Environmental impact on the life of a polymeric composite with polyamide matrix and glass fibres

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Abstract. Polymer construction materials in composite design achieve high strength, have high chemical and thermal resistance as well as resistance to UV radiation. Due to the fact that polymer composites are often used for a long time outdoors, they are exposed to the weather and living organisms. The polymer composite PA66 + GF30 was used in the experiment. The composite consists of a polyamide matrix (PA) and a short glass fiber. Samples of the composite were subjected to accelerated aging in a UV chamber under precisely defined conditions. After UV degradation, the samples were still exposed in wet soil. After exposure, the samples were evaluated for a change in weight and a change in absorption in boiling water. Changes in the surface topography of the samples were evaluated using a light microscope.

1. Introduction

Composites are extensively used as materials in making aircraft, electronic packaging to medical equipment, and space vehicle to home building [1]. Composites consist of two or more components, insoluble in each other, which are combined to form a useful engineering material possessing certain properties not found in the constituents [2]. Polymer composites generally consist of thermoplastic or thermoset matrix with organic (e.g., wood flour, chicken feather) or inorganic (mineral or glass materials) fillers (particulates or fibers) [3]. Thermoplastic polymers in composites usually consist of polyolefins such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC), or of polyesters such as PLA and polyhydroxyalcanoates (PHA), of which PHB is the most common. Thermosets include acrylics, polyesters/vinyl esters, epoxies, polyurethanes, amines, furans, phenolics. Glass Fibre Reinforced Polymers (GFRPs) is a fibre reinforced polymer made of a plastic matrix reinforced by fine fibres of glass. Fibre glass is a lightweight, strong, and robust material used in different industries due to their excellent properties. Although strength properties are somewhat lower than carbon fibre and it is less stiff, the material is typically far less brittle, and the raw materials are much less expensive [4]. Its bulk strength and weight properties are very favorable when compared to metals, and it can be easily formed using moulding processes [5].

Polyamides have been selected due to the balance of physical and chemical properties against cost. Injection moulding, using mould flow, is well suited for mass production of components with
Polyamide 66 (PA66) has interesting properties, including heat resistance, a high strength, toughness, and good wear resistance, and is therefore widely used for sliding parts in automobiles or industrial machines, such as gears and bearing retainers. Unreinforced PA66, which does not contain reinforcement fibers, is used for sliding parts. In addition, reinforcement fibers such as glass fibers (GFs) or carbon fibers (CFs) may be added to PA66 to increase its strength and stiffness, and thus meet the requirements for a downsizing of parts under severe conditions. To use such parts under a high-temperature environment, such as inside an engine compartment of an automobile, it is necessary to understand the temperature dependence of the tribological properties.

Polymers used for outdoor applications deteriorate due to the combined effects of photolysis and pursuant photo-oxidative reactions, more commonly known as UV degradation. The rate of degradation is dependent on exposure conditions such as sunlight intensity, temperature and relative humidity, as well as the structure of the polymer itself and associated impurities. UV degradation manifests itself as a change in the physical characteristics of the bulk polymer. Weathered polymers show yellowing, embrittlement, cracking and hazing. In order to minimize UV degradation, UV screeners are added to the bulk polymer during processing. In general, these protect by absorbing UV light themselves thereby reducing the amount of UV light that can be absorbed by the chromophores present in the polymer.

2. Experimental material and methods
A commercial polymer composite, polyamide 66 (trade name PA66 + GF30 or Nylon 6/6 glass fiber reinforced) was used as the experimental material. The matrix of the composites is made of polyamide 66 (PA66) and the reinforcement is made of chopped glass fibers (GF). The fiber length is 4 mm and the fiber diameter is 10 μm. The content of glass fibers in the matrix was 30%.

Polyamide type PA66 with the addition of 30% glass fibers is a material that is used for the production of abrasion-resistant and dimensionally stable components, pulleys, but also for the production of highly loaded structural elements, etc. Among other things, this material is used in the electrical, automotive and engineering industries. It excels in high strength, abrasion resistance, high dimensional stability and relatively low absorbency.

