



An effect of surface segregation of polyhedral oligomeric silsesquioxanes on surface physical properties of acrylic hard coating materials



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ABSTRACT

An effect of surface segregation of polyhedral oligomeric silsesquioxanes (POSS) on surface physical properties was investigated. Hard coating layer with various MA₈POSS loadings was prepared on a bilayer of soft layer and PMMA substrate via a UV curing process. The scratch resistance of the coating layer showed specific properties. When MA₈POSS loadings in the coating layers were less than 10 wt %, the coating layers showed a great performance in scratch resistance. While MA₈POSS loadings were higher than 10 wt %, the surface performance was deteriorated. This is because the outermost surface of the coating layer was covered by MA₈POSS molecules when the MA₈POSS loadings were higher than 10 wt %, resulting in uncompleted curing reaction caused by large steric hindrance of MA₈POSS.

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1. Introduction

Hard coating materials for polymers with high transparency and scratch resistance that were prepared by acrylic derivatives have been widely used for various applications such as optical lenses, displays for electronic devices, automobile parts, etc. [1–5]. In general, they are prepared onto base materials by coating mixture of acrylates derivatives and photocatalyst dissolved in an organic solvent, cured by ultraviolet (UV) irradiation. The curing reaction leads to the formation of a three-dimensional network, resulting in a high scratch resistance [6,7]. So far, performance of these coating

materials was improved on the basis of hybridization with inorganic compound having good miscibility with the acrylates derivatives [8–10]. Polyhedral oligomeric silsesquioxane (POSS) is among the best candidate to improve the properties. POSS is organic-inorganic hybrid material, which has cubic cage with the silicon atoms at the corners and oxygen atoms interspersed along the edges. Multifunctional groups can be introduced into the eight corners, leading to a tunable performance [11–16]. Recently, acrylate functionalized POSS with long alkyl chains has been widely used as inorganic nanocomposite in hard coat agent [17,18], because long alkyl chain and acrylate groups are expected to promote miscibility and reactivity for hard coat agents.

The scratch resistance has closely related to a degree of conversion in the curing reaction [6,7]. It is widely accepted that the degree of conversion decreased with increasing steric hindrance surrounding the acrylate groups [19]. As POSS having large steric hindrance, the curing reaction might be suppressed when high concentration of POSS was added to the hard coat agents. Also, the surface free energy of acrylate functionalized POSS is relatively smaller than that of hard coat agents. When the POSS molecules are

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mixed with hard coat agents, it is expected that they preferentially segregate to the surface, leading to a high concentration of POSS. This phenomenon suppresses the curing reaction. However, an effect of the curing reactivity caused by surface segregation on scratch properties for hard coating materials is still unclear. In this study, we will report preparation of hard coating layer including methacrylate functionalized POSS on a bilayer of soft layer and PMMA substrate, and discuss the effect of surface segregation on the scratch properties.

2. Experimental

2.1. Materials

Pentaerythritol triacrylate (PETA), 1-hydroxycyclohexyl phenyl ketone (photo-initiator), trimethylolpropane ethoxylate triacrylate (soft base layer) and poly (methyl methacrylate) (PMMA) substrates were provided by Kaneka Corporation (Osaka, Japan). Multi-functional methacrylate-POSS (MA₈POSS) was purchased from Hybrid Plastics (Hattiesburg, MS). All materials were used as received. The chemical structures of PETA and MA₈POSS molecule are shown in Fig. 1.

2.2. Sample preparation

PETA/MA₈POSS hard coating layers were prepared by UV curing technique with varying MA₈POSS loadings. PETA and MA₈POSS were mixed with 5 wt % of photo-initiator and magnetically stirred at room temperature for 30 min. The mixture was coated on bilayer of 5 μm soft layer and 2 mm PMMA substrate using Mayer rod applicator. The films were exposed under UV light with gradually increased light intensity to inhibit film deformation for 30 min. The thickness of PETA/MA₈POSS coating layers was 30 μm.

