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Highly filled biocomposites based on ethylene-vinyl acetate copolymer and wood flour

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Abstract. Recently, there is a great interest in the world to biodegradable materials based on synthetic polymers in a composition with natural fillers. Highly filled polymer composite materials based on various grades of synthetic block copolymer of ethylene vinyl acetate with wood flour were under investigation. Five grades of ethylene-vinyl acetate copolymer differing in the content of vinyl acetate groups and a melt flow index were used in this work in order to find the best one for highly filled biocomposites. Wood flour content in biocomposites was 50, 60, 70 weight %. The rheological and physico-mechanical characteristics of the resulting biocomposites were studied.

1. Introduction

Superconcentrates are polymer composites with a high filler content. They are intended to be added to pure polymer during the manufacture of finished products in order to impart a certain color or improve the functional characteristics of the product. Today, the most widely uses superconcentrates of dyes, they also called as masterbatches. Superconcentrates of oxo-degrading additives, UV stabilizers, antistatic agents, antioxidants, flavors, etc. are also manufactured. The idea of creating superconcentrates of biodegradable composites based on synthetic polymers with biodegradable fillers has not been studied well.

The most common biodegradable materials, based on synthetic polymer and natural filler, are the composites with wood flour. A number of works are known where composites, based on synthetic polymers filled with wood flour, were studied. Such materials have a wide range of applications in packaging sector (films, bags, containers etc.), in automotive and electronic industry, for furniture, suitcase, grinding discs, safety helmets [1]. Such materials are rather widely described [2-4].

In the previous work it was found, that the particle size of lignocellulosic filler has influence on physical properties and biodegradation of biocomposites based on polyethylene. It was found that as filler particle size decreases, the rate of biodegradation decreases [5]. Sometimes, it is proposed to use not only one polymer, but a mixture of two or more polymers, as a polymer matrix in such biocomposites, for example blend of polyethylene and polypropylene was used as a polymer matrix in the work of E. Mastalygina [6]. In the other work the blend of polyethylene with ethylene with vinyl acetate copolymer was used as a matrix [7]. Superconcentrates contain a small amount of synthetic polymer and after adding superconcentrate to the other pure polymer the composite with two blended polymers and the filler is being obtained.

Currently, a lot of works have been devoted to improving the compatibility, as well as the mechanical and rheological properties of wood-polymer composites, but a little amount of works studied highly-filled biocomposites [8-10].

2. Materials and methods

It was studied the influence of the chemical composition and physical properties of the matrix on the main properties of highly filled composites with wood flour. Five different grades of the ethylene vinyl acetate copolymer (EVA) from LG Chem, supplied by OOO Ecoplastics (Moscow, Russia), differing in the content of vinyl acetate (VA) groups and in the melt flow index (MFI) were taken as matrix (table 1).

Table 1. Characteristics of different trademarks of ethylene vinyl acetate copolymer (EVA). Characteristics were provided by LG Chem.

No	EVA trademark	VA content [weight %]	Melt flow index (MFI), [g/10 min] ASTM D 1238	Tensile strength, [MPa] ASTM D 638	Elongation at break, [%] ASTM D 638	Density, [kg/m^3] ASTM D 1505	Melting temperature, [^{o}C] DSC
1	ES28005	28	5	13.5	800	0.951	72
2	EA28025	28	25	9.5	850	0.951	69
3	EA28150	28	150	4.0	900	0.946	70
4	EA19150	19	150	7.0	800	0.940	80
5	EC15006	15	6	16.0	800	0.936	89

Three EVA trademarks (ES28005, EA28025, EA28150) have the same content VA groups, but different MFI, while two other trademarks (EC15006 and EA19150) differ both by MFI and the content of VA. The effect of these two parameters on the properties of highly filled composites was studied.

As a filler for superconcentrates, wood flour (a mixture of deciduous and coniferous trees) was used because it is wide-spread cellulose-containing filler. Wood flour was supplied by OOO Novotop (Moscow, Russia). Wood flour contains 46% cellulose, 20% lignin, 29% pentosans, 5% polyuronic acid, residual ash content is 10% [11]. Wood flour was filtered by electromagnetic sieve shaker Matest A059-02KIT (Italy) through a sieve with a mesh diameter 0.1 mm.

The main difficulty in processing composites based on thermoplastics and wood flour is the propensity of untreated wood particles to form large agglomerations. Therefore, using traditional methods of mixing, the fibers distribute poorly in the polymer matrix, and it leads to a significant decrease in the reinforcing action of fibers [12]. There are several methods for mixing polymers: extrusion, milling, compounding on a Brabender-type plastograph. In the work [13], various methods of mixing polymer materials were considered, and it was concluded that milling provides the best distribution of the components into the polymer matrix. Therefore, in this work for mixing EVA and wood flour heated mixing rolls UBL6175BL (China) were used. A series of composites was prepared: EVA + wood flour 50%, 60 and 70% with all the used above EVA trademarks. Milling processing mode: mill roll temperatures T1 / T2 = 130/150 ℃, roll speed 8 rpm.