Degradation testing of polymeric materials is one of the most important tests in terms of life estimation. Aging tests can be performed under real conditions of polymer use or artificial conditions of accelerated aging are used, which provide faster results. The artificial aging test was performed on a Cofomegra Solarbox 1500e. The device guarantees accelerated artificial aging according to the specified parameters in accordance with the standard. The parameters that were set at the beginning of the test are given in table 1.

| Table 1 Cofomegra Solarbox parameters |
|---------------------------------------|
| **Exposure time** (hrs.) | **Dry phase** (min.) | **Wet phase** (min.) | **Black panel temperature** (°C) | **Radiation** (W/m²) |
| 500 | 40 | 5 | 65 | 250 |

The extent of damage to plastic by the action of a biologically active environment can be determined by visual evaluation of the appearance of the test body, a change in weight, a change in physical properties. These methods are suitable for materials with a smooth surface, porous samples such as foam products are unsuitable. Test specimens, which had been weighed in advance, were placed in a beaked and completely covered with soil, which was then flooded with distilled water. The exposure time was 2 weeks. At the end of this time, soil sample were taken, cleaned and weighed.

The water absorption test for plastics is carried out in cold (method A) and in boiling water (method C) (EN ISO 62). The method consists in determining the weight gain of test pieces immersed in cold and boiling water over a prescribed time. The test specimens should have the same shape and dimensions.
At least 3 immersion test bodies shall be tested the prescribed time into the water container. After the time has elapsed, they are removed from the water, dried and weighed to the nearest 1 mg. The amount of water absorbed by the test specimen in mg is calculated using method A (X₁) and C (X₂) according to formula 1:

\[ X_{1,2} = m₂ - m₁ \text{ (mg)} \]  

(1)

Amount of water absorbed by the test piece per unit of surface in mg. cm⁻² is calculated using method A (X₅) and method C (X₆) using formula 2:

\[ X_{5,6} = \frac{m₂ - m₁}{A} \text{ (mg. cm⁻²)} \]  

(2)

The amount of water absorbed by the test specimen in% is calculated using method A (X₉) and method C (X₁₀), using formula 3 [12]:

\[ X_{9,10} = \frac{m₂ - m₁}{m₁} \cdot 100 \text{ (%)} \]  

(3)

The topography of the samples was also evaluated on a light microscope.

3. Experimental results and discussion

All test specimens were weighed before the start of the experiment. The first set of samples was placed in a beaker with wet soil for 2 weeks. The second set of samples was first exposed UV radiation (500 hrs.) and then placed in a beaker and wet soil for 2 weeks. At the end of the exposure period, soil samples were taken, cleaned and prepared for weighing. The values of the resulting masses are recorded in table 2. The value of \( m₁ \) is the mass recorded before the exposure of the sample to the soil, the value of \( m₂ \) is the mass of the sample after its exposure in the soil and the last row of the table indicates the difference between these values (Δm).

|          | PA6.6 + 30 GF | PA6.6 + 30 GF + 500 UV |
|----------|--------------|------------------------|
| \( m₁ \) (g) | 1.9852       | 1.9314                 |
| \( m₂ \) (g) | 2.0924       | 2.6011                 |
| Δm (g)    | 0.0442       | 0.1745                 |

Further testing was testing for absorbency and changes in absorbency due to UV radiation. The test specimens were weighed at the beginning of the absorbency test. Absorbency in the boiling water was realized. The exposure time in boiling water was 30 minutes, followed by cooling in cold water for 15 minutes and the samples were weighed again. The change in weight (absorbency) and the amount of water absorbed by the surface of the test sample were evaluated. The results of the measurements are given in table 3 and 4.

|          | PA6.6 + 30 GF | PA6.6 + 30 GF + 500 UV |
|----------|--------------|------------------------|
| \( m₁ \) (g) | 2.4115       | 2.3976                 |
| \( m₂ \) (g) | 2.4360       | 2.4430                 |
\[ \Delta m \ (g) \quad 0.0245 \quad 0.0454 \]

| Table 4. Amount of water absorbed by the surface of the test specimens |
|---------------------------------------------------------------|
| | PA6.6 + 30 GF | PA6.6 + 30 GF + 500 UV |
| m (%) | 1.0160 | 1.8936 |

From the measured values, it can be said that for the PA6.6 + 30 GF composite, the change in weight after exposure in soil was also recorded in the evaluation of water absorption. After exposure of the samples to UV radiation, this change in weight was even more pronounced in both tests. Changes in the surface of the samples due to UV radiation and microorganisms were also confirmed by observing the surface changes using a light microscope. The surface of the samples was observed in reflected light on an Axio Imager A1m microscope from Zeiss. In figure 1 we can see surface of the sample without degradation effect of the environment. The surface of the sample is homogeneous, see traces of injection and solidification of the material in the mold.

