Influence of Fly Ash Fillers on Impact Resistance of Epoxy Matrices

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Abstract. In the first part of this work the impact of different materials is discussed. Relations for Charpy type tests are shown. Main part is devoted to enhance impact properties of epoxy matrix by Fly Ash. For their mechanical activation the high frequency ball milling is used.

Keywords: Fly Ash Fillers, Epoxy Matrix, High Frequency Ball Milling, Charpy Tests, Impact Toughness

1 Introduction

It is well known, that epoxy resins obey excellent mechanical properties and are used in the construction, transportation, and furniture industries. They have also high adhesiveness and excellent chemical and heat resistance, making them a common material for adhesives and high-performance coatings. Epoxy resins are cured with by using of Hardeners. There is great effort for using safer epoxy resins and hardeners from bio-based, sustainable alternative sources. For enhancing of mechanical properties of these resins the particle-based micron and sub microns fillers are often used. One of low-cost fillers are based on Fly Ash. Main problem here is special structure of raw form of this filler particles composed from highly porous core capped by practically nonporous spherical shell having low specific surface area. Main aim of this work is investigation of mechanical activation of Fly Ash by high frequency ball milling (destroying of shell) and changing of their concentration on enhancement of impact toughness of epoxy matrix.

2 Impact of materials

Impact experiments involve impacting the test material with a sudden blow of the impactor, which simulates the reaction of the material to high speed loading [2]. used Impact energy (J/m) and impact force (kJ/m²) are mainly used to describe impact effects [1]. Impact toughness is related to standard toughness (the area over the working curve, i.e. the integral of the stress as a function of strain to the point of failure) and the ability
of the material to absorb energy due to sudden loading. The impact is therefore mainly conditioned by the toughness of the material.

It can be stated that the toughness of a material is a property that demonstrates the material's ability to absorb mechanical energy from the outside, especially impact energy, through plastic deformation. In low-deformable materials, shock energy is dissipated by the propagation of stress waves. Toughness is measured as the energy required for plastic deformation and fracture. This amount of energy can be measured by the impact test method. During testing at different contact velocities, three types of material reactions to the impactor can usually occur [5]: rebound, penetration and perforation. The first phenomenon (i.e., rebound) occurs when the impact energy is insufficient to infiltrate the material and the impactor bounces back. However, the impactor will transfer a certain amount of impact energy to the material and damage it. In the second case (i.e., penetration) the energy of the impactor is further increased and it can penetrate the material. In this case, the impactor transfers its total energy to the material. In the third case (i.e., perforation), the energy of the impactor is sufficient to completely penetrate the material and some energy is lost due to friction between the material and the impactor.

For materials with low ductility such as thermoset-based composites, and ceramics three modes of failure are most commonly observed:

1. Cracking and peeling – from the point of impact, a pressure shock wave propagates from the point of impact and is reflected as a tensile wave from the rear interface of the material (plate) with air. Cracking occurs near the rear interface when the tensile stress in the reflected (tensile) wave exceeds the strength of the material.

2. Punching a hole – results in a nearly cylindrical hole punched in the material, nearly the size of the impactor. In metals, this usually occurs due to large shear forces at the edge of the moving part of the material (the packing), which lead to adiabatic softening and shear failure. In ceramics, this type of failure is a consequence of the so-called conical cracking mechanism.

3. Radial fracture – if the tensile strength in the material is less than the compressive strength, radial cracking occurs due to tensile radial stresses. This mode of failure is often observed in both ceramics and high strength (low formability) metals.

Low velocity (LVI) is defined as an impact velocity that allows static material response analysis to be used. For rigid lightweight structures (composite) with a high resonant frequency, the upper limit for low speed classification can be in the order of tens of m/s [6]. For very flexible material structures this limit can be of the order of cm/s or less [7]. The weight, material and shape of the impactor (the impacting body) must also be specified for impact resistance evaluation [3].
For the experimental determination of impact resistance, the impact is frequently caused by the free fall of a body of impactor of a suitable shape (Charpy type tests see. Fig. 1)

![Fig. 1 Principle of Charpy test](image)

The test device consists of a pendulum end-loaded with an impactor (hammer) which is lowered from a specified height to strike the specimen. The energy transferred to the material can be derived by comparing the difference in the height of the pendulum at the beginning $h_f$ and after the fracture $h_i$ (see Fig. 1).

