Chapter 5

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AGING OF POLYMERIC COMPOSITES
IN LABORATORY CONDITIONS

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. The composite contains $10 - 30$ % 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.

Key words: UV aging, polymeric composites, glass fibres, mechanical properties

5.1. Introduction

Weathering is a broad term that is applied to the changes that take place in a polymer on exposure out of doors. The main agents of weathering are sunlight (particularly ultraviolet radiation), temperature, thermal cycling, moisture in various forms, and wind. The main degradation is brought about by ultraviolet light, assisted by contributions from the visible and near-infrared portions of the electromagnetic spectrum.

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In particular the near-infrared radiation accelerates degradation reactions by raising the temperature (ADLER J., NELSON L. 1989, BILLMEYER F.W. JR. 1984).

All of the factors involved in weathering, including both the amount of intensity of sunlight, vary both seasonally and geographically. To understand fully and predict the weathering behavior of any polymer requires information about exactly how these factors vary and how they then contribute to the overall degradation process (CROMPTON T.R. 1989).

Solar radiation experienced by polymers at the Earth's surface has two components, direct radiation from the sun and indirect radiation from the sky. At all parts of the Earth's surface, solar irradiance is highest at noon, when the sun is highest in the sky. The actual intensity, though, varies geographically. This is due not only to regional variations in the amount of direct sunlight, but also because the clarity of the atmosphere varies geographically, depending on the amount of water vapour or polluting gases that are present locally (HEARLE J.W. 1982).

5.2. Experimental material

As an experimental material was used a composite of polymeric matrix (PA+PAI) and filler (glass fiber). The glass fiber strand have manufacturing marking GF 672, fiber diameter is 10 μm and the fiber length of 4 mm. They were supplied by three types of composite to be different in filler loading (10 %, 20 % and 30 %). It is a modern material that should be used in interior and exterior of cars. It should also resist UV radiation due to the addition of UV stabilizers. The experimental implementation of mechanical and thermal tests, samples in the form of rods and paddles which were produced from the granules of the polymer injection molding technology.

5.3. Experimental conditions and methods

UV degradation. 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 (Fig. 5) ensure continued maintaining of artificial climatic conditions (day and night cycles, changing humidity, drought and wet, etc.)

Fig. 5.1. SolarBox 1500 E with flooding

A source of light radiation 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, 750 and 1000 hours.

Experimental methods. The test samples were evaluated by the selected mechanical parameters (Vicat temperature and hardness) regarding the effects of UV radiation. The same parameters were assessed after 3 runs (500, 750 and 1000 hours) of UV radiation acting on the sample. The test also included evaluation of the structure and changes in the structure before and after UV irradiation.

5.4. Experimental results and discussion

Test Vicat softening temperature was conducted on a test for heat test. The test sample is placed under the tip, which is connected via a vertical shaft with a micrometer to an accuracy of 0.01 mm. Then, the tip load, and the thermometer was read the temperature when the needle has penetrated the material to a depth of 1 mm. Of each sample were made three measurements and are determined by the final arithmetic value (Tab. 5.1).

Table 5.1. Vicat temperature

Filler content	Vicat temperature [°C]			
	0 UV	500 UV	750 UV	1000 UV
10 %	231	234	243	243
20 %	240	241	244	248
30 %	242	243	246	249

Hardness test was conducted durometer CV-3000 LDB. Loading force was set to 250 kp, injection time was 10 seconds and the indentation diameter balls of 5 mm. Measured by the average of the

indentation beads. The microscope was counted using a scale diameters which are perpendicular to each other, then the resulting hardness was calculated. Each sample was made 5 measurements. The final hardness is shown in Fig. 5.1.
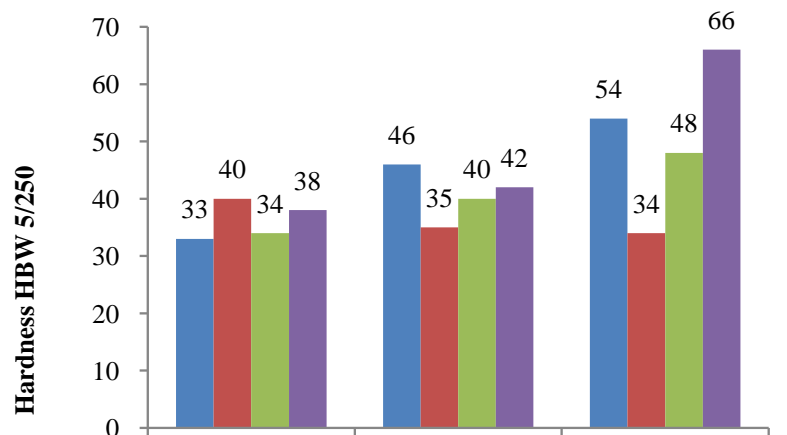

Fig. 5.2. Effect of UV radiation on the change in hardness

UV radiation caused us changes in structure and material degradation.

