

Thermoplastic Composites with Reduced Discoloration and Enhanced Fire-Retardant Property

Peng Cheng, Liqing Wei, Hongyu Chen, Ruomiao Wang

Abstract—This paper discusses a light-weight reinforced thermoplastic (LWRT) composite with superior fire retardancy. This porous LWRT composite is manufactured using polyolefin, fiberglass, and fire retardant additives via a wet-lay process. However, discoloration of the LWRT can be induced by various mechanisms, which may be a concern in the building and construction industry. It is commonly understood that discoloration is strongly associated with the presence of phenolic antioxidant(s) and NO_x . The over-oxidation of phenolic antioxidant(s) is probably the root-cause of the discoloration (pink/yellowing). Hanwha Azdel, Inc. developed a LWRT with fire-retardant property of ASTM E84-Class A specification, as well as negligible discoloration even under harsh conditions. In addition, this thermoplastic material is suitable for secondary processing (e.g. compression molding) if necessary.

Keywords—Discoloration, fire-retardant, thermoplastic composites, wet-lay process.

I. INTRODUCTION

THERMOPLASTIC based composite materials are proving themselves well-suited for many building and construction purposes. These materials have been used for building products in large amounts since World War II and their significance is increasing [1]. New types of products and new applications in building and construction are constantly being developed [2]. Polyolefin-based composite materials offer a combination of properties not easily found in other types of building materials. They are lightweight, moldable, chemical-resistance, weather-resistance, and electrical-resistance; most of them are naturally clear. In addition, LWRT offers a high degree of wearability and ease of maintenance for interior building purposes, such as ceiling tile and office furniture. Although LWRTs are not considered as materials with superior fire-retardant property, they can be combined with other fire-retardant (FR) additives (such as magnesium hydroxide and aluminum hydroxide) and, thus, can achieve a high level of flammability resistance.

Hanwha Azdel, Inc. developed moldable polyolefin-fiberglass composites with excellent flame retardant property (FR-LWRT). The current standard LWRT is considered as a material with good sound absorption but it can only pass ASTM E84, Class B specification. Some building and

construction applications require ASTM E84, Class A specification product with natural white surface. The as-produced composite sheet may be a porous fiber-reinforced thermoplastic comprising discontinuous reinforcing fibers, one or more FR additives. Optionally, the composite sheet can be molded via low pressure processes, such as pressure forming, thermal forming/stamping, vacuum forming, compression forming and autoclaving [3].

II. EXPERIMENTAL

A. Materials and Manufacturing Process

The new FR-LWRT was manufactured using the same wet-lay process as standard LWRT. In the manufacturing process, chopped glass fibers, polyolefin resin, and compounded FR additives were combined in an aqueous slurry. Afterwards, the agitated aqueous slurry was disposed onto a wire support, and a web was formed by removing the excess water. Followed by evacuation, drying, pressing, and consolidation, a thermoplastic composite sheet was produced. Surface skins, such as PET scrims, can be added through an in-line lamination process during the consolidation step [4]. FR-LWRT with various areal weights and as-produced thicknesses can be produced by adjusting manufacturing parameters.

B. Discoloration Test

In an effort to grade the discoloration degree of the trials, the samples were sent to TexTesT, LLC (Columbus, GA) for gas fade (accelerated aging) test according to AATCC 23 standard dated in 2015 [5]. It is basically the method of assessing color fastness to burnt-gas fumes. The fume chamber is fueled by natural gas, in which the NO_x concentration is around 2-3 ppm. The average temperature inside the chamber is around 60°C. The relative humidity is in the range of 60-65 % (see Fig. 1 for details). At the same time, the samples were also placed in storage area subject to field aging, where the typical NO_x concentration is 0.2 – 0.3 ppm. The primary NO_x sources are gas/propane powered appliances/equipment (e.g. forklifts) and space heaters.

After the samples underwent gas fade or field aging test, a colorimeter (HunterLab) was used to measure the color difference before and after the aging tests. Hunter L, a, b color scale is based on the Opponent-Color Theory [6]. The output is converted with an analog circuit into values of L, a, b. The value of L measures lightness and varies from 100 (white) to 0 (black), where a low number (< 50) indicates dark and a high number (> 50) indicates light; a measures redness (positive value), gray (0), and greenness (negative value); b measures