![Figure 1. PA66 + GF30 - surface, 0 UV, 200x](image)

Samples under the influence of UV radiation (250 hrs.) changed the character of the surface (figure 2). We can identify emerging cracks on the surface of the samples. Cracks are preferably formed at the locations of the protrusion that have formed during the process of injecting the samples into the mold.
After exposure in the UV chamber, the test specimens were placed in wet soil for 2 weeks. These samples showed the most significant change in the character of the surface compared to the original samples (figure 3). The density of surface cracks increased. The individual cracks joined together to form a network for the failure of the samples. In figure 3 we can see that the character of the matrix has also changed.

4. Conclusions

Based on experiments performed on the polymer composite PA66 + GF30 after exposure to UV radiation and subsequently in wet soil, we can conclude:

- After exposure of the polymer composite in wet soil, we can state increasing in weight in both cases. In the case of samples without UV radiation, the weight gain was 5% compared to the original weight.
- In the case of samples that were first exposed to UV radiation and then exposure to soil, we observed a change in weight of 35%.
- In the boiling water absorbency test, absorbency was recorded for samples without UV radiation of 1% and for samples after UV radiation of 2%.
Polyamides are characterized by absorbency, which depends on the concentration of amide groups. This property was confirmed by storing the samples in wet soil as well as in the absorbency test. At the same time, UV radiation caused changes in the topography of the surface, the formation of cracks. Cracks allow easier entry of the liquid into the matrix and thus changes in properties.

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References
[1] Shaw A, Sriramula S, Gosling P D, Chryssanthopoulo M K 2010 Composites Part B, 41, 446 – 453.
[2] ASTM. Standard Terminology Relating to Plastics, ASTM: West Conshohocken, PA, USA, 2012, p. D883
[3] Brebu M 2020 Environmental Degradation of Plastic Composites with Natural Fillers – A Review, Polymers 2020, 12(1), 166. https://doi.org/10.3390/polym12010166
[4] Jarukumjorn K, Suppakarn N 2009 Effect of glass fiber hybridization on properties of sisal fiber polypropylene composites, Compos: Part B, 40 (2009), pp. 623 - 627
[5] Dwivedi U K, Navin chand 2009 Influence of MA – g – PP on abrasive wear behaviour of chopped fiber reinforced polypropylene composites, J Mater Process Technol, 209 (2009), pp. 5371 - 5375
[6] Lates M T, Velicu R, Gavrila C C 2019 Temperature, pressure, and velocity influence on the tribological properties of PA66 and PA46 Polyamides, Materials, 12 (20) (2019), p. 3452
[7] Habrman M, Ráž K, Kalina T 2019 Effect of the cascade injection molding on the filling behaviour, Manufacturing Technology, volume 19, issue 6, 2019, pp. 936-940
[8] Chval Z, Raz K, Sedlacek F. 2019 Dimension Stability of Thin-Walled Parts from 3D Printed Composite Materials, Structural Integrity, vol. 5, 2019, pp. 91-92.
[9] Ray B C, Prusty R K, Rathore D K 2018 Fibrous polymeric composites: environmental degradation and damage, CRC Press, ISBN 978-1-4987-8401-6
[10] Ray B C, Rathore D 2014 Durability and integrity studies of environmentally conditioned interfaces in fibrous polymeric composites: Critical concepts and comments, Advances in Colloid and Interface Science, vol. 209, p. 68-83
[11] Mahato K K, Dutta K, Ray B C 2018 Static and Dynamic Behavior of Fibrous Polymeric Composite Materials at Different Environmental Conditions, Journal of Polymers and the Environment 26, p. 1024-1050
[12] Standards EN ISO 62 (640112) Plastics. Determination of water absorption in water