Corrosive effect of environmental change on selected properties of polymer composites

I. Markovičová and V. Zatkalíková
University of Žilina, Faculty of Mechanical Engineering, Department of Material Engineering, Univerzitná 8215/1, 01026 Žilina, Slovakia
lenka.markovicova@fstroj.uniza.sk

Abstract. The development of composite materials and the related design and manufacturing technologies is one of the most important advances in the history of materials. Composites are multifunctional materials having unprecedented mechanical and physical properties that can be tailored to meet the requirements of a particular application. Ageing is also important and it is defined as the process of deterioration of engineering materials resulting from the combined effects of atmospheric radiation, heat, oxygen, water, micro-organisms and other atmospheric factors. The present article deals with monitoring the changes in the mechanical properties of composites with polymer matrix. The composite was formed from the PA matrix and glass fibers (GF). The composite contains 10, 20 and 30% of glass fibers. The mechanical properties were evaluated on samples of the composite before and after UV radiation on the sample. Light microscopy was evaluated distribution of glass fibers in the polymer matrix and the presence of cracks caused by UV radiation.

1. Introduction

Modern structural composites, frequently referred to as advanced composites, can be distinguished from commodity composites because of their frequent use of more exotic or expensive matrix materials and higher-priced reinforcements such as carbon/graphite, and they can be found in more structurally demanding locations that have a greater need for weight savings [1-3]. They are a blend of two or more components. One component is made up of stiff, long or short fibers, and the other, for polymeric composites, is a thermoplastic or a resinous binder or matrix that holds the fibers in place.

The fibers are strong and stiff relative to the matrix and are generally orthotropic (having different properties in two different directions) [4-7]. These properties are most evident when the components are shown in Figure 1. Polymers are widely used in many industrial fields and in outdoor applications all polymers degrade. The degradation rate depends on the environment (especially sunlight intensity, temperature and humidity) and on the type of polymer. There are some problems such as photo-yellowing and the decrease in mechanical strength after long term irradiation by ultra-violet (UV).

This so-called UV-degradation is due to combined effects of photolysis and oxidative reactions [8]. There are many studies on the photo-degradation of polymers induced by UV irradiation. It is important to study the depth profile of the degradation in order to see the attained depth of the degradation and the effects of the additives.
Rheology and its experiments reveal information about the flow behaviour of liquids but also the deformation behavior of solids, because it is the typical behaviour of polymers. Changes induced by the environment with degradation effect can be evaluated by rheological measurements which monitor changes in viscoelastic properties of the tested polymers. The fundamental of rheological characteristics is viscosity which defines the internal resistance of material against its creep generated by external forces. It is necessary to realize the dual character of majority of polymer materials from viscoelastic point of view. The action of external force on the ideal viscous material results in its deformation i.e. irreversible locomotion (movement) of macromolecules and after removal of the external force material retains its „new” shape. The action of external force on the ideal elastic material results in its deformation but after the removal of the external force, the material returns to its original shape. Polymers are generally characterized by the viscoelastic nature, which means that external forces cause partly permanent (viscosity element of polymer) and partly reversible (elastic element of polymer) deformation [9, 10].

2. Experimental material
The experimental materials are composites with the PA+PAI (polyamide + polyamidimide) matrix with 10 %, 20 %, 30 % (% = vol. %) of glass fibers coded GF 672 with diameter 10 µm and length 4 mm. The composites are estimated for interior and exterior details of cars, then it is expected their UV stability. The matrix includes also UV stabilizer. The structures of the tested composites were observed by SEM (Scanning Electron Microscopy). The surface of the samples was covered with a carbon layer. In Figure 2, the surface state of the composites with various content of GF is shown and distribution of GF in cross section also. Inhomogeneity of the tested composites increases with amount of GF. We can see the fibres are distributed periodically in composite with 10 % of GF (Figure 2a). Higher fibre content (30% GF) causes heterogeneity of the matrix-fibre system (Figure 2c). The individual glass fibres after removal from the matrix, leaving regular oval holes (Figure. 2a, b), with a higher volume of glass fibres is made up of holes.
Testing degradation of polymeric materials is one of the most important tests to the lifetime of polymer product. Ageing tests can be either in real conditions of use of the polymer in a particular application, or using artificial accelerated ageing conditions. Accelerated ageing methods provide test results significantly faster natural aging tests. Testing is based on exposing test bars to man-made climate. After a fixed interval of exposure changes are detected in end points (aesthetic, physical, electrical, etc.). The apparatus for man-made weather ageing ensure continued maintaining of artificial climatic conditions (day and night cycles, changing humidity, drought and wet, etc.). The apparatus SolarBox 1500e which was used in the experiment has the following characteristics: a source of light guarantees a radiant flux of radiation intensity 550 W.m$^{-2}$. The source of light is a xenon arc lamp, but other sources of radiation are allowed too. The device must be equipped with a thermometer built into the black panel, which senses the temperature of the black panel. The black panel temperature of exposure time was selected at 65 °C the liquid phase lasted for 102 minutes and the wet phase for 18 minutes. If it necessary wetting by distilled or deionised water can be applied. The numbers of man-made climate factors that simultaneously affect the test bars is selected by the test program. Test runs continued for a period fixed in the testing program. The duration of the test was 500 and 1000 hours [11].

