Polymer Systems Associated with Agricultural Byproducts

PhD dissertation
(Written by Gábor Dogossy)

Theses

Thesis 1 I adapted the Kelly-Tyson formula well-known in the literature for short fiber reinforced composites, applied for the determination of the critical fiber length of circular cross section fiber reinforcements, and this way it became applicable for systems associated with sheetlike particles (T1):

$$\frac{b_c}{h} + \frac{1}{\alpha} = \frac{\sigma_f}{\tau}, \qquad \text{(T1)}$$

where b_c is the critical value of the longer side of the sheet, h is the thickness of the sheet, α denotes a proportionality factor between the sides of the sheet ($a_c=\alpha b_c$), σ_f is the tensile strength of the associating material, τ is the shearing strength valid for the interface.

I determined the geometrical and strength properties of maize hull required for maize hulls longer than 0.62 mm to function as reinforcing material, and the results are the following:

the value of the proportionality factor between the sides of the maize hull (α) (based on 1000 measurements, determined with Student distribution) at 95% confidence interval around the average value is $\alpha=0.43\pm0.012$; the tensile strength of maize hull containing 11.8 weight% cellulose and 33 weight% hemi-cellulose determined with elementary tensile test is in the $\sigma_{MH}=42.07\pm16.4$ MPa interval, and based on literature data (K. Van de Velde; J Thermoplast Compos, 14, 2001, 244-260) considering the smallest possible shear strength that can be applied on a reinforced composite of the given characteristics ($\tau=3.8$ MPa).

Thesis 2 I revealed that the acoustic emission test (AE) can be applied to characterize the failure process of agricultural byproduct associated PE systems.

a.) I found out through AE tests carried out at different associating material content that there is a linear relationship between the filler content and the number of acoustic events occurring in a unit time.

b.) I verified that the number of acoustic events detected in the AE tests is in linear relationship with the tensile strength of the composite.

c.) I proved with measurements that three different, major failure modes can be separated in maize hull associated PE systems based on the amplitude curves detected during the tests:

- I. matrix deformation (below 25 dB)
- II. pull-out of the associating material (26-40 dB)
- III. breakage of the associating material (above 40 dB)

Thesis 3 I found in case of PE matrix composites produced in melt mixing technology and having different associating material content that the initial geometrical properties of the associating material change to a great extent. I proved that the proportionality factor, α, defined in the Kelly-Tyson formula modified for sheetlike particles as reinforcements takes the exponential form revealed by (T2) for the different associating materials between 0 and 30 weight% associating material content:

$$\overline{\alpha} = \alpha_A \cdot e^{-\frac{TA_t}{A}} + \alpha_0 , \qquad \text{(T2)}$$

where TA_t is the amount of associating materials in the composite in weight percent, α_A, A and α_0 are constants characterizing the associating material.

I showed that in case of maize hull association (as reinforcement) proportionality factor $\overline{\alpha}$ follows the function defined above with a correlation factor of 0.9916 if the constants are: $\alpha_A=-0.1546$, $A=10.8311$ and $\alpha_0=0.5851$; in case of ground sugar cane bagasse association correlation is 0.9949 if the constants are: $\alpha_A=0.1066$, $A=13.1174$ and $\alpha_0=0.4730$; and in case of ground maize hull association correlation is 0.9961 if the constants are: $\alpha_A=0.1074$, $A=13.0615$ and $\alpha_0=0.5824$. Grinding was carried out with grinder equipped with a sieve of 0.2 mm hole size.

Thesis 4 I proved that thermoplastic starch (TPS) softened with 21 weight% maltitol and 10.6% glycerin loses its plastic property obtained in the production after the third day (between the 72^{nd} and 84^{th} hour, depending on the humidity of the environment), and it becomes rigid. The reason for this phenomenon is that the polymer aims at equilibrium moisture content depending on the humidity of the air. During this process (in the examined period of 160 hours) tensile strength and tensile stiffness increases linearly, while specific elongation decreases according to function (T3) composed of two parts:

$$\varepsilon_T(t) = 1.32 + (28.79 - 1.32) \cdot e^{-0.0689 \cdot t}, \qquad \text{(T3)}$$

where ε_T is the change in time of the specific elongation belonging to the maximal stress of the tensile diagram, and t is the time passed after production.

The process can be divided into the following two specific domains:

The first phase of the process (the first 24 hours), during which water diffuses out of the TPS, described by the exponential part of the function is material-dependent,

the second term shows the value characteristic of the equilibrium, hence is partly material dependent, and is partly a function of the current value of the equilibrium moisture content of the environment.

Thesis 5 Based on literature data, I developed a new, sugar cane bagasse associated composite with thermoplastic starch matrix softened with maltitol and glycerin. The tensile strength of the composite reaches that of PE, while the other mechanical properties of the composite (tensile, bending stiffness, bending strength, Charpy impact strength) exceed the similar parameters of PE severalfold in case of the following production conditions: 1500 bar injection pressure, 350 bar holding pressure, 135 cm^3/s injection rate, 50 s residual cooling, and zone temperatures in the range of 90-120°C.

Thesis 6 I proved that the common application of maize hull and sugar cane bagasse (at 30 weight% associating agent content) in polyethylene matrix composites, as well as in the 10.6 weight% glycerin and 21 weight% maltitol softened thermoplastic starch, hybridization occurs in the following way:

a) The application of sugar cane bagasse and maize hull of two different grain sizes (average grain sizes: 5.94x2.35 mm and 0.07x0.04 mm) results in a negative hybrid effect in case of most mechanical properties. I experienced better results for the different grain size maize hull, since it showed positive hybrid impact for Charpy impact strength, bending strength and bending modulus, while the other properties depended on the ratio of the different associating materials.
b) Thermoplastic starch softened with glycerin and maltitol shows the best results in terms of producibleness and brittle fracture properties in case of the composition given above; however a negative hybrid effect is experienced in the mechanical properties compared to the starch softened only with maltitol and only with glycerin.