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Effect of methacryloxypropyl and phenyl functional groups on crosslinking and rheological and mechanical properties of ladder-like polysilsesquioxane hard coatings

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ABSTRACT

The rheological and mechanical properties of photocurable ladder-like polysilsesquioxanes containing phenyl and methacryloxypropyl groups (LPMA) were investigated. LPMAs with various ratios of the two functional groups were synthesized through the hydrolysis and condensation reactions. The chemical structures of the synthesized LPMAs were confirmed using H^1 NMR and FT-IR spectroscopy. The basic rheological properties of the LPMA solutions provided information about their flow properties prior to the curing stage, which was relevant for their application as a hard coating. The curing behaviors of the LPMA solutions under UV irradiation were scrutinized using real-time rheological measurements and rigid-body pendulum tests. These results were well correlated with the surface mechanical properties of the final cured LPMA films measured via nano indentation and scratch tests. The phenyl group was found to play a role in providing rigidity to the cured films, and the methacryloxypropyl group affected crosslinking performance. The physical properties of LPMA samples could be improved for application as a promising inorganic-organic hybrid coating by tuning the ratio of two functional groups.

1. Introduction

Radiation curing technology has been highlighted as a useful hardening method for curable coatings that reduces the risk of thermal damage on sensitive materials, such as woods, papers, and plastics. The UV irradiation process has several advantages, including its high curing rate, good energy efficiency, low gas emissions, and the superior anti-scratch features of the cured products, which make this technique effective for the production of organic coating materials (e.g., epoxy, ester, ether, urethane, etc.) [1–3].

Organic coating products with densely crosslinked networks sometimes exhibit critical inherent defects, such as low heat or oxidation resistance and yellowing phenomena [4–6]. To compensate for these vulnerable points, inorganic-organic hybrid materials in which inorganic components reinforce the organic coatings have been explored. Their remarkable optical properties, scratch resistance [7,8], and anti-abrasive characteristics [9–11] have expedited the development of hybrid coating materials.

Silicon-based polysilsesquioxanes could be classified into random branched silsesquioxanes, i.e., polyhedral oligomeric silsesquioxane (POSS) and ladder-like structured polysilsesquioxane (LPSQ). Among them, LPSQs have attracted great attention as promising inorganic-organic coatings for their superior thermal, chemical, and mechanical stabilities, which result from their unique double-stranded siloxane backbone structures [12]. It has been previously reported that LPSQs with various functional groups have been synthesized, and their structural and physical properties have been characterized by various methods [13–16]. However, the real-time curing behavior of LPSQs during the photo-curing process and the relationship between their rheological and mechanical properties have not been fully elucidated yet. To shed light on the complicated network features of inorganic-organic coatings, and optimally tune the cured film properties and coating performance, real-time analysis during the curing process is required [17–19].

The in-situ crosslinking kinetics of various UV- or thermal-curable materials can be featured by techniques such as photo or thermal differential scanning calorimetry (DSC), real-time Fourier-transform infrared spectrometry (FT-IR), rotational rheometry, and rigid-body

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pendulum testing. DSC is generally used to detect the onset and peak point of thermal or photo-induced crosslinking via reactive heat flow during the initiation and propagation steps. Real-time FT-IR, also known as RT-IR, can be useful to monitor the conversion rate and degree of coating materials [20,21]. These methods, however, have critical limitations in describing detailed network formation. Therefore, real-time curing measurements using a rigid-body pendulum tester and a rotational rheometer could be useful alternatives to identify the curing features of various coatings. A rigid-body pendulum tester equipped with a UV lamp can be used to evaluate the curing rate and rigidity of thin films [22–25]. The period and logarithmic damping ratio of a pendulum placed on the coated film change with time during the curing process. A rotational rheometer with a UV irradiation module can monitor the viscoelastic response of bulk curable materials against oscillatory strain [26–29]. The obtained elastic modulus (G’) is an indicator of solid-like behavior, and its evolution during curing quantitatively describes the development of a crosslinking network.

In this study, various types of ladder-like structured poly(phenyl-co-methacryloxypropyl) silsesquioxane (LPSQ) were synthesized through well-known hydrolysis and condensation reactions [13–16] incorporating different ratios of the phenyltrimethoxysilane and methacryloxy-propyltrimethoxysilane monomers. The chemical structure of the LPSQs synthesized with different phenyl and methacryloxypropyl functional group contents (referred to as LPMAs) and ratios of the functional groups are presented in Fig. 1 and Table 1. All the LPMA samples, regardless of their original phases (liquid or solid), were dissolved in tetrahydrofuran (THF). Subsequently, the real-time rheological and mechanical characteristics of various LPMA coatings were monitored during all curing steps, focusing on the effect of the functional group (phenyl and methacryloxypropyl) ratio. Before the UV curing process, the basic properties of the LPMA solutions, i.e., their shear viscosities (η) and elastic and viscous moduli (G’ and G’’) were measured using a rotational rheometer [17–19]. Their real-time curing behaviors were characterized using a rotational rheometer [22–25] and a rigid-body pendulum tester [26–29] equipped with UV irradiation modules. The indentation hardness and depth-force curve of the cured LPMA films were quantitatively determined using a nano indentation tester. Finally, the anti-scratch properties of the cured films were predicted using a nano scratch tester equipped with a built-in atomic force microscope (AFM) and optical microscope. The overall physical properties of the LPMAs were interpreted and correlated on the basis of the property measurements obtained through the entire UV curing process [30–35].

