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Synthesis and characterization of a new adhesion-activator for polymer surface

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Abstract

We developed a new type of adhesion-activator, Lichlor-6, consisting of lithium chlorohexylisocyanurate (LCI) and lithium dichloroisocyanurate (LDI), which can be soluble in water very well (more than 30 g/water 100 g), to replace trichloroisocyanuric acid (TCIA) which is only soluble in organic solvent. LDI acts as an adhesion-activator and LCI is used as additive to improve wetting ability of LDI on the polymer surface. The surfaces of styrene-butadiene rubber (SBR) and ethylene vinyl acetate (EVA) were treated with Lichlor-6 solution and bonded together using water-soluble polyurethane adhesive. Contact angle measurements, attenuated total reflectance-FTIR spectroscopy and scanning electron microscopy were carried out to characterize the treated surfaces. Tear resistance was also tested to compare adhesion strengths. After treatment with 16 wt% solution of Lichlor-6, the water contact angles decreased from 89° and 88° to 34° and 36° for SBR and EVA, respectively. The treatment with the higher concentration of Lichlor-6 produced the more marked chemical and morphology modifications on the SBR and EVA surfaces. The increased surface roughness of SBR and EVA caused by the treatment with Lichlor-6 have larger effects on the decrease of the contact angle than chemical modification. Tear resistance values obtained are 4.9, 6.5, 8.4 and 10.2 kgf/2 cm for the treatment with 0, 2, 5 and 8 wt% solutions of Lichlor-6, respectively, and the tested tear resistance is almost inversely proportional to the larger one between the two contact angles of SBR and EVA surfaces.

Keywords: Adhesion-activator; Trichloroisocyanuric acid; Styrene-butadiene rubber; Ethylene vinyl acetate

1. Introduction

So far trichloroisocyanuric acid (TCIA) has been used as an adhesion-activator to treat polymer surface for enhancing the adhesion between polymers. TCIA has to be used by dissolving in organic solvent and it produces chlorine due to unstableness in ambient condition. Unfortunately, TCIA is only soluble in organic solvents such as acetone and chloroform which are harmful. So these problems require a new type of adhesion-activator to get an improved environmental condition.

Chlorination with TCIA is a common surface treatment to improve the adhesion of synthetic vulcanized styrene-butadiene rubber (SBR) to polyurethane (PU) and epoxy adhesives [1,2]. TCIA has been used as an adhesion-activator to chlorinate the polymer surfaces to improve the adhesion between them and the surface treatment of SBR with TCIA has been widely studied in different conditions. Romero-Sanchez et al. [1] used ethyl, propyl and butyl acetates as solvents for TCIA to chlorinate SBR and found that the solvent is a key factor in the effectiveness of the chlorination of SBR containing zinc stearate and paraffin wax. They clarified that the solvents with slower evaporation rate led to more pronounced modifications on the SBR and the increase in TCIA percentage in the chlorinating solution

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produced more marked modifications on the SBR surface. It has been considered that the surface treatment of SBR with TCIA produces chemical structure change and surface morphology modifications that enhance the adhesion between SBR and EVA or PU [3–9].

One of the most applications of adhesive has been done in the footwear industry. The bottom of a footwear usually consists of two layers that are bonded together using adhesive. One layer is made of SBR and the other layer is made of EVA or PU. In order to improve the adhesion between the two layers a kind of adhesion-activator is usually applied to treat the surfaces of the layers. However, it must be noticed that TCIA is only soluble in organic solvents and the organic solvents may cause considerable hazards to health by absorbing harmful vapors. In order to avoid using harmful organic solvent, we synthesized a new type of adhesive-activator, Lichlor-6 (chlorine releasing agent), consisting of lithium chlorohexylisocyanurate (LCI) and lithium dichloroisocyanurate (LDI), which can be soluble in water very well. LDI acts as an adhesion-activator and LCI is used as an additive to improve wetting property of LDI on the polymer surface.