3. Experimental results and discussion

The Vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. The test specimen must be between 3 and 6.5 mm thick and at least 10 mm in width and length. Of each sample were made three measurements and are determined by the final arithmetic value (Table 1). From the test results, we can see that the Vicat softening temperature slightly increased after 1000 hours of UV radiation.

| Table 1. Vicat temperature. |
|-----------------------------|
| Filler content | 0 hrs. UV | 500 hrs. UV | 1000 hrs. UV |
| 10% | 231 | 234 | 243 |
| 20% | 240 | 241 | 248 |
| 30% | 242 | 243 | 249 |
The impact strength test measures the amount of force needed to break a specimen introduced through a swinging pendulum. The samples had the following parameters: width: 10 mm, thickness: 4 mm and a length of 80 mm. The test took place at a temperature of 23 °C (23 ± 2 °C). Results of measurements are shown in Figure 3.

![Impact strength test](image)

**Figure 3.** Effect of UV radiation on the change of impact strength.

The results show that the impact resistance to the most impact volume of glass fibers, wherein the amount of the impact strength values increase. The values of impact resistance by the action of UV radiation halved. One of the important properties of the polymer material is the impact strength, which is a combination of strength, plasticity, and durability of the material. When polymers mechanical resistance is dependent on the speed with which a force is applied to the material. At lower speeds the polymer occurs to a relatively large deformation, while at higher speeds has a brittleness of the material, because the mechanical energy is not enough to dispose the material. Because of this feature, the polymer is gradually becoming a better design choice for a variety of applications [12].

Experimental data were obtained by using an oscillatory rheometer Physica MCR301 with convection heating device CTD 450. The main advantage of this measuring method is in simultaneous monitoring of all mentioned parameters, e.g. G’, G”, tan δ and η* [13, 14, 15]:

- G”(Pa) - loss modulus is a measure of deformation energy used up by sample during shear process and shows irreversible deformation energy, presents the viscous behaviour of tested material.
- G’(Pa) - storage modulus is a measure of the deformation energy stored by samples during the shear process is showing reversible deformation behaviour, represent elastic behaviour of tested material. The complex modulus is expressed by the equation:
  \[
  |G'| = \sqrt{(G')^2 + (G'\prime')^2}.
  \]

- η* - complex viscosity represents ratio of η’ expressed elastic behaviour of polymeric and η’’ viscous one [16,17]:
  \[
  |\eta'| = \sqrt{(\eta')^2 + (\eta'\prime')^2}.
  \]

The measurements were provided by Frequency Sweep test (FS) to study changes of viscoelastic properties, changes of molecular mass and its distribution after various types and time of degradation. The sample was placed between two parallel plates with diameter of 25 mm, in 1 mm distance from each other. Measurements were carried out at the temperature of 320 °C and following conditions: amplitude of γ = 5%, angular frequency of ω = 500 – 0.051/s. The principle of the mentioned evaluation is shown in Figure 4 [10].
The process of degradation is followed by changes of molecular weight (as networking or macromolecular chains breaking) which should be reflected in the measured parameters. As seen in Figure 4, the values of complex dynamic viscosity $\eta$ and storage modulus $G'$ and loss modulus $G''$ can be compared by measuring. Furthermore, we are able to monitor the position of the intersection of the curves characterizing the state of both modulus and indicate the transition from viscous deformation behaviour to the more elastic behaviour. This intersection is qualitative characteristics of the material [16]. The polymer degradation can results in changes of the values of measured characteristics. Shift of the modulus intersection in horizontal direction provides information about the average molecular weight and shift of the modulus intersection in the vertical direction signals the difference in the molecular weight distribution.

Rate and depth of PA + PAI composite with different content of glass fibres degradation after exposure in UV chamber (after 1000 hours) was evaluated by Frequency Sweep test (FS). The differences in viscosity and modulus defining plastic and elastics properties of PA + PAI samples are shown in Figure 5, 6. In Figure 5 it is illustrated difference of rheological parameters of PA + PAI composite with different content of glass fibres (0 hrs. UV radiation) expressed in the position of a cross point (COP) of loss and storage modulus. The COP is moved to lower angular frequencies with increasing molar mass. The vertical shift of the COP indicated changes in distribution of molar mass.

The effect of exposure of the composite PA + PAI simulated atmospheric conditions of intense radiation was clearly observed as a change in viscosity values and as a change of the position of point COP. The viscosity of samples after exposure in the UV chamber shifted towards lower values (Figure 6). It also was recorded by shifting the COP. The intersection of the loss and storage modulus of the samples after exposure to the UV chamber, shifted towards longer and more branched-chain. Differences between visco-elastic properties of specimens in initial state are higher than after exposition. It means increasing of elastic properties and drop of plastic ones. The composites are more brittle, include more cracks and the so the fibres are liberated from their positions.
Figure 5. Differences in rheological properties of PA + PAI with different content of GF without UV radiation.