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yellowness (positive value), gray (0), and blueness (negative value). The overall color change (ΔE), commonly referred to as fading or discoloration, was calculated as the vector difference between two points, see (1)-(4):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

$$\Delta L = L_{\text{sample}} - L_{\text{original}} \quad (2)$$

$$\Delta a = a_{\text{sample}} - a_{\text{original}} \quad (3)$$

$$\Delta b = b_{\text{sample}} - b_{\text{original}} \quad (4)$$

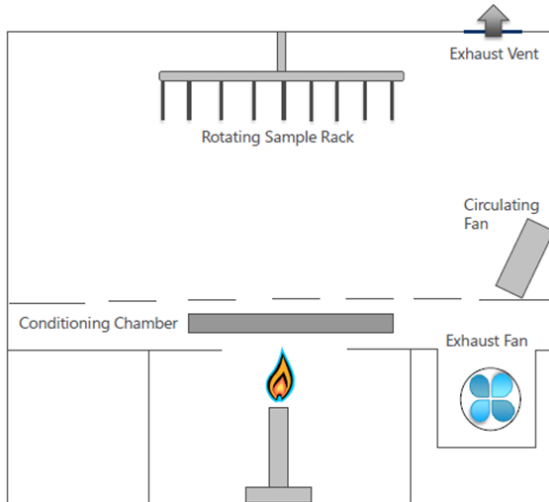


Fig. 1 Atmospheric fume chamber for gas fade test

C. Flammability Test

ASTM E84 test is commonly used for the comparative surface burning behavior of building and construction materials, which is applicable to exposed surfaces such as walls and ceilings. The test was conducted with the material surface exposed face down to the ignition source [7]. The purpose of this test is to evaluate the relative burning behavior of the material by observing the flame spread along the specimen. A large testing specimen of exposed area (0.457 m \times 7.32 m) was used for allowing realistic fire involvement of material surfaces and the development of physical and failures that may influence the flammability performance during the testing method [7]. ASTM E84 is a wind-aided test, and the air velocity is 73.2 ± 1.5 m/min (air temperature = 23 °C, and 50% relative humidity). The specimens were placed directly on the tunnel ledges and supported by rods and wire. The testing furnace is considered under calibration when a 10 min test of red oak decking will pass flame out the end of the tunnel in 330 ± 15 s. Based on the flame propagation, a comparative dimensionless flame spread index (FSI) is calculated from the areas under the flame spread distance – time plot. The areas for reinforced cement board (SDI = 0) and red oak flooring (SDI = 100) are used for the calculation of the smoke developed index [7]. Flame speed and smoke

developed index were reported after this test. There is no relationship between these two measurements. The International Building Code classifications are listed below.

The as-produced materials were cut into plaques, and the plaques were sent to an external certified lab for ASTM E84 test. After the test, the specimens were removed from the tunnel, examined and disposed of.

TABLE I
ASTM E84 CLASSIFICATION

Classification	Flame Spread Index (FSI)	Smoke Developed Index (SDI)
A	0-25	0-450
B	26-75	0-450
C	76-200	0-450

D. Physical Properties

The physical tests were performed on disks with 99 mm diameter based on Hanwha Azdel internal standard procedure. Basically, the areal weight (g/m², 5 replicates), ash content (weight percent, 5 replicates), as-produced density (g/cm³, 5 replicates), and as-produced thickness (mm, 5 replicates) of the FR-LWRT were measured.

III. MANUFACTURING PROCESS

The FR-LWRT was produced via wet-lay process similar to the manufacturing process of LWRT. In this process, all the components are combined in an aqueous solution, forming a slurry. Then, the pulped slurry was discharged to a forming belt. A web comprising of polypropylene, fiberglass, and FR additives is formed. Typically 20 – 35 wt.% of FR additives are introduced. The web went through drying (melting the polypropylene), compression, and consolidation processes before packaging. The surface outer layers, such as protective/decorative layers [8] or adhesive layers, could be laminated via an in-line lamination process onto either one side or both sides depending on the end-use application. In this paper, two outer skin layers are non-woven scrims.

IV. RESULTS AND DISCUSSION

A. Physical Properties

The physical properties (areal weight, as-produced thickness, as-produced density, and ash content) of the FR-LWRT panels were measured during production to ensure that the products meet the target. Because the as-produced FR-LWRT composite has a porous structure with a high voidage, the densities of the materials are significantly lower than a fully consolidated material. The areal weight, thickness, and density were comparable for FR-LWRT and standard LWRT (as shown in Table II). Since the FR additive was essentially comprised of metal hydroxide, it left certain amount of ash after burning, so the ash content of the FR-LWRT is higher than the standard LWRT.

Tensile properties were measured based on the ASTM D638 method. The tensile properties (for as-produced materials) are shown in Fig. 2. For FR-LWRT, the FR additive acted as a filler, thus, the chemical interaction of FR-LWRT

was weaker than that of Standard LWRT. That is probably why the tensile properties of the FR-LWRT(s) were lower than the standard LWRT.

TABLE II
PHYSICAL PROPERTIES OF FR-LWRT COMPOSITES

Material ^a	Areal Weight (g/m ²)	Thickness (mm)	Ash content (%)	Density (g/cm ³)
FR-LWRT-A	1034 ± 11	3.03 ± 0.06	59.6 ± 0.3	0.34
FR-LWRT-B	1017 ± 8.0	3.06 ± 0.10	60.6 ± 0.3	0.33
Standard LWRT	1002 ± 2.6	2.93 ± 0.04	52.4 ± 0.2	0.34

^aAll the samples were laminated by scrim layers on both sides.

