

LONG-TERM DEGRADATION OF COMPOSITES EXPOSED TO LIQUID ENVIRONMENTS IN AGRICULTURE*

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Polymeric particles composites with hard inorganic particles are abrasion resistant materials which can be used in the sphere of agriculture – e.g. for functional areas in renovation or as resistant layers. Silicon carbide waste particles were used in the present experiment, replacing the primary filler with waste without significant changes in the mechanical properties. The present paper describes the effect of immersion of polymeric particles composites with epoxy matrix in liquids on selected mechanical properties. Overall, it explains the change of hardness and resistance of abrasive wear, a typical kind of wear in the sphere of agriculture.

abrasive wear; mechanical properties; waste recyclation



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INTRODUCTION

In the sphere of agriculture, the used materials are often exposed to various aggressive substances and environments. Therefore, it is important to study their degradation processes in order to determine general features of their behaviour. The degradation process influences final mechanical properties of the materials which could lead to a limited state (Müller, 2013).

The polymeric matrix of composite particles systems can be formed by epoxy resins. The mechanical properties of epoxy resins and their ability to resist to various types of contaminants speak for their application in the sphere of agriculture. According to Ducháček (2006), epoxy resins are of medium resistance to degradation media action. It is in accordance with Doležal (1981) who stated that epoxy resins from bisphenol A are not susceptible to weather degradation for up to two years of exposure. Bonniau and Bunsell (1981) studied three types of glass epoxy composites: water diffusion leading to saturation has been shown to occur under humid conditions for two of them, the third composite was seen to degrade in the presence of water. In general, it could be stated that the absorption of polymer matrix composites by liquids (e.g. water) and the determination of saturation

are difficult to describe. Chemicals act on polymers in the following ways (Mleziwa, 1993; Joannes et al., 2014):

- sorption on the surface
- diffusion into the polymer
- physical or chemical interactions.

Unlike the organic fillers, the inorganic ones reduce polymers hygroscopicity (Mleziwa, 1993). The inclusion of hard inorganic particles into the epoxy matrix increases its abrasive wear resistance and hardness. In order to increase the wear resistance of two-component epoxy and polyester resins, Valášek, Müller (2012) used Al_2O_3 particles (waste particles 52–147 μm in size). As fillers, different types of waste (e.g. chips which were taken away from an endless saw) can be used as well (Valášek, Müller, 2013a, b). Basavarajappa et al. (2010) also describe a significant influence of Silicon carbide particles (SiC) on resultant resistance of polymer matrix to three-body abrasion. Mohan et al. (2012) describe a similar experiment in which SiC particles increased the wear resistance of polymers. One of possible application areas of these materials is the renovation of parts of agricultural machines.

The aim of the experiment is to verify the hypothesis that during the exposure to various environments,

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the waste filler does not accelerate substantially the degradation process and that the individual phases of interaction ensure the expected properties in the composite lifespan. This paper describes the effect of immersion of composites used in agriculture in liquids on hardness (Brinell) and abrasion resistance changes (two-body abrasion).

MATERIAL AND METHODS

The two-component epoxy resin Eco-Epoxy 1200/324 (DCH - Sincolor, a.s., Karlovy Vary, Czech Republic) functioned as the matrix. The curing agent P11 based on bisphenol A was chosen. The values stated by the manufacturer: viscosity 30–80 Pa·s (23°C), epoxy group content 3.0–3.4 mol·kg⁻¹, epoxy weight equivalent 290–330 g·mol⁻¹. As a filler, the SiC particles – waste of mechanical surface preparation (abrasive particles from blasting – not a dangerous waste) were used. The surface preparation is an important technological process (Müller, 2011; Novák, 2011). The microparticles size after the grit blasting process measured using a stereoscopic microscope was 86.25 ± 23.18 μm. Density of SiC waste particles corresponded to 3.2 g·cm⁻³, density of epoxy resin to 1.15 g·cm⁻³. The tested samples were prepared with 30 volume per cent (vol%) of the filler in the matrix. About 35 vol% of the SiC used in epoxy resin was taken as the limit of a probable application of the mixture (high saturation of the resin by the filler). The tested samples were casted into forms from a two-component silicone rubber. Rise of air bubbles during the mechanical preparation of the mixture (mixing) was eliminated in an ultrasonic vat. Hardening proceeded according to the technological requirements of the resin producer. After curing, the individual samples were placed in a relevant medium (liquids and environments).

Density and porosity

The theoretical density of the composites systems was calculated on the basis of the physical relationships, the actual density was stated on the basis of the ratio of weight and volume of the trial objects. An important first-class quality parameter of the composite system – the porosity (P) – was calculated according to the theoretical and real composite density.

