Progress in Organic Coatings 77 (2014) 184–193

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Synthesis and characterization of silicone-modified polyester as a clearcoat for automotive pre-coated metals

Yong-Hee Lee [a], Hyun-Joong Kim [a,b,*], Steven Schwartz [c], Miriam Rafailovich [d], Jonathan Sokolov [d]

[a] Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science Seoul Natioal University, Seoul 151-921, Republic of Korea
[b] Research Institute for Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Republic of Korea
[c] Department of Physics, Queens College, Flushing, NY 11367-1597, USA
[d] Chemical & Molecular Engineering, Department of Materials Science & Engineering, State University of New York at Stony Brook, NY 11794-2275, USA

ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form 17 August 2013
Accepted 12 September 2013
Available online 15 October 2013

Keywords:
Polyester
Pre-coated metals
Formability
Deep drawing
Clearcoat
Semi-removable

ABSTRACT

Four types of silicone-modified polyester resins were synthesized for cleanable characteristics with silicone intermediate, which has a long chain, to extend the polymer chains of the resins. These resins were formulated to make polyester/melamine heat-cured coatings to control the formability. The characteristics, viscoelastic behavior and flexibility of the resins were measured by DMA and tensile test. The contact angle measurement can be measured by the water repellence of the coating surface, which is a standard method to evaluate cleanable characteristics. The surface free energy was calculated by the contact angle measurement, and the surface analysis of each cured coating was evaluated using an XPS. Silicone-modified polyester coatings were coated on the cold rolled steel sheets to verify their formability, using a deep drawing test. Results showed that the storage modulus decreased, and the glass transition temperature shifted to a lower temperature with increasing contents of silicone intermediate. So, silicone intermediate provides lower stiffness and higher softness to polyester coating. To analyze the formability, we calculated F_U (the forming coefficient based on strain energy) and F_ε (the forming coefficient based on strain). When F_U and F_ε are both larger than 1, the polyester coatings have good formability. CSiPE-3 and CSiPE-5 had good formability. Also, CSiPE-5, which had the highest amount of silicone intermediate, had 93.5° of water contact angle, and had 26.5 mN/m of surface free energy and had 5.5 N/25 mm of the peel strength. So, it is implied that silicone intermediate can give a low surface energy and peel strength to polyester coatings. From those tests, the polyester/melamine coating of CSiPE-5 that had 0.5 mol of silicone intermediate had good formability and low peel strength, which are semi-removable characteristics. So, it would be an appropriate coating as a clearcoat for automotive pre-coated metals.

1. Introduction

Pre-painted or coil-coated metals (PCM) have been used in many applications, such as household electric appliances, building materials and others. In this system, the wet coating process can be eliminated by using a roll coating process, making it possible to circumvent the problem of air pollution arising from evaporation. In addition, a pre-coated metal system offers other advantages, such as improved productivity and energy saving; thus the use of PCM has been spreading [1,2]. One of the most important properties of PCM is its formability. If the film on coated PCM parts is damaged, the products are rendered useless [3]. Polyester resins crosslinked with melamine resins or isocyanates are widely used for improvement resistance to abrasion and scratching.

The interest in developing organic–inorganic hybrid coatings has been increasing, because of the unique properties obtained from combining inorganic and organic components into a single coating system. One approach is a sol–gel process, involving the hydrolysis and condensation reaction of metal alkoxides [4,5]. Sol–gel provides an easy, cost-effective and efficient way to incorporate inorganic components into an organic binder. The other is using nanoparticles dispersed in organic binder [6,7]. The incorporation of inorganic nanofillers in an organic coating is often reported. Organic–inorganic hybrid materials improve properties such as toughness, impact strength, tensile strength, and thermal stability [8].

In this study, we designed an organic–inorganic hybrid resin with a silicone intermediate. We synthesized a silicone-modified

* Corresponding author at: Laboratory of Adhesion and Bio-Composites, Program in Environmental Materials Science, Seoul National University, Seoul 151-921, Republic of Korea. Tel.: +82 2 880 4784; fax: +82 2 873 2318.
E-mail address: hjokim@snu.ac.kr (H.-J. Kim).