The velocity of the impactor $V_o$ at the moment of impact can be easily determined from a simple relationship

$$V_o = \sqrt{2gh_f} \tag{1}$$

here $h_f$ is the initial impactor height and $g$ is the gravitational acceleration (9.81 m s$^{-2}$). It is also possible to formally determine the velocity $V_i$ after the impactor overshoots from the height $h_i$ to the level of the cracked sample.

$$V_i = \sqrt{2gh_i} \tag{2}$$

The impact energy $E_r$ depends on both the drop height $h_f$ and the impactor mass $m$.

$$E_r = mg h_f = mV_o^2/2 \tag{3}$$

Therefore, $E_r$ and $V_o$ can be changed independently of each other. From Eq. (3) it can be seen how the height of the fall is related to the speed of the impactor at the moment of impact. The energy of the impactor after the return oscillation to the level of the cracked material $E_i$ is then

$$E_i = mg h_i = mV_i^2/2 \tag{4}$$

The impact energy $E_a$ absorbed by the material during impact is simply
\[ E_a = m g (h_f - h_i) = m (V_o^2 - V_i^2)/2 \] (5)

Standard devices working on the Charpy pendulum principle only have the ability to record the initial (maximum) angle of the pendulum with the impactor \( \alpha \) and the highest angle of the pendulum after breaking through the sample \( \beta \).

The impact energy \( E_a \) absorbed by the material is then calculated from the angle of the hammer in the initial (\( \alpha \)) and final (\( \beta \)) position, the weight of the impactor \( m \) and the length of the arm \( L \). The impact energy \( E_a \) absorbed by the material is then calculated according to the relationship

\[ E_a = m g L (\cos(\alpha) - \cos(\beta)) \] (6)

This energy is still usually corrected for friction losses (comparison of impact energy without sample with calculation) [9]. Impact toughness \( F_c \) per cross-section unit is thus related to the total impact energy absorbed (by the material-sample) \( E_a \) (measured, for example, as the loss of potential energy of the impactor during impact) and the original cross-section of the material.

\[ F_c = E_a / (t \ b) \] (7)

where \( t \) is the thickness of the specimen and \( b \) is a its length between the supports.

During three-point bending, let the impact force \( F \) act on the center of the sample of thickness \( t \), width \( b \) and active length \( l \) (the distance between the supports), which causes a deflection \( p \). Assuming the validity of Hooke's law, the energy \( E_a \) absorbed in the sample can be expressed as [8]

\[ E_a = F \ p/2 \] (8)

If \( F \) is expressed by bending stress \( \sigma = (3F \ l)/(2 \ b \ t^2) \) [8] and deflection \( p = (F \ l^3)/(4 \ E \ b \ t^3) \) [8], the impact energy is expressed as

\[ E_a = \frac{\sigma^2}{18 \ E} \ b \ t \ l \] (9)

where \( E \) is initial Young's modulus in tension. For the impact energy \( u \) per unit volume (the total volume is \( b \ t \ l \)) it is then simple

\[ u = \frac{\sigma^2}{18 \ E} \] (10)

So \( u \) does not depend on the dimensions of the sample.

Since composites reinforced with continuous inorganic fibers and thermoset matrices exhibit an almost linear impact-deformation diagram until failure, it is appropriate to use energy \( u \) as a characteristic independent of the geometry of the samples.
In work [8], it was found that the ratio $I/t$ has an effect on the impact properties for composites reinforced with unidirectional continuous fiber.

To determine the impact dynamics at low speeds, a model of an elastic body composed of a combination of a spring with stiffness $K$ and an impactor mass $m$ is commonly used [4]. For this model, the maximum impact force of $F_M$ is equal to

$$F_M = V_o \sqrt{Km}$$

(11)

For this model, the maximum contact force increases linearly with the speed of the impactor at the point of impact [1].

Comprehensive analysis of toughness and its mechanisms in epoxy resins was recently published in [10]. Composites and resins with higher impact toughness have generally higher ability to absorb energy during fracture and prevent crack propagation. The cured epoxy resins are a multiphase system with the sizes of the phase are in the order of sub-microns or microns. Coarser filler particles can also act as stress concentration points, involves the generation of crazes and shear bands [10].

