



Stability of acrylic polyurethane coatings under accelerated aging tests and natural outdoor exposure: The critical role of the used photo-stabilizers

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ABSTRACT

The effect of photo-stabilizers on the crosslinking and weathering durability of acrylic polyurethane coatings based on the HSU 1168 acrylic polyol and the Desmodur N-75 polyisocyanate has been investigated. The aging of these coatings under accelerated weathering conditions and natural outdoor conditions upto a decade has been compared. Our findings showed that photo-stabilizers had a negligible effect on the conversion of isocyanate groups during the photocrosslinking but enhanced the aging resistance. Coatings containing photo-absorbers exhibited an excellent weathering durability, upto 72 cycles upon accelerated aging and 10 years in natural outdoor exposure, while the unstabilized coatings appeared serious cracks, damages and chalking after 48 cycles of accelerated aging and after 5 years in outdoor weathering exposure. The degradation of coatings was also investigated by monitoring atomic force microscopy, weight loss and gloss loss, cracking, blistering and flaking of the coating. The degradation of coatings in the surface of natural and accelerated was compared by using Atomic force microscopy coupling with nanoscale infrared spectroscopy (AFM-IR) by following oxidized products on the coating surface.

1. Introduction

Organic coatings are used in a large variety of applications to protect the surface of various substrats. Acrylic binders have attracted substantial interest of scientists and manufactures due to their advanced characteristics, including good weathering durability, high transparency, excellent mechanical properties and chemical stability. The commercial acrylic resins for industrial coatings are mainly used in outdoor conditions. It is well known that the solvent-borne acrylic coatings, which are largely employed in industrial maintenance such as steel structures, fuel tanks and automotive finishes, consist of thermoset acrylic binders (acrylic-melamine), two pack polyurethanes (acrylic-polyurethane) and thermoplastic acrylic polymers (acrylate-methacrylate copolymers). To minimize the levels of polluting substances released into the atmosphere, in recent decades, end-users have tried to develop eco-friendly solvent-free coatings such as UV-curable systems and water-borne coatings, etc [1–11]. However, in some application

fields, the solvent-based coatings are still commonly used and developed due to its super-high quality such as high gloss, transparency, hardness and mechanical properties, chemical and weathering resistance. Acrylic polyurethane coatings are highly recommended in various applications including automotive clearcoats, industrial maintenance topcoats, general metal, wood furniture and flooring. The most common coating type is two-component system, where an acrylic polyol solution is mixed with a polyisocyanate solution just before applying to the protective substrates. The coating then was cured by a combination of solvent evaporation and chemical crosslinking to form a durable urethane bonds. These two-component polyurethane systems are dominant technology in automotive refinishing, thank to its low temperature process and its good physical properties and excellent substrate/coating adhesion. A large number of acrylic polyurethane coatings could be synthesized using various kinds of polyisocyanates and polyols [10–13].

However, outdoor organic coatings could be degraded under the

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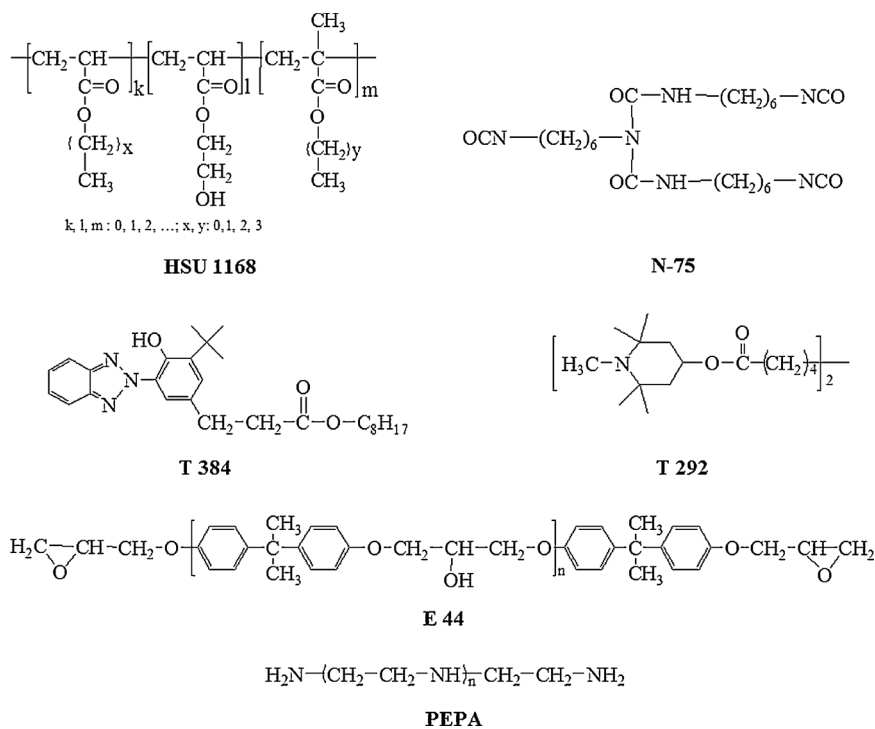