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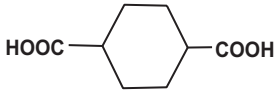
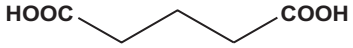
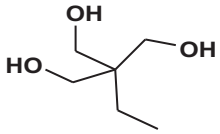
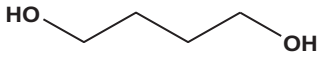
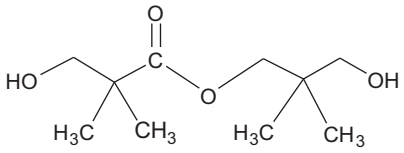
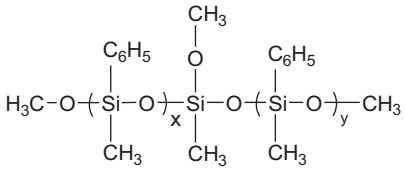
http://dx.doi.org/10.1016/j.porgcoat.2013.09.004

Table 1
Raw materials used for synthesis of silicone-modified polyester resin.

Function	Materials	Abbrv.	Chemical structure	M_n (g/mol)	Supplier
Acid	1,4-Cyclohexane-dicarboxylic acid	1,4-CHDA		172	Tokyo Chemical Industry
	Adipic acid	AA		146	Samchun Pure Chemical
Alcohol	Trimethylol-propane	TMP		134	Tokyo Chemical Industry
	1,6-Hexandiol	1,6-HD		118	Samchun Pure Chemical
	2,2-Dimethyl-1,3-propanediol mono(hydroxypivalate)	HPHP		204	Tokyo Chemical Industry
Silicone	Silicone intermediate	SI-IM		1000	Dow Corning

polyester resin from polyester resin and silicone intermediate, by methylol reaction between —OH and —CH_3. Silicone intermediate is an inorganic material, and branched polyester resin is organic material. Silicone modified polyester coatings are able to be used as an automotive clearcoat. The surface free energy of polyester coatings was calculated by the contact angle measurement. Also, the peel test was measured for the surface properties, and was used to determine any correlation with cleanable ability. The elongation, tensile strength and viscoelastic properties of synthesized resins of free-coated film were measured. The formability of PCMs was evaluated using a cylindrical drawing test. The stress and strain of the coatings were calculated from the deep drawing results. Finally, the relationship between the contents of silicone intermediate and the formability of the polyester coatings was discussed.

2. Experimental

2.1. Materials

Table 1 presents the chemical structures and basic information of the raw materials used for the synthesis. A silicone intermediate (DC 3037, M_n = 1000, Dow Corning, USA) was prepared to control the flexibility of the main chain. 1,4-cyclohexanedicarboxylic acid (1,4-CHDA, Tokyo Chemical Industry, Japan), adipic acid (AA, Samchun Pure Chemical, Republic of Korea), trimethylol propane (TMP, Tokyo Chemical Industry, Japan), 1,6-hexandiol (1,6-HD, Samchun Pure Chemical, Republic of Korea), and 2,2-dimethyl-1,3-propendiol mono(hydroxypivalate) (HPHP, Tokyo Chemical Industry, Japan) were used without further purification. Butylstannoic acid (FASCAT 4100, Arkema Inc., USA) was used as a catalyst to catalyze polymerization, and to prevent a transesterification reaction during the polymerization [8].

Hexamethoxy-methylmelamine (HMMM, Cytec Industries Inc., USA) was used as the curing agent, and Nacure blocked acid catalyst (NACURE 1953, King Industries, Inc., USA) was used.

2.2. Synthesis of silicone-modified polyester resin

The synthesized scheme of silicone-modified polyester resin is shown in Scheme 1 and the formulations are listed in Table 2. Polyester was synthesized from polybasic alcohols and polybasic acids with the following procedure, which consisted of two synthetic processes. One was the fusion process, and the other was the solvent process. The synthesis took place in a 500 mL round bottom flask equipped with a four-necked flask, having a mechanical stirrer, thermometer, condenser and water trap. The condenser and water trap were meant to remove condensed water during the poly-condensation reaction.

The synthesis of polyester has two steps. The first step is to the synthesized base polyester resin remaining —OH group. 1,4-CHDA, AA, TMP, 1,6-HD, HPHP were charged into a dried reactor, and the reaction temperature was set to 150 °C with stirring for 2 h under N_2 purge. Subsequently, the reaction temperature was increased from 150 to 210 °C, at the rate of 0.5 °C/min. During the fusion process, all raw materials were melted, and the condensed water was collected. After finishing the fusion process, it was converted into solvent process, by adding xylene. The solvent process was carried out to collect condensed water, and to make a low acid value. The reaction temperature was set to 220 °C. During the solvent process, the acid value was measured by 0.1 *N* KOH. The reaction temperature was maintained for several hours, until the acid value was under 20 mg KOH/g resin [9].

The second step is a methylol reaction between the–OH group of polyester resin, and the —CH_3 of silicone intermediate, with catalyst. Silicone intermediated was charged into a synthesized