Degradation

For the experimental definition of the effects of immersion in liquid chemical, the standard ČSN EN ISO 175 (2011) (Plastics – Methods of test for the determination of the effects of immersion in liquid chemicals) was modified. A long-duration test was used. The time between the individual intervals was 16 weeks starting from the day of curing (0–16–32–48–64 weeks). The test temperatures were 23 ± 2°C.

For the laboratory experiment, the following liquids were chosen:

- agricultural fertilizer – Cererit
- methyl-ester
- petrol
- diesel
- semi-synthetic used oil 10W-40 Mogul
- water

The chosen fluids are commonly used in the sphere of agriculture. The tested specimens were exposed to the laboratory conditions (standard) as well as to the outdoor environment.

For each specimen, the percentage increase or decrease in mass (A₁) was calculated immediately after the removal from the liquid using the formula:

$$A_1 = \frac{m_2 - m_1}{m_1} \times 100$$

where:

m₁ = weight before immersion (g),

m₂ = weight immediately after removal from the liquid (g) (ČSN EN ISO 175, 2011).

After the determined exposure time, the test specimens were pulled up from the degradation medium, washed, dried out, and tested according to the relevant standards (hardness, two-body abrasion).

Hardness

In order to determine hardness of the composites systems, the standard ČSN EN ISO 2039-1 (1998) was used as a guide. The tested specimens sized 35 × 25 × 9 mm. A ball of hard metal 10 mm in diameter was used. The specimens were tested under a 2.452 kN loading force for 30 s.

Abrasive wear resistance

The two body abrasion was tested on a rotating cylindrical drum device with the abrasive cloth

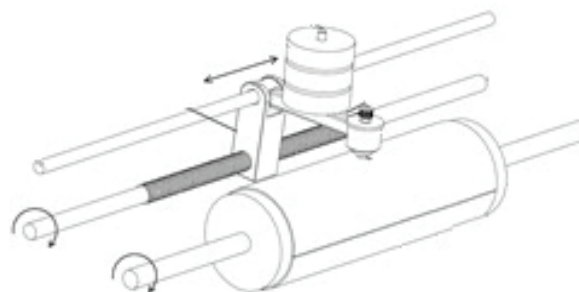


Fig. 1. Schema of equipment for two-body abrasive wear testing

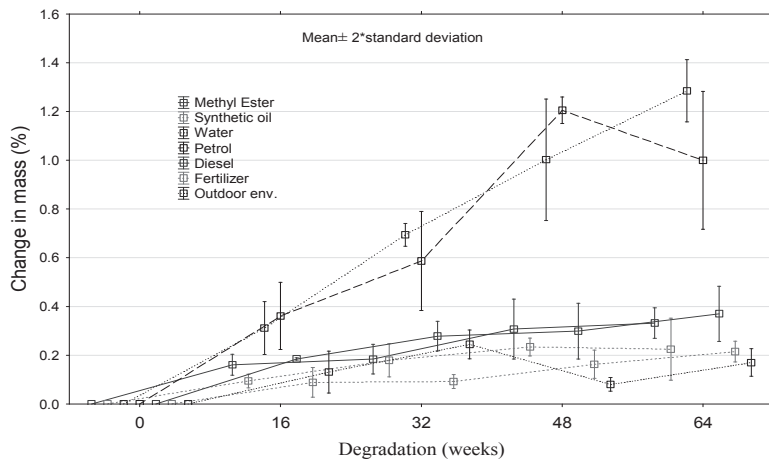


Fig. 2. Absorption (A₁) of filled systems for each fluid

of P220 grain size (Al₂O₃ grains) according to the standard ČSN 62 1466 (1993). The testing machine with the abrasive cloth consists of the rotating drum on which the abrasive cloth is affixed by means of a bilateral adhesive tape (see Fig. 1).

The testing specimen is secured in the pulling head and during the test it is shifted by means of a mowing screw along the abrasive cloth from the left edge of the drum to the right. The testing specimen is in contact with the abrasive cloth and it covers the distance of 60 m. During one drum turn by 360° the testing specimen is provoked left above the abrasive cloth surface. The following impact on the tested specimen simulates the concussion. The pressure force is 10 N. The diameter of the tested specimens was 15.5 ± 0.1 mm and their height was 20.0 ± 0.1 mm. The mass decreases were measured on analytic scales weighing with the 0.1 mg accuracy. The volume decreases were calculated on the basis of the detected volume and the density of the composites systems.

The test results of the chosen mechanical properties were statistically processed.

RESULTS

After 64 weeks of exposure time, the laboratory environment did not influence any of the evaluated mechanical and physical properties. The presence of air bubbles in the composites systems was evident. Porosity values of SiC composites systems corresponded to 6.8 ± 1.8% (density 1.77 g·cm⁻³).