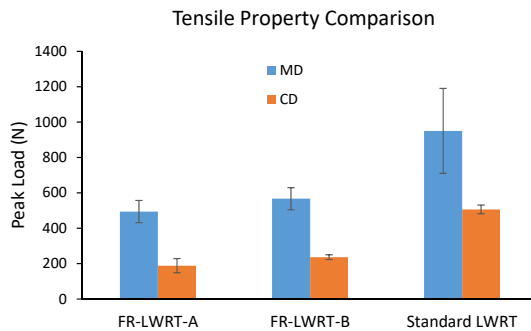


Fig. 2 The tensile peak load (tested by ASTM D638 method) performance comparison of FR-LWRT and Standard LWRT

B. Discoloration Studies

TABLE III
DISCOLORATION TESTS (AFTER GAS FADE AND FIELD AGING) OF FR-LWRT

Material	ΔE 72 h gas fade	ΔE 1 month field aging	ΔE 6 month field aging
FR-LWRT-A	19.7	9.7	12.5
FR-LWRT-B	5.4	0.4	0.8
Standard LWRT	4.8	0.4	1.7

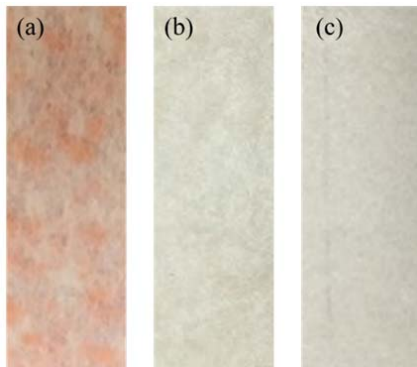


Fig. 3 Specimens after 72h gas fade (a) FR-LWRT-A; (b) FR-LWRT-B; (c) Standard LWRT

The discoloration of the FR-LWRT samples, before and after aging, was evaluated by HunterLab colorimetry (shown in Table III). As mentioned earlier, ΔE takes into account the overall difference between L , a , b values. For FR-LWRT-A and FR-LWRT-B, the FR additive loadings were the same, which was confirmed by the ash content listed in Table II. As shown in Table III, the degree of discoloration of FR-LWRT-

B was much lower than that of FR-LWRT-A. The corresponding pictures of the specimens after 72 h exposure of gas fade (accelerated aging with continuous NO_x) are shown in Fig. 3. The fundamental reason is that the phenolic antioxidant(s) present in the FR & polyolefin masterbatch could react with an oxidizing agent (e.g. NO_x) to provide a pink/yellow compound (e.g. quinone), which was not desirable [9]. If the concentration of the oxidized species exceed a certain level, color change will be discernible by human eyes.

C. Flammability Performance

After the FR-LWRT panels were produced, test samples were cut into plaques and then sent to an external certified lab for ASTM E84 test. Extreme care was taken during the sample preparation step before sending to the external lab. The top and bottom side of FR-LWRT were considered as identical. The testing results are listed in Table IV. It can be seen that the FR property of FR-LWRTs could pass ASTM E84 class A specification while standard LWRT was in the range of Class B. Two major reasons may explain this difference. First, during burning, the metal hydroxide would be decomposed into metal oxide and water vapor. The water vapor would absorb the heat and reduce the surface temperature. Second, the FR additives incorporated in FR-LWRT will alter the thermal inertia (thermal conductivity and heat capacity) [10]. In essence, the thermal conductivity of the FR additives was approximately two orders of magnitude higher than the LWRT composites. Hence, the overall thermal conductivity of FR-LWRT was much higher than standard LWRT. The FR-LWRT allows the heat to be dissipated effectively through the bulk, rather than propagate through the surface.

Based on the ASTM E84 results, the relative burning behavior of FR-LWRT-B (with negligible discoloration) can be considered as the same as FR-LWRT-A (both flame spread and smoke density developed were close to each other). By adding the non-pinking FR additive (FR-LWRT-B), the FR property of Standard LWRT could be enhanced from ASTM Class B to Class A.

TABLE IV
ASTM E84 TEST RESULTS OF FR-LWRT

Material	ASTM E84
FR-LWRT-A	Class A
FR-LWRT-B	Class A
Standard LWRT	Class B

V. CONCLUSION

A grade of LWRT, FR-LWRT, has been developed by incorporation of metal hydroxides. This new grade passes ASTM E84 Class A, which is suitable for interior building materials. By reducing the color change to a negligible level, the fire retardancy property of the new product was not affected. The natural clear exterior surface can be a great candidate for serving building and construction applications.

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