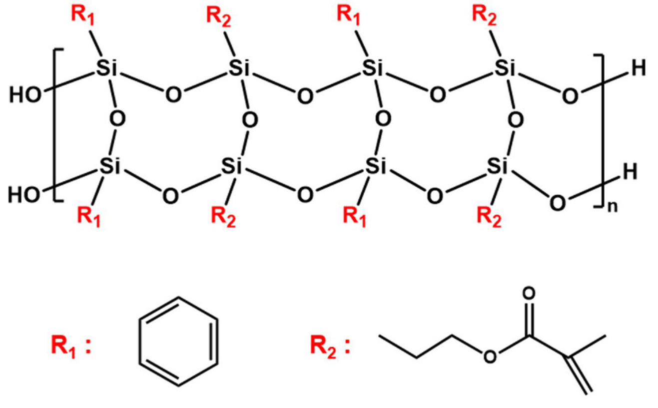

Fig. 1. The chemical structure of ladder-like polysilsesquioxane with the phenyl (R_1) and methacryloxypropyl (R_2) functional groups.

Table 1
LPMA samples with various molar ratios of phenyl and methacryloxypropyl functional groups.

Sample	Molar ratio of side groups (mol %)[a]		M_w[b] (kg mol^{-1})	Remark
	Phenyl	Methacryloxypropyl		
LPMA19	10	90	7	Liquid type
LPMA28	20	80	9	
LPMA46	40	60	15	
LPMA64	60	40	24	Solid type
LPMA82	80	20	13	
LPMA91	90	10	9	

[a] Calculated by ^{1}H NMR.
[b] Analyzed by GPC using polystyrene standard.

2. Experimental

2.1. Materials

Phenyltrimethoxysilane (PTS, Dynasylan® 9165, Evonik), 3-methacryloxypropyl-trimethoxysilane (3-MPTS, Dynasylan® MEMO, Evonik), tetrahydrofuran (THF, 99.9%, Sigma-Aldrich), dichloromethane (DCM, 99.5%, Daejung Chemical), deuterated chloroform ($CDCl_3$, 99.8%, Sigma-Aldrich), anhydrous magnesium sulfate ($MgSO_4$, 99%, Daejung Chemical) and Irgacure®184 (BASF) were used as purchased. Potassium carbonate (K_2CO_3, 99.5%, Daejung Chemical) was dried in a vacuum oven at 40 °C overnight prior to use. Deionized (DI, 18.2 MΩ cm) water was prepared with the Millipore Milli-Q purification system.

2.2. Synthesis of LPMAs and preparation of LPMA solutions

The ladder-like structured LPMAs were synthesized through the conventional hydrolysis and condensation reactions using PTS and 3-MPTS monomers, according to previously reported synthetic procedures [13–16]. Briefly, a mixture of K_2CO_3 (0.04 g, 0.29 mmol), DI water (4.8 g, 0.267 mol), and THF (8 g, 0.110 mol) was prepared in a 100 mL round-bottomed flask. Next, a mixture (0.08 mol) of PTS and 3-MPTS was added to the prepared solution mixture with purging nitrogen gas and vigorously stirred at room temperature for 96 h. After the reaction, the mixture was separated into a colorless aqueous and a cloudy organic phase. Then, the viscous product in the organic phase was dissolved in DCM and extracted with DI water three times. After DI water was removed, the drying agent ($MgSO_4$) was added to the product solution, which was stirred overnight and subsequently filtered out. DCM was then evaporated off at 40 °C from the product solution to obtain the final product of LPMA. The ratio of the functional groups of LPMAs was systematically controlled by adjusting the composition of each monomer, as shown in Table 1. The UV curable methacryloxypropyl group enables LPMA films to have a high crosslinked network by the UV curing process and the phenyl group also plays a significant role in the enhancement of the mechanical properties and rigidity of the cured LPMA films [13–16]. The synthesized LPMAs were dissolved in THF with the weight ratio of 60:40 and then Irgacure®184 (1 wt% of LPMA solutions) was added as a photoinitiator to observe the crosslinking behavior of various LPMA solutions during the curing process.

2.3. Characterization of LPMAs

A gel permeation chromatography (GPC) system was used to measure weight average molecular weight (M_w) of the synthesized LPMAs. GPC analysis was carried out at a flow rate of 1 mL min^{-1} at 40 °C. Polystyrene (M_w: 1,440; 2,980; 7,600; 20,300; 46,900; 120,000; 271,000; 715,000) was selected as a standard material to calibrate the column. The LPMAs were dissolved in $CDCl_3$ and their chemical structures were characterized using ^{1}H nuclear magnetic resonance (^{1}H