### 3 Experimental part

As material for matrix the epoxy resin 520 CHS and hardener TELALIT 492 in weight ratio 100:27 were selected. Epoxy 520 is based on bisphenol A and contains at least 28% bio-carbon, which comes from renewable sources. This unique resin is obtained by the production of epichlorohydrin from glycerin. Viscosity at 25°C is 12-14.5 Pa.s. The inorganic particles of Fly Ash (FA) were selected as fillers. FA from SILO Transport Pilsen was used, as raw filler. This FA had a light gray color and a density of 2 g/m$^3$. Mechanical activation of the FA particles was carried out using a Fritsch Pulverisette 7 planetary ball mill in sintered corundum vessels. Zirconia balls with a diameter of 10 mm were used, grinding took place in dry and wet conditions for 30 min., mass ratio of balls and filler 5:1. The speed was 850 rpm.

A predetermined amount of particles (1, 2, 3, 4 and 5% by weight) was firstly mixed with the hardener and then the hardener/filler mixture was added to the desired amount of epoxy resin. Mixing was carried out for 5 minutes using a Hanna magnetic stirrer. To determine the influence of particles concentration and milling conditions, a series of samples mixed using ultrasound (ultrasonic fly ash) were prepared by casting into glass molds. All composite samples were cured for 24 h at room temperature and then at 60 °C for 15 h.

The FA particle size distribution was measured using EDS analysis and using a Horiba 920 device working on the principle of light scattering. Deionized water was used as the dispersion medium. The dispersion was sonicated for 5 minutes. The microstructure of the particles was observed on a scanning electron microscope (SEM) Hitachi-model TM-3000 and (SEM) TS5130-Tescan at an accelerated voltage of 20-30 kV.
The impact toughness $F_c$ (see eqn. 7) was tested on the Charpy Labtest CHK 50J device according to the ČSN EN ISO 179-1 standard [9]. Friction losses determined during calibration are 0.02 J and speed $V_0 = 2.9 \text{ m s}^{-1}$. All measurements were carried out under climatic conditions of $(20\pm2) \degree \text{C}$ and relative humidity $(40\pm2) \%$.

4 Results and Discussion

Raw FA EDS spectra are shown in Fig. 1.

Fig. 2 Elemental quantitative analysis of FA

The largest portion is represented by silicon dioxide and aluminum oxide with traces of other metal oxides. Based on spectrum analysis, the fly ash was classified as category F (ASTM C618), which is based on the total amount of silica and alumina greater than 70%.

The particle size distribution of fly ash is shown in Fig. 3. Fig. 3A is for raw FA, Fig. 3B is for FA dry milled 30 minutes and Fig. 3C is for FA wet milled for 30 minutes.

Fig. 3 SEM images and particle size distribution of FA (A) unmilled fly ash, (B) dry milled, (C) wet milled
It is clear that the particle size was greatly reduced after milling. No milled FA with a particle diameter about 10 µm was converted to particles smaller than 1000 nm after dry milling and below 500 nm after wet milling. It is clear from the surface structure of the FA particles shown in the SEM images that grinding disrupted a large part of the spherical shell of the raw FA and subsequently resulted in a nano/micro material with more active surfaces.

Fc impact toughness results for raw FA, wet milled FA and dry milled FA are shown in table 1.

<table>
<thead>
<tr>
<th>Concentration [%]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw FA</td>
<td>0.016</td>
<td>0.018</td>
<td>0.016</td>
<td>0.015</td>
<td>0.017</td>
</tr>
<tr>
<td>Dry milled</td>
<td>0.023</td>
<td>0.018</td>
<td>0.039</td>
<td>0.0325</td>
<td>0.038</td>
</tr>
<tr>
<td>Wet milled</td>
<td>0.08</td>
<td>0.055</td>
<td>0.063</td>
<td>0.058</td>
<td>0.05</td>
</tr>
</tbody>
</table>

It is clear that the wet milled FA have the impact toughness much over to the impact toughness of the epoxy resin itself which had value 0.021 J mm\(^{-2}\). In table 1 are visible nonsystematic changes of impact toughness. These changes can be caused by the random presence of voids in the samples, which act as stress concentration centers. The main factor influencing impact toughness is therefore particle fineness but destroying of surface shell increase mainly other mechanical characteristics as dynamical moduli. It was found that real part of the complex modulus \(E'\) increased from 2813.04 MPa (without FA) to 4487.07 MPa (raw FA), to 4596.73 MPa (dry milled FA) and to 4639.25 MPa (wet milled FA) at 1, 5 Hz frequency for 3 wt % FA concentration at 40 °C.

5 Conclusion

The work is mainly devoted to impact characteristics at low strain rates, as is typical for Charpy type tests. The influence of various factors on the impact of thermosets are discussed.

The impact toughness is used for the selection of suitably mechanically activated Fly Ash that improves the impact characteristics of epoxy matrices.

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References


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