

# Effects of accelerated environmental aging on glass fiber reinforced thermoset polyurethane composites

J. Nicholas, M. Mohamed, G.S. Dhaliwal, S. Anandan, K. Chandrashekhara\*

Department of Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA

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## ABSTRACT

In the present study, the effects on the microstructure and the impact behavior of thermoset polyurethane composite material, exposed to an accelerated aging environment, were assessed. A combined hygrothermal and ultraviolet (UV) chamber is used in an accelerated aging procedure to simulate temperate climate conditions. The samples were manufactured using a vacuum assisted resin transfer molding (VARTM) technique using a novel two-part polyurethane resin (Methylene diphenyl diisocyanate/Polyol) infused into plane weave E-glass fiber mats. Samples were exposed to the UV/moisture rich environment for 250, 500, 750 and 1000 h. Effect of UV exposure on color change of composite specimens was evaluated using colorimetry. The rate of color change and the total change in color for the fiber reinforced composite was shown to be much less than that of pure polyurethane. Optical microscopy observations revealed that the color change was limited to surface discoloration due to the fiber reinforcement limiting degradation to the surface polymer matrix microstructure even after extended UV-exposure. The accelerated aging effect on the glass fiber reinforced polyurethane was examined using low velocity impact tests to evaluate impact properties of the material throughout the aging process. The test showed that the bulk composite material was resistant to the UV aging by demonstrating no significant change in impact properties due to the accelerated aging process.

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## 1. Introduction

Polyurethane (PU) composites have become an accepted alternative in the infrastructure industry, especially for applications requiring high strength-to-weight ratios and durability. Polyurethanes have several factors that make them desirable polymers for composites. PU systems are a low cost, high performance polymer. Polyurethane durability contributes significantly to the long lifetime of many products. This longevity of PU products life cycle leads to a resource conservation, an important environmental considerations that often favor the selection of polyurethanes. Another significant factor in the success of polyurethane is the ability to produce PU in various forms, from flexible, easily deformed to rigid load bearing materials. Polyurethanes made from petroleum-based polyols and isocyanates have achieved widespread applications in foams, coatings, structural materials and in composites due to their excellent abrasion resistance, toughness, strength, cost benefits and potential environmental reliability [1,2].

By use of various polyols and polyisocyanates, polyurethanes can be created to be both thermoplastic or thermoset polymers, and their mechanical, thermal, and chemical properties can be designed for the intended purpose [2–4]. There is a wide range of isocyanates and polyols commercially available thus leading to almost unlimited possibilities for polyurethane material formulations. Because of the inherent versatility in polyurethane synthesis, the properties of this class of polymer can be easily engineered to their intended application's environments and make an excellent component for a fiber reinforced composite material [5–7]. Two serious threats to the potential durability of composite laminates are their susceptibility to environmental exposure and to impact damage [8].

One potential use of polyurethane composites is in structural applications. Many structural applications will involve exposure to environmental effects such as moisture and ultraviolet (UV) exposure cycles, which lead to a reduction of the physical and mechanical properties of the polymer [9]. Many efforts have been made to investigate the effects of UV on polyurethane and improve the UV stability PU [9–18]. UV exposure has been shown to change the color of the PU material caused by the photo-oxidation of Methylene diisocyanate (MDI) in the central methylene group

\* Corresponding author. Tel.: +1 573 341 4587.

E-mail address: [chandra@mst.edu](mailto:chandra@mst.edu) (K. Chandrashekhara).

leading to the formation of hydroperoxides that then lead to the formation of quinine-imide structures, known as strong chromophores, resulting in the discoloration of the PU [14]. Jana and Bhunia [18] have studied the effects of UV aging on physico-mechanical properties of two part thermoplastic polyurethane. The results showed after 720 h of UV aging that there was an increase in surface roughness of samples and some ridges were observed to form on the surface. As the UV aging increased to 2160 h the surface roughness increased further and large holes formed that significantly reduced the mechanical properties. It has also been found that photo-oxidation of PU surface leads to an increase in surface free energy and its polar component; simultaneously, water adhesion to polymer increases significantly during UV-irradiation. These phenomena increase the potential for degradation during the aging process [2]. Studies have shown that the degree that the environment affects the polymer depends on the specific chemical properties of the polymer and that there is a direct link between physico-chemical and mechanical change with extended environmental exposure [8,10,18–21]. Connolly et al. [19] studied the changes in physical properties due to UV, environmental exposure and chemical exposure for polyurethane (PU) and unsaturated polyester–urethane hybrid (UPE-PU) resin-based profiles with identical glass fiber reinforcement. The study showed varying results depending on the chemical characteristics of the polymer. With new formulations of PU being used to make polymer composite there is a need to study how the environment affects these new materials.