The changes in colour and other appearance attributes (crazing, blisters, and other effects) after the degradation (64 weeks) were not determined. The physical and mechanical changes are described below. The absorption of filled epoxy resin for each fluid (and outdoor environment) is presented in Fig. 2 (A₁). The highest values of absorption after 64 weeks were recorded in water (1.3%) and petrol (1.2%). The lowest values after 64 weeks were recorded in fertilizer (0.2%) and in outdoor environment (0.17%).

Hardness and abrasive wear resistance of the unfilled resin compared with the SiC composites systems with 30 vol% SiC (before degradation) is shown in Fig. 3. The inclusion of 30 vol% of SiC particles led

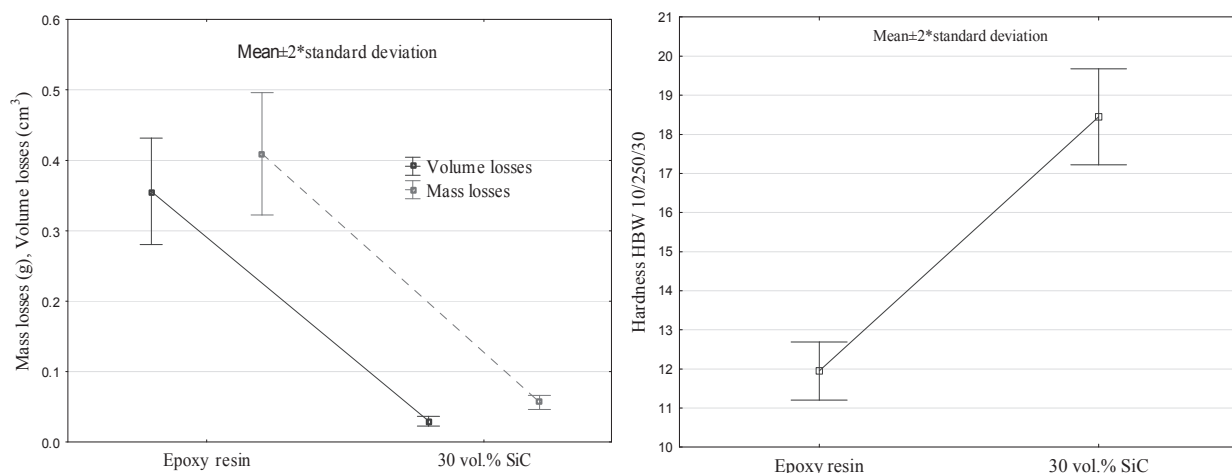
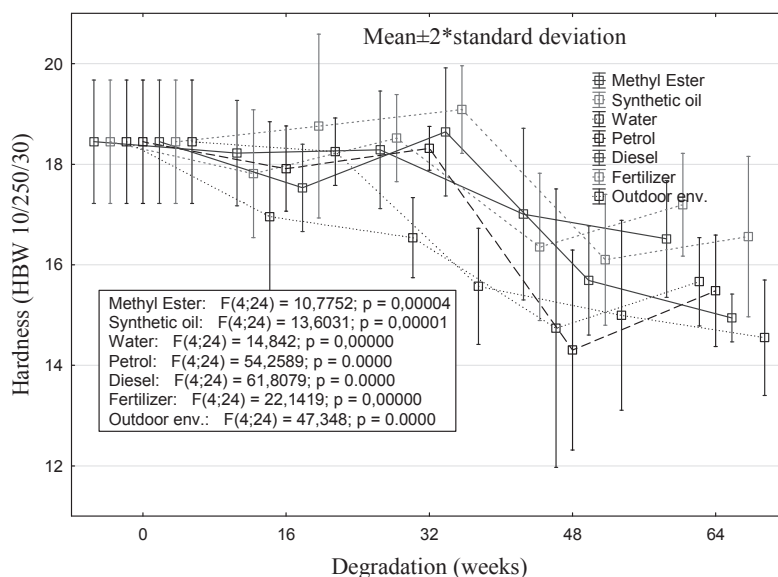


Fig. 3. Hardness and abrasive wear resistant of filled and unfilled systems

Fig. 4. Hardness – changes during the degradation



to the 54% increase of hardness. SiC particles led to the decrease of mass losses by 88% (increase of the abrasive wear resistance).

The change in hardness of the composites systems during the degradation (0–64 weeks) is visible in Fig. 4. In all cases, the degradation leads to a decrease of hardness values compared to resin before degradation. A significant decrease occurred after 32 weeks of degradation. The lowest value of hardness was recorded after 48 and 64 weeks for the outdoor environment, petrol, and water.

