Degradation of strength properties of epoxy resin filled with natural-based particles

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Abstract. Degradation of polymeric materials can be considered as a limiting factor for their use. Mechanical characteristics of epoxy resins are reduced, for example, by the action and changes of temperature or humidity. Degradation also occurs in composite systems where the epoxy resins function as matrices, i.e. in polymer composite materials. If a natural filler is used together with the epoxy resin, we refer to these materials as biocomposites, where also the natural character of the filler material greatly affects the degradation process. The paper focuses on the description of the shear strength of the resin filled with particles prepared from the seeds of dates of Phoenix Dactylifera plant. The degradation was evaluated experimentally in laboratory conditions via the climatic chamber. The experiment describes composites with a particle size of filler 100-200 μm with a concentration of 5 - 10 wt%. As the number of degradation cycles increased, the tensile strength of both the unfilled and the filled epoxy resin decreased. After 5 weeks, the drop was up to 50%. The presence of the particles did not significantly affect the shear strength compared to the non-filled resin. The described way of utilization of the natural-based particles is the possibility of material utilization of secondary natural materials.

1. Introduction

At present, in the area of material engineering, the emphasis is placed on saving primary resources that can be readily replaced by secondary resources. The possibility of this substitution is filled with natural materials. A very promising area is the possibility of using secondary products on a natural basis in composite systems. [1, 2]

Natural materials can be in form of both particle and fiber in the composites. Particles are mainly used to optimize abrasive wear, they can increase shear strength or cohesive characteristics of the resulting material [3, 4]. Factors affecting the resulting properties of the composite system include particle size, morphology, surface properties and, last but not least, their concentration in the material. [5-7]

Secondary raw materials on a natural basis can substitute primary sources. Their meaningful use is also desirable from an economic point of view. Such materials can be considered, for example, as seeds that are produced during the processing of Phoenix Dactylifera plants, that is, dates [8]. Said et al. [9] describe that there are many scraps of Phoenix Dactylifera, which is produced on such a secondary basis - for example, in Algeria it refers to 85,000 tons/year. Such secondary products can be used energetically, another possibility is their material utilization where they can substitute materials
such as wood - wood flour, which is used in the field of material engineering to reduce the price of material while maintaining the required mechanical characteristics. An example of a similar substitution may be, for example, the work of Crespo et al. [10] who uses secondary products in composite systems in the form of almond husks, obtained as a by-product of the agri-food industry. The use of Phoenix Dactylifera particles in composite systems is described, for example, by Al Maadeed [11]. Polymeric materials, including epoxy resins, that are exposed to a specific environment for a certain period of time, somehow change their properties - they degrade. Degradation processes are caused by a variety of factors, including temperature, humidity, chemical effects, weather effects, and more. Materials, also polymers, lose their required properties by acting of named factors, which is reflected, for example, by a decrease in mechanical characteristics.

The aim of the experiment was to assess whether particles based on secondary renewable raw materials prepared from date seeds affect the shear strength of epoxy resin on steel adherents, and also to assess the degradation process of these composite systems in comparison with the unfilled resin.

2. Materials and Methods

Seeds of the dates can be considered as a secondary commodity resulting from the processing of Phoenix Dactylifera plants. Dates can be considered as a fruit that has been used for many years in a row and its use is still up to date. Effective use of all commodities arising during dates processing is important from the economic point of view of the entire process.

The seeds of dates grown in China were crushed with a knife mill at a speed of 20,000 rpm·min⁻¹, dried at temperature 105 °C and subsequently fractionated by analytical sieves. The fraction was formed between sieves of 100 and 200 μm.

The two-component epoxy resin was used as a matrix. This resin evinces excellent adhesion to a variety of materials and is therefore suitable for use in composite systems. The prepared microparticles were mechanically mixed with the epoxy resin to obtain the desired concentration of these particles in the composite system, namely 5 and 10 weight percent (wt%). The resulting composite mixture was applied to conventional carbon steel sheets (S235J0). These sheets were blasted before application of the composite mixture and their roughness was assessed by roughness parameters Ra and Rz, steel sheets were also cleaned and degreased prior to application of the composite composition. The degradation of the specimens was carried out in the climatic chamber according to the standard CSN EN ISO 9142, where the particular cycles were changed. Each cycle consisted of individual parts, see Tab. 1. There was always a rapid change of the desired parameters between the different parts of the cycle, within 15 minutes. These time periods are counted in the total cycle time, which corresponds to 24 h. Total 35 cycles (840 h) were performed, corresponding to 5 weeks. Samples were removed from the temperature chamber every 7 cycles - 1 week.

| Parameter  | 1 part | 2 part | 3 part |
|------------|--------|--------|--------|
| Temperature [°C] | 70     | -40    | 70     |
| Humidity [%]    | 90     | -      | 50     |
| Time [h]        | 16     | 3      | 5      |

The adhesive strength of the composite system on the steel adherent was evaluated according to CSN EN 1465 after removal from the degradation chamber - by defining the shear strength of these joints. After this destructive test, the types of disruption were assessed.