Residual impact damage from tool falling during manufacturing or installation, hail damage or other low velocity impact event greatly affects the mechanical properties of composite materials. Many studies have been performed to investigate both numerically and experimentally the low velocity impact damage modes of composites such as surface indentation, matrix cracking, fiber breakage, delamination and fiber shear-out [22–25]. These damage modes can be difficult to visually detect and are known to be detrimental to the mechanical properties of the composite with the greatest effect on the compressive strength after impact as found by Challenger [26] and Ghelli et al. [27]. Several studies have been concentrated on the understanding of the low velocity impact behavior of laminate composites subjected to environmental conditioning [8,28–31]. These studies have shown a degradation of impact resistance due to exposure to aging environment. Pang et al. [31] report that after UV radiation the glass reinforced epoxy impact specimens were more vulnerable to impact induced damages. In their study, extensive delamination, interfacial debonding and matrix cracking occurred in the UV attacked specimens. Kim et al. [8] investigated the internal damage and compressive residual strength variation of accelerated-aged woven Glass/Phenolic composite laminate by impact loading. The results show that, as aging time increases, initial failure energy and residual compressive strength decrease. As aging cycles increase, failure initiation energy is decreased due to surface degradation caused by ultraviolet light. These studies have found that exposure to the aging environment has enhanced the damage effects of the polymer composites tested. Although studies have been conducted to evaluate the affect of aging on the impact properties of a number of composite systems, there is currently a lack of understanding of the affect of UV radiation on the impact properties for glass fiber reinforced thermoset PU.

The present work is aimed to examine the aging behavior of new generation thermoset PU composite exposed to accelerated weathering conditions. Glass fiber reinforced flat plates specimens are fabricated, conditioned, impacted and examined using microscopy. The effect of accelerated aging on the microstructure and impact resistance properties of composite laminates are studied by

comparing samples with varying exposure times to a control sample that was not subjected to the aging environment.

### 1.1. Materials and manufacturing

In this work, woven fiber based composites were chosen because they offer improved performance over unidirectional type composites. The woven fiber structure increases resistance to matrix splitting and delamination growth from impact damage [32]. The plain weave E-glass fiber mats, coated with a sizing to ensure compatibility with the PU resin system, were obtained from Owens Corning Inc., OH.

Low viscosity thermoset polyurethane resin system compatible with VARTM was obtained from Bayer MaterialScience, PA. The two-part PU resin system consists of two components. Component A is an Isocyanate (NB#840859 ISO) namely, Methylene diphenyl diisocyanate (MDI-Aromatic). Component B is a Polyol (RTM NB#840871). The mix ratio by weight for the A and B components is 92:100 (manufacturer recommended). The major challenge in using this PU resin system for vacuum infusion processes is moisture sensitivity. The isocyanate portion of the reacting components tends to react with water to produce carbon dioxide, which results in foaming. To address this issue, the mold is heated to 200 °C and cooled in a dry environment to room temperature ensuring removal of all moisture from the mold. Also to remove adsorbed moisture, and prevent void formation, E-glass fibers and all bagging materials used are dried at 110 °C for several hrs prior to manufacturing. Six panels, measuring 12 in. × 12 in., with six layers of E-glass fiber are manufactured utilizing a double bag VARTM process. Fig. 1 shows the VARTM process setup.

Fiber reinforcement layup is prepared on a rigid aluminum mold with a layer of removable plastic flow-enhancement medium to reduce fill time. A layer of peel ply is used to facilitate easy removal of manufactured part. The layup was sealed using a vacuum bag under a 28 in. Hg vacuum. The layup was infused at room temperature and cured at room temperature (24 °C) for 8 h, followed with the post curing cycle of 70 °C for 1 h and 80 °C for 4 h, the final thickness of the composite plate was measured to be 3 mm (0.118 in.). Specimens were cut to the required sizes from the panels manufactured.

### 1.2. Accelerated aging

To study the effect of in use environmental aging on the polyurethane composite samples a simulated accelerated aging environment was created using a QUV Accelerated Weathering Tester. The tests were performed in accordance with ASTM G154. The tester chamber is equipped with UVA-340 fluorescent bulbs to

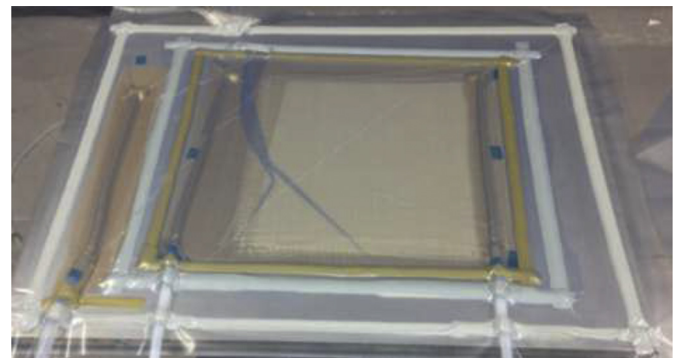


Fig. 1. VARTM double bag setup with full vacuum applied before resin infiltration.

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