographs were obtained using a 30 μ m \times 30 μ m scanner and a rectangular silicon cantilever with an average spring constant of 4.0 \times 10¹ N/m.

Contact angle measurements using ca. 0.3 μ L of water (*w*) and diiodomethane (*d*) were obtained at RT with a CA-X contact angle meter (Kyowa Interface Science Co., Ltd.). Images of each droplet were obtained after 60 s of deposition. The surface tension of both water ($\gamma_w = 72.8 \text{ mJ m}^{-2}$, $\gamma_w^d = 29.1 \text{ mJ m}^{-2}$, $\gamma_w^p = 43.7 \text{ mJ m}^{-2}$) and diiodomethane ($\gamma_d = 50.8 \text{ mJ m}^{-2}$, $\gamma_d^d = 46.8 \text{ mJ m}^{-2}$, $\gamma_d^p = 4.0 \text{ mJ m}^{-2}$) [14] were used to calculate the surface free energies of the films according to the extended Fowkes equation [15,16].

The surface molecular orientations of the polymer films on PET substrates were investigated by infrared (IR)-visible sum frequency generation spectroscopy (SFG). A mode-locked Nd:YAG laser PL2143D (EKSPLA) with a wavelength of 1064 nm and a pulse width of 25 ps was used as the master light source. A tunable IR beam was generated by an AgGaS₂ crystal having a difference-frequency mixing of the fundamental light excited by the Nd:YAG laser using the output of a PG401 VIR/DFG optical parametric oscillator/amplifier system (EKSPLA). The visible and IR beams were overlapped on the sample surface at incidence angles of 70° and 50°, respectively. The SF output signal was filtered using a holographic notch filter and a monochromator (MS257, Oriol instrument) and they were subsequently detected by a photomultiplier tube (R649, Hamamatsu Photonics K. K.).

In-plane and out-of-plane X-ray diffraction (XRD) measurements were taken for PEVODC films on silicon wafers using a Rigaku SmartLab X-ray diffractometer equipped with a 9 kW (45 kV, 200 mA) rotating anode CuK α source ($\lambda = 0.154 \text{ nm}$) and a scintillation counter. For in-plane XRD, i.e., grazing incidence X-ray diffraction (GIXD), the incidence angle was set to 0.19° and the diffracted X-ray was collected at a detection angle of 1.31°. For the in-plane 2θ range lying between 0.5° and 10° ($q = 0.36\text{--}7.11 \text{ nm}^{-1}$) the increment was 0.01°, and for

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