2.3. Characterization

A progressive load scratch test (ISO 19252) was conducted at room temperature using scratch machine KK-02 (KATO Tech Co., Japan) with 1 mm in diameter stainless steel spherical tip. Normal load was linearly increased from 1 to 20 N. Scratch velocity and scratch length was set at 100 mm/s and 70 mm, respectively. Five tests were performed per each condition. To observe surface damage feature on the coating layer surfaces, VK-X200 laser scanning microscope (Keyence Corporation) was used. Degree of conversion of each coating layer was evaluated using attenuated total reflectance infrared (ATR-FTIR) (Spectrum One FT-IR Spectrometer, Perkin Elmer Instrument, USA) equipped with an ATR accessory (Ge crystal, 45°). Each spectrum was collected with 4 cm⁻¹ resolution and 64 scans in the range of 4000–650 cm⁻¹. Flexural properties were measured at room temperature with crosshead speed of 1 mm/min. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) (PHI-5000 VersaProbe II, ULVAC-PHI Inc., Japan) was utilized to investigate the chemical composition of the

coating layer surfaces using monochromatic Al Kα source (15 kV and 25 W). The static contact angle was measured at room temperature using automatic contact angle meter DSA10 (Krüss, Ltd.). 2.0 μL of water and diiodomethane droplet were deposited onto the coating layer surfaces. The mean value was calculated from 8 measurements.

3. Results and discussion

3.1. Effect of MA₈POSS loadings on scratch resistance

The progressive load scratch test according to ISO 19252 was performed to evaluate surface fracture behavior of the hard coating layer containing MA₈POSS on bilayer of soft layer and PMMA substrate. This test method provides valuable information about scratch damage transitions and quantitative data for scratch resistance indicated by critical normal load for onset of scratch damage mechanisms [20]. Details of scratch damage transitions of each coating layer containing various MA₈POSS loadings were carefully observed using laser scanning microscope. Fig. 2 shows a typical surface damage transition of the hard coating layers. In all coating layer systems, two damage transitions including abrasion in first region and coating delamination in second region were seen along the scratch groove as normal load linearly increased from 1 to 20 N. The damage transition in the first region began from no damage to abrasion due to smooth indentation of scratch tip, and the abrasion became more severe with increasing the normal load. The damage transition in the second region, i.e., coating delamination was observed as the normal load further increased. At this region, the scratch tip was ploughed through the coating layer surface, resulting in the removal of the coating layer from the substrate. Subsequently the substrate was exposed and damaged by penetration of the scratch tip.

To clarify the effect of MA₈POSS loadings on the scratch resistance, the surface damage at 14 N of normal load was compared as shown in Fig. 3. It was clearly seen that only abrasion damage was observed in the coating layers containing 3 to 10 wt % of MA₈POSS loadings and the lower MA₈POSS loadings led to milder abrasion damage (Fig. 3b–e). Whereas coating delamination was observed in PETA coating layer (Fig. 3a) and the coating layers containing MA₈POSS at high loadings (>10 wt %) (Fig. 3f–g). These results were correlated to the scratch coefficient of friction (SCOF) (Fig. 4). The SCOF which is defined as the ratio of the tangential force to the normal force, is used to determine the scratch resistance for the coating layer [21]. The high fluctuation of the SCOF at a beginning stage was related to the inertia effect as the scratch tip experienced sudden change in speed from 0 to 100 mm/s [2]. In the PETA coating layer and the coating layers containing MA₈POSS higher than 10 wt %, the slope of the SCOF curves at scratch length about 50 mm (14 N of Normal load) rose dramatically. This region was related to the beginning of coating delamination. After that, the large fluctuation was observed due to the penetration of scratch tip through the coating layer and substrate deeper [2,22]. While, the SCOF curves of the coating layers with MA₈POSS less than 10 wt % were lower than those of the coating layers containing high MA₈POSS loadings. This related to the occurrence of abrasion. These results indicated that the amount of MA₈POSS loadings affected surface damage behavior. The incorporation of MA₈POSS loadings into the coating layers less than 10 wt % resulted in mild damage and lower SCOF.

To demonstrate how the coating layers are able to withstand scratches in quantitative method, a critical normal load at onset of scratch damage transition is the common parameter for defining the scratch resistance [23]. In this work, coating delamination was chosen as an interesting damage mechanism. As mentioned above, at this point, the coating layer was removed from the substrate,

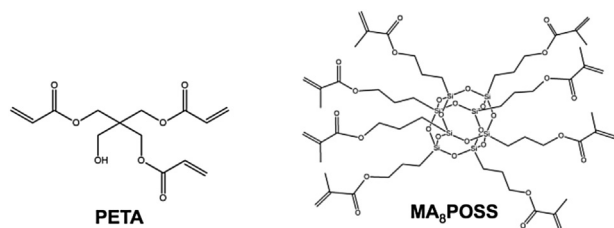


Fig. 1. Chemical structures of PETA and MA₈POSS.

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