2. Experimental

2.1. Materials

All chemicals used in this experiments were purchased from Aldrich Chemical Company, Inc., USA, and used as received.

*2.1.1. Synthesis of hexylisocyanuric acid **3** [10]*

To a suspension of cyanuric acid (98%) **1** in water, $LiOH \cdot H_2O$ (98%) was added followed by stirring for 3 h at 100 °C. After cooling to room temperature, the precipitated product was filtered and washed with water. The product was dried at 110 °C for 24 h to give white crystals **2**. The lithium salt **2** was dissolved in MeOH (99%) at 50 °C, and then 1-bromohexane (98%) was slowly added to the solution. After refluxing for 24 h the reaction solution was concentrated in vacuo. The residue was diluted with ethyl acetate (99.8%) and extracted with water to remove the unreacted lithium salt. The organic layer was concentrated in vacuo and then, the residue gave the white solid **3** after several washing with benzene (99.5%) to remove the remaining 1-bromohexane.

*2.1.2. Synthesis of dilithium hexylisocyanurate (LHXIC) **4***

To a solution of hexylisocyanuric acid **3** in EtOH (99.5%), $LiOH \cdot H_2O$ in water was slowly added at 60 °C. After cooling to room temperature the reaction solution was evaporated in vacuo to give the white solid **4** in a quantitative yield.

*2.1.3. Preparation of mixture solution of Lichlor-6 (chlorine releasing agent) Consisting of Lithium Chlorohexylisocyanurate **6** and Lithium Dichloroisocyanurate **7***

Dilithium hexylisocyanurate (LHXIC) **4** dissolved in water was loaded to a beaker with a pH meter (320, METTLER TOLEDO, UK). TCIA **5** was slowly added to the solution under vigorous stirring. The final pH of the product solution was 7.65 ± 0.12. White powder of Lichlor-6 was finally obtained by freezing and drying the solution [11].

Synthetic procedures and chemical structures of each product are shown in Fig. 1. The structures of all products were identified with fourier transform nuclear magnetic resonance (FT-NMR) spectrometer (JNM ECP-400, Jeol, Japan) and Fourier transform infrared (FT-IR) spectrometer (SPECTRUM 2000, Perkin Elmer, England).

According to the chemical structure of synthesized adhesion-activator, it is referred to as Lichlor-6, in which Li, chlor and 6 stand for lithium, chlorine, hexyl group, respectively. SBR and EVA for this study were used as substrates.

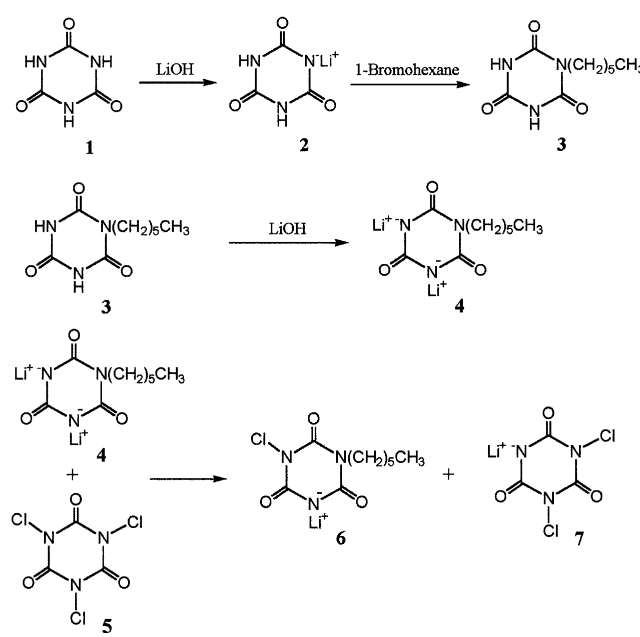

Fig. 1. Synthetic procedures and chemical structures of hexylisocyanuric acid **3**, dilithium hexylisocyanurate (LHXIC) **4** and preparation of Lichlor-6 consisting of lithium chlorohexylisocyanurate **6** and lithium dichloroisocyanurate **7**.