Figure 6. Differences in rheological properties of PA + PAI with different content of GF after 1000 hrs. UV radiation.
4. Conclusions
Based on the experiments performed on composite PA + PAI with different content of the filler (GF) we can conclude:

- From the observation of the morphology of the composite show that the increased volume of glass fibers cause the fibers form clusters and their distribution is uneven. Fracture and irregularities are formed on the surface of the laminate of the matrix observed. The combination of UV radiation and higher glass fiber content rise to cracks, which gradually spread matrix. This caused a degradation of the matrix and the peeling in the form of flakes.

- The softening point of the composite increases with the content of glass fibers. UV radiation has had no significant impact on softening point, there was only a slight change in the material properties. The biggest change in the softening point was the composite containing 10% filler wherein the temperature is increased from 231 °C to 243 °C. This may be caused by changes in the structure and also the partial crosslinking chains.

- In examining the impact strength material with an increasing volume of glass fibers increases. After UV irradiation, this value clearly decreased, although the figures are volatile and vary. This is due to the partial cross-linked polymer by the action of UV radiation and also heterogenous distribution of glass fibers.

- Rheological measurements sensitively monitor changes in the structure of studied polymers due to degradation effect in different environment. This was reflected in the measured rheological parameters and variables like viscosity, molecular weight changes and their distribution, modulus characterizing elastic and plastic properties.

- UV radiation causes - decrease in viscosity values, the formation of long or branched chains, confirming the displacement of the COP point in regions with a broad molecular weight distribution.

- The changes by the effect of environment with present UV radiation reduce products quality and life time. The possibility of reducing degradation processes is in using of effective UV stabilizers and increase adhesiveness of GF to matrix.

Acknowledgement
The research was supported partially by Slovak Academy of Science grant VEGA No. 1/0533/15 and No. 1/0123/15.

References
[1] Peters S T, Humphrey W D and Foral R F 1999 Filament Winding Composite Structure Fabrication 2nd ed. SAMPE Publishers Covina.
[2] Brown R T 1987 Engineered Materials Handbook, vol. 1 Composites Theodore Reinhart Tech. Chairman ASM International.
[3] Birley A W, Haworth B and Batchelor J 1992, Physics of Plastic Carl Hanser Verlag Munich.
[4] Gupta P K 1988 Glass Fibers for Composite Materials Fibre Reinforcements for Composite Materials A. R. Bunsell Ed. Elsevier Publishers.
[5] Petru M, Broncek J, Lepsik P and Novak O 2014 Experimental and Numerical Analysis of Crack Propagation in Light Composite Materials Under Dynamic Fracturing Communications - Scientific Letters of the University of Zilina 16 (3A) 82-89
[6] Dresslerova Z, Pulcek P and Uhricik M 2016 Effect of Heat Treatment on the Behavior of AZ31 and AZ91 Magnesium Alloys During the Cyclic Loading Proc. of Materials Today 3 (4) 965-968

[7] Raz K, Zahalka M and Chval Z 2017 Injection molding quality improvement by advanced virtual simulations Manufacturing Technology 17 ISSN 1213-2789 79-83

[8] Denisov E T 1982 In: Scott G. Editor Developments in polymer stabilization 5 London Applied Science 23-40

[9] Carraher Ch E Jr 2007 Introduction to Polymer Chemistry Taylor and Francis Group ISBN 0-8493-7047-2 USA

[10] Wollny K 2006 Comparison of a propylene reinforced with glass fiber and pure polypropylene over a temperature range from -150 to +180°C Anton Paar Germany GmbH

[11] Markovicová L, Zatkalíková V and Vasko A 2016 Accelerated Aging of Polymeric Composites in Laboratory Conditions Manufacturing Technology 6 (5) 1033-1037

[12] Kanie T, Fujii K, Arikawa H and Inoue K 2000 Flexural properties and impact strength of denture base polymer reinforced with woven glass fibers Dental materials 16 Issue 2 150-158

[13] Mezger T G 2006 The Rheology Handbook 2 Hannover Vincentz Network ISBN 3-87870-174-8 299

[14] Vojsovičová M, Liptákóvá T and Zatkaliková V 2011 Rheological characteristic of thermoplastic polymer after degradation In Communications Scientific Letters of the University of Zilina 13 EDIS Publishing Institution of Zilina University ISSN 1335-4205 32-35

[15] Lelovics H and Liptáková T 2010 Rheological properties of acrylic bone cement SmartSet®HV In Communications Scientific Letters of the University of Zilina 12 EDIS Publishing Institution of Zilina University ISSN 1335-4205 85-89

[16] Carraher C E 1996 Polymer Chemistry An Introduction 4/e Marcel Dekker Inc. New York 53