Electron microscopy (Tescan Mira 3 GXM) was used to describe morphology and particle size and was used to describe the interfacial interaction between the matrix and microparticle particles prepared from date seeds and to evaluate the fracture areas after a destructive test. To verify the hypothesis whether the presence of particles prepared from date seeds affect shear strength compared to a non-filled resin and whether the degradation process affects the resulting shear strength of the composite...
system on steel adherence, ANOVA and T-test were used. The truth of the hypothesis H0 that the
given factor does not affect the observed quantity indicates parameter p > 0.05.

3. Results and Discussion

Description of topography and particle size are crucial to the resulting properties of composite systems.
The shape and size of the particles influence both the cohesive and adhesive characteristics of the
composite system. Particle based on seeds of dates have an irregular shape that supports mechanical
interfacial bonding. The particle size is indicated by the following Tab. 2. The mean particle size was
148.83 ± 28.87 μm, ranging from 67 μm to 197 μm.

| Particle size [μm] | <100 | 100-119 | 120-139 | 140-159 | 160-179 | 180-200 | 200+ |
|--------------------|------|---------|---------|---------|---------|---------|------|
| Observations [%]   | 7    | 9       | 16      | 31      | 25      | 12      | 0    |

Prior to the degradation evaluation, the strength of the unfilled epoxy resin (12.28 ± 0.69
MPa) was compared with the system filled with 5 wt% (12.37 ± 0.60 MPa) and 10 wt% (12.36 ± 0.83 MPa). At the
significance level α = 0.05 it was shown that there is no statistically significant difference between unfilled resin and composite systems where the parameter for the composite 5 wt% was p = 0.82, and the H0 hypothesis for 10 wt% was p = 0.86. Roughness parameters and surface cleanliness are among the basic factors influencing
the adhesion strength between the composite system formed by the matrix of epoxy resin and
the used adherent. Optimizing these factors is crucial for interfacial interaction on this
interface. The basic parameters of the roughness of the blasted steel sheet prior to the
application of the composite system corresponded to Ra = 2.31 μm and Rz = 11.93 μm.

![Figure 1](image_url)

Figure 1. The dependence of the values of shear strength of filled and unfilled resin on
degradation time.
In the case of a non-filled resin, the shear strength dropped by 5.36 MPa. In the composite system with 5 wt% of particles caused a decrease of 6.12 MPa and 10 wt% in the system reached 6.29 MPa. The lowest shear strength after 5 weeks of exposure was recorded in the composite system with 10 wt% of the filler - value 6.07 ± 0.98 MPa. Statistical comparison of the degradation process, i.e. comparison with a data set that was not subject to degradation at a significance level α = 0.05, is shown in the following Table. 3.

Table 3. T-test: Effect of degradation on shear strength - parameter p.

| Degradation (weeks) | 1  | 2  | 3  | 3  | 5  |
|---------------------|----|----|----|----|----|
| 0 wt%               | 0.57 | 0.10 | 0.00 | 0.00 | 0.00 |
| 5 wt%               | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 |
| 10 wt%              | 0.24 | 0.00 | 0.02 | 0.00 | 0.00 |

After the first week of degradation, the decrease in shear strength values was statistically demonstrated in the resin filled with 5 wt% of the particles. After the second week of degradation, a statistically demonstrable decrease in shear strength was observed in both composite systems. In the case of non-filled resin, the decrease was only apparent after 3 weeks of degradation.

The interfacial interaction was evaluated by electron microscopy, on fracture surfaces after the destructive tests, see Fig. 2. The nature of the infringement was in most cases an adhesive type of failure. Failure thus occurred at the interface of filled resin and steel adherent. An increase in interaction at this interface could be achieved, for example, by another treatment of steel adherents prior to application of the resin, but blasting and subsequent surface degreasing are common treatments of materials where the epoxy resin is applied. [4, 5]

Figure 2. Interfacial interaction assessment – SEM: Mag 2.48 kx (left), Mag. 2.83 kx (right).
From Fig. 2 is apparent, that there is a good interfacial interaction between used particulate filler and the epoxy resin. For example, chemical surface treatment of particles could increase this interaction with natural fillers [2]. The experiment showed that natural particles create good interactions with epoxy resins that lead to the formation of composite systems with the desired properties - there is no reduction in shear strength - this assumption confirms a number of works [1, 9, 11]. The described way of using natural secondary materials is environmentally sensitive. Particles prepared from the Phoenix Dactylifera plant by processing the seeds, for example, can substitute the use made of a wood flour.

4. Summary
The effect of temperature changes in the range of -40 °C to +70 °C, along with changes in the humidity of 50 to 90%, significantly affected shear strength. This exposure of the test specimens in the degradation chamber for 5 weeks resulted in a decrease in the strength of the non-filled resin by 43.6%. For composite systems filled with microparticles prepared from date seeds, this drop was 49.5% (5 wt%) and 50.9% (10 wt%). A slight increase in the rate of the degradation of shear strength was observed as a result of the presence of a particulate filler from the date processing. However, the natural-based microparticle filler does not significantly affect the shear strength of the resin prior to degradation.

5. References
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