The statistical evaluation (hardness) of individual degradation periods (16–64 weeks) compared with values before degradation is given in Table 1. H_0 describes the zero hypotheses – there is no statistically significant difference among the compared data sets.

The changes in values of volume losses are apparent from Fig. 5. Values of mass losses significantly changed only in the case of water and petrol. These fluids increased mass losses by about 0.017 g (water after 48 weeks) and 0.021 g (petrol after 48 weeks).

The statistical evaluation (mass losses) of individual degradation periods (16–64 weeks) compared with values before degradation is given in Table 2.

DISCUSSION

The degradation of resins which are used as adhesives has been described by several authors. Müller, Valášek (2012) describe a significant negative influence of the liquid contaminants on values of lap-shear tensile strength of bonded joints. Significant changes of the adhesive bond strength occurred within 15–45 days depending on the adhesive and agents (Müller, Herák, 2010, 2013; Müller, 2013). However, degradation of composites does not affect the interaction with the adherent (steel sheet). Degradation of the composites can be affected by used filler.

The conducted experiment confirmed that the filled epoxy resin used is resistant to degradation processes in the used liquids. The influence of the degradation media increased the standard deviation. After 64 weeks of degradation there was no significant loss of the monitored physical and mechanical properties. However, in the interval of 0–64 weeks some degradation media affect the mechanical properties: the highest decrease of hardness was caused by water (20.1%) and by petrol (22.5%). The outdoor environment reduced hardness of filled resin by 21%. Water and petrol also led to

Table 1. T-test - Hardness

H_0 ; p>0.05 0 : 16-64	Degradation (weeks)			
	16	32	48	64
Methyl ester	0.58	0.66	0.01	0.00
Synthetic oil	0.12	0.82	0.00	0.00
Water	0.01	0.00	0.00	0.00
Petrol	0.12	0.62	0.00	0.00
Diesel	0.02	0.61	0.00	0.00
Fertilizer	0.53	0.07	0.00	0.00
Outdoor env.	0.51	0.00	0.00	0.00

Table 2. T-test – Mass losses (two-body abrasion)

H_0 ; p>0.05 0 : 16-64	Degradation (weeks)			
	16	32	48	64
Methyl ester	0.93	0.06	0.23	0.38
Synthetic oil	0.44	0.44	0.93	0.22
Water	0.02	0.04	0.00	0.01
Petrol	0.41	0.13	0.02	0.01
Diesel	0.20	0.63	0.34	0.68
Fertilizer	0.96	0.73	0.70	0.51
Outdoor env.	0.23	0.13	0.14	0.29

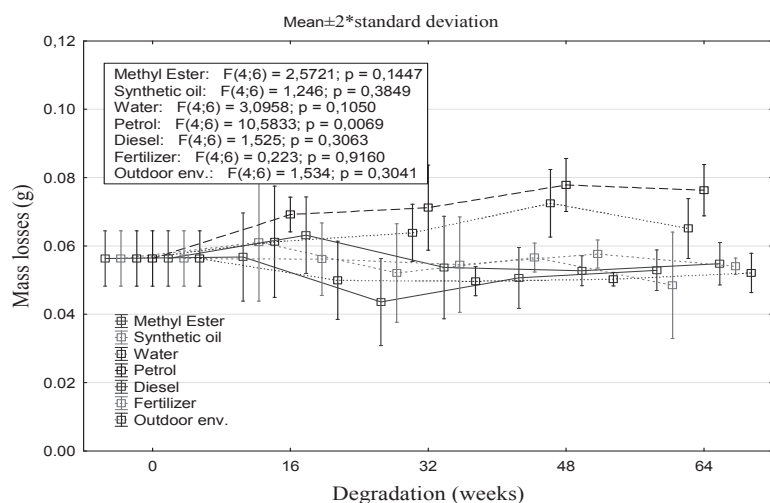


Fig. 5. Resistance to abrasive wear (mass losses) – changes during the degradation

the highest decrease in resistance to abrasive wear. Other liquids did not change the resistance to abrasive wear – there is no statistically significant difference among compared sets of data. Thus these materials with epoxy resin as the matrix offer a sensitive way of material recycling.

CONCLUSION

On the basis of the laboratory experiment, the degradation process of composites systems in liquids can be summarized as follows:

- Qualitative estimated changes (changes in colour and other appearance attributes changes in colour and other appearance attributes) were not observed.
- Waste material used in the epoxy matrix increases their significance.
- Composites were susceptible to degradation in water and in petrol – the average change in weight corresponded to 1.3% (water) and 1.0% (petrol). The composites hardness decreased to 14.69 HBW 10/250/30 (water) and 14.30 HBW 10/250/30 (petrol). The influence of the degradation media increased the values of mass losses caused by two-body abrasion – 0.0778 g (petrol) and 0.0725 g (water).

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