Fibers started to separate from the matrix and pulled out and left by a row in the blanks - hole. At higher glass fiber content had holes tend to be linked. The fibers are broke, segregated and were pulling without residue matrix, due to poor adhesion interface fiber – matrix (Fig 5.3). Degradation is gradually spread from the material surface to the center. The material causing rupture of which initiates have just glass fibers and the cracks gradually spread from the surface of the matrix (Fig.5.4b, c).

Coloring cracks us determine its depth. At the beginning of fine hairline cracks emerged that the picture can be seen as white with a slight hint of blue. Prolonged exposure to UV radiation has been associated crack spread and in depth. These cracks can be seen in the figures as deep black. The biggest changes in the structure (degradation) we can see a

material with 10% glass fiber content, where most of the matrix to which the UV radiation is the most evident effect (Fig. 5.5).
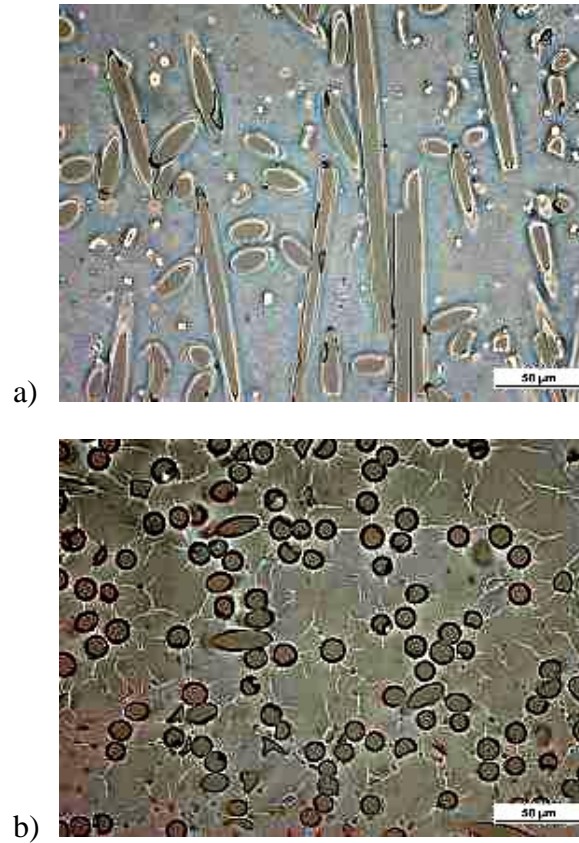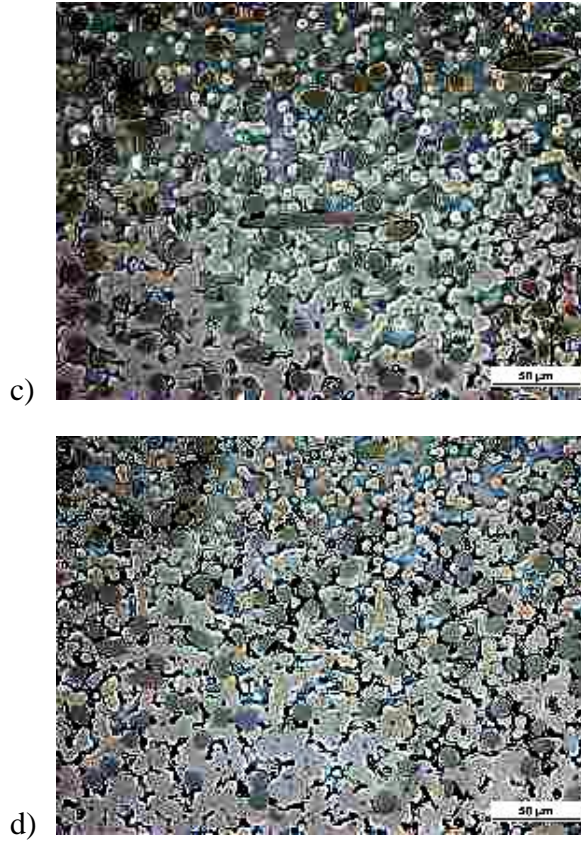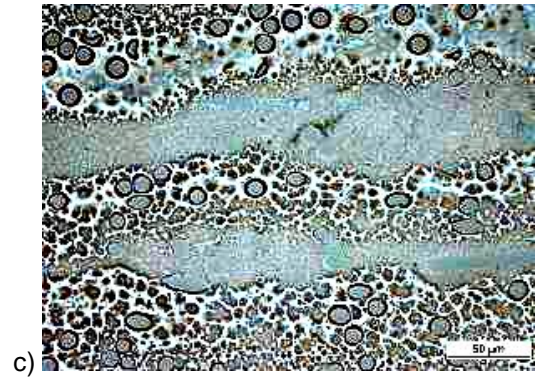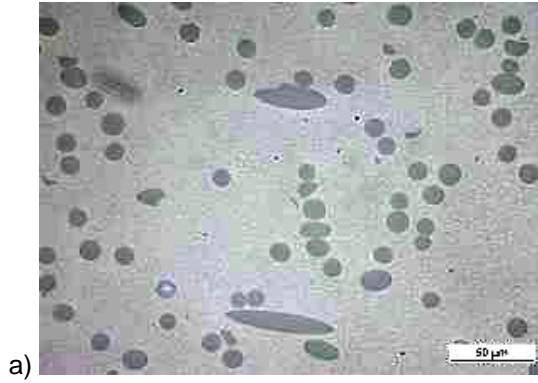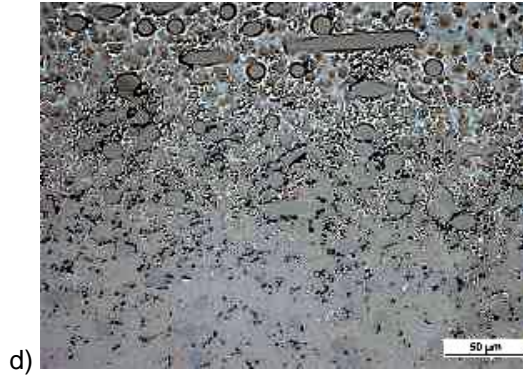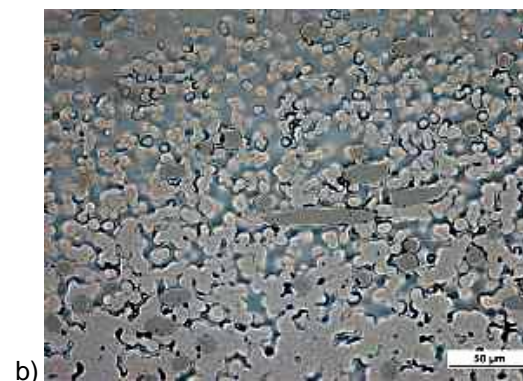