Fig. 1. Chemical formula of used materials.

effect of weathering environmental factors such as UV-light, oxygen, heat, humidity and pollutants, which could deteriorate their bulk properties as described in our previous publications [11–14]. Among these factors, UV irradiation is considered as a major contributor to the degradation of the materials. The aging behavior of acrylic coating has been widely investigated and the degradation mechanisms of these resins are related to several processes such as scission of side chain ester groups, cross-linking of the polymer backbone, oxidation processes leading to new hydroxyl and carbonyl functionalities [11–15]. The main drawbacks of acrylic polyurethane coatings relate their urethane bonds which are susceptible to the photooxidation and hydrolysis [13–15]. In recent years, researchers have tried to overcome these disadvantages through different strategies. Among that, the addition of additives such as pigments, organic UV absorbers, hindered amine light stabilizers (HALS) or functional nanoparticles (nano TiO₂, nano ZnO, etc) into the coating formulations is one of the most effective ways to enhance photo-stability of coating [2,13,16–24]. Acting as UV absorbers, these nanoparticles exhibit superior chemical stability under UV radiation, compared to other organic UV absorbers. For outdoor exposure, since the nanoparticles do not decompose and release out of coating during outdoor weathering, it might offer a long UV protection. However, in the presence of active oxygen and humidity, photocatalytic reactions leading to the degradation of coating surface were commonly observed [11,25], expressed by gloss loss and chalking. The chalking phenomenon consists in a friable powder on the coating surface caused by the disintegration of the binding medium due to degradative weather factors. These unwanted effects not only affect the decorative properties but also on the protective ability of the coatings. For this reason, organic photo-stabilizers, dealing with benzophenone or benzotriazole derivatives and HALS, are frequently incorporated in the coating formulations to enhance photo-stability in outdoor conditions.

Nowaday, there is still an open question without satisfactory answer about the relationship between the accelerated aging test in laboratory and the outdoor exposure conditions. The theoretical models, developed in the laboratory, were scarcely proven and validated in real outdoor conditions. These natural testings are often long, upto a decade and very expensive due to the maintenance fee for a continuing long time.

Although there are already several publications reported on the degradation and enhancing the photo-stability of coating under accelerated aging [2–34], the natural outdoor weathering aging of coatings is still limited and thus there is a lack of information about the degradation and photo-stability behavior of acrylic polyurethane coating in climate conditions. In this study, the crosslinking process and the influence of an UV absorber and a HALS on the weathering durability of acrylic polyurethane coatings during UV/condensation accelerated aging and natural outdoor exposure were spectroscopically followed. The data on the accelerated aging were compared to those, taken at a natural testing station upto a decade, to show their relationship. The degradation of coatings was also investigated by monitoring weight loss and gloss loss, cracking, blistering and flaking of the coating and AFM-IR. This work provides insights on photoaging of stabilized acrylic polyurethane coating and photo-protective efficiency of photo-stabilizers upon accelerated aging and natural outdoor weathering exposure, especially on the surface by using mainly nanoscale AFM-IR technique.

2. Materials and methods

2.1. Materials

HSU 1168 acrylic polyol (HSU 1168) solution, with 65 wt% containing 4.3 wt% of hydroxyl groups content was supplied by Industrial Resins Company A&P (Taiwan) and desmodur N-75 polyisocyanate (N-75) solution containing of 75 wt% containing 17 wt% of isocyanate group content was purchased from Bayer. An organic photo-stabilizer mixture consisting of a benzotriazole-UV-absorber (2-(2-hydroxy-3-tert-butyl-5-propionic axit isooctyl ester) -2H-benzotriazol, Tinuvin 384) and a hindered amine light stabilizer (bis (1, 2, 2, 6, 6-pentamethyl-4-piperidiny)l) sebacate, Tinuvin 292) from Ciba was added in the clear-coat (top layer) formulations to enhance its photo-stability. E-44 epoxydiane resin (E 44) having molecular weight of 500 g/mol and epoxy content of 4 mol/kg, a curing agent of polyethylene polyamine (PEPA) and ferric oxide (Fe₂O₃) pigments from China were used to fabricate a primer coat. Ti-Pure R-902 rutile TiO₂ pigments (R-902) were supplied

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