a)

b)

Fig. 5.3. The action of UV radiation on the degradation of the polymer composite, the glass fiber content of 30%

c)

d)

Fig. 5.3. The action of UV radiation on the degradation of the polymer composite, the glass fiber content of 30%

a)

b)

c)

d)

Fig. 5.4. The action of UV radiation on the degradation of the polymer composite, the glass fiber content of 20%
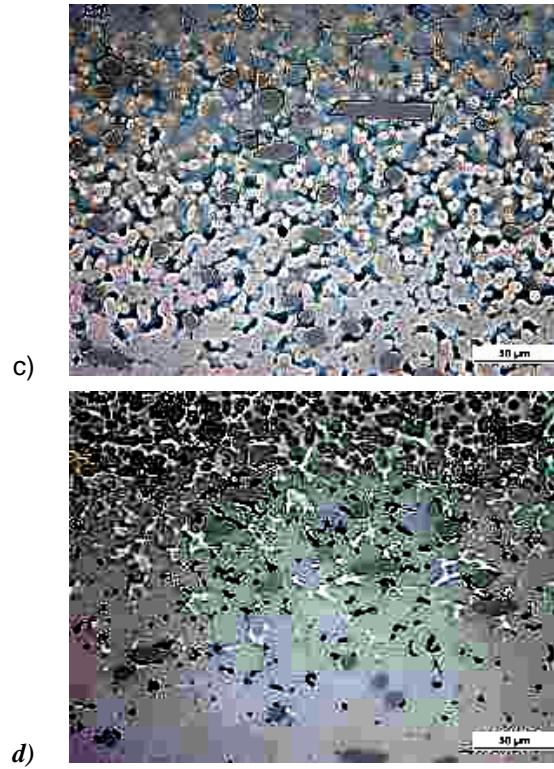

a)

b)

c)

d)

Fig. 5.5. The action of UV radiation on the degradation of the polymer composite, the glass fiber content of 10%

5.5. Conclusion

Based on the results of the experiment we can say that 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.

Hardness (HBW) of the composite depends mainly on the content and distribution of the glass fibers in the polymer matrix. HBW largest composite reached the 30% filler loading, whereas in the matrix occupy the bulk of the glass fibers as the filler content of 10%, which was occupying a larger volume of polymer matrix. The filler content of 10% HBW value slightly fluctuated. After 500 hours of UV HBW is slightly increased, after 750 hours of UV HBW it decreased to its original value, and after 1000 hours of UV irradiation was again to the small increase. At 20% and 30% filler content HBW hand the value after 500 hours of UV irradiation, and then decreased gradually decreased. It could result in a partially crosslinked chains to UV radiation. HBW values depended mainly from the point at which the measurement was carried out, whether it was a place where there was more accumulated fiberglass or was it a polymer matrix.

The optimum amount of filler for the composite is a glass fiber content of 30%, whereas the content of the best values were registered endpoints. As for the structure, are in the filler content of a site having marked heterogeneity in the distribution of the filler, be toxic to the mechanical properties of the composite. UV radiation is one of the most aggressive modes of degradation of polymers, which in the case of the composite expressed considerable degradation of the matrix in the glass fiber content of 10% even at the time of UV radiation 500 hours.

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