The rheological properties of the obtained composites were studied by measuring the melt flow index (MFI). MFI was determined according to the standard [14]. The load is 2.16 kgf, the melt temperature is 190^{o}C.

The obtained composites were pressed on a hydraulic press Biolent RP-12 (Russia) at a temperature of 140 ℃ and pressure 40 kgf/cm^2 for 1 minute. As a result, flat sheets of square form with a thickness of 0.3 to 0.6 mm were prepared.

Samples for mechanical tests were cut from the sheets. Measurement of strength and elongation was performed according to ISO 527-4 [15] by the universal testing machine GOTECH AI-7000M

(Taiwan) at a deformation speed of 100 mm/min. Eight specimens were tested for the tensile and flexural properties of each composite, standard deviation was calculated. The density of the composites was studied by the hydrostatic weighing method in accordance with standard [16].

3. Results and discussion

Table 2 shows the measurement data for MFI of composites, with a filling of 50% and 70%. The MFI values are very low even at 50% wood flour content in the composite. Nevertheless, as a result, it was confirmed that with an increase in the MFI of the polymer matrix, the MFI of highly-filled composite increased. With a filling of 70%, the flow was not observed at all.

Table 2. Melt flow index of composites based on EVA and wood flour.

Filler content [weight %]	EVA trademark	Melt flow index (MFI) [g/10min]
0	28005	5
	28025	25
	28150	150
	19150	150
	15006	6
50	28005	0.08
	28025	0.28
	28150	0.65
	19150	0.15
	15006	0.03
70	28005	Not flow
	28025	Not flow
	28150	Not flow
	19150	Not flow
	15006	Not flow

The high viscosity of the composite is due to the fact that wood flour particles are in the form of fibers, i.e. a high L/D ratio (the ratio of the length of the particle to its diameter). It is also possible that part of the filler starts to degrade at the test temperature (190°C) [17]. According to the literature, wood flour starts to undergo thermal degradation (loses 3 wt.%) at 240-250°C in nitrogen atmosphere [18], but this temperature can be lower in the air and under mechanical treatment. Also, with an increase in the content of VA groups in EVA matrix, the MFI of highly filled composite increases. VA groups have good adhesion to the wood flour, that is why biocomposites with the higher VA content have better distribution of wood particles in the matrix and as a consequence less viscosity of biocomposite.

Table 3 shows tensile strength and elongation at break of EVA composites with wood flour. It can be concluded that the viscosity of the polymer matrix has a significant influence on the strength of the composites, the higher the MFI of the matrix, the lower the tensile strength of the composites because MFI is directly related to molecular weight distribution (MWD) of the polymer [19]. Also, the strength of the composites depends on the content of VA groups in the polymer matrix, the lower content of VA groups, the higher the tensile strength. It may be explained, because with an increase in the content of VA groups in EVA, its crystallinity degree decreases and the modulus of elasticity increases [20]. The content of the filler does not significantly affect the strength of the composites up to 60% of the filling, however, for a number of composites, a significant reduction in strength at 70% filling was found. The elongation at break of the composites depends on the MFI of the polymer matrix (the

higher the MFI, the lower the elongation), the VA content (the elongation is higher at a high VA content) and the filler content in the composite (the smaller the filler content, the higher the elongation). The density of the composites tends to increase with the increasing filler content. This is due to the higher real density of wood flour (1.54 g/cm^3), compared to the density of pure EVA (0.95 cm^3).

Table 3. Mechanical characteristics of composites on the basis of EVA and wood flour with the filling of 50, 60 and 70 weight %.

Filler content [weight %]	EVA trademark	Tensile strength [MPa]	Elongation at break [%]	Density [kg/m^3]
50	28005	3.3 ± 0.2	57.5 ± 5.8	1.147 ± 0.002
	28025	2.9 ± 0.2	26.4 ± 4.9	1.145 ± 0.001
	28150	2.4 ± 0.1	9.4 ± 5.3	1.141 ± 0.003
	19150	3.1 ± 0.2	4.2 ± 1.3	1.140 ± 0.003
	15006	3.8 ± 0.5	5.5 ± 1.6	1.134 ± 0.002
60	28005	3.3 ± 0.2	9.4 ± 1.6	1.185 ± 0.002
	28025	2.8 ± 0.2	8.3 ± 0.1	1.179 ± 0.003
	28150	2.7 ± 0.2	4.3 ± 0.8	1.184 ± 0.001
	19150	2.8 ± 0.2	1.7 ± 0.1	1.171 ± 0.001
	15006	4.1 ± 0.9	2.0 ± 0.6	1.089 ± 0.011
70	28005	3.4 ± 0.3	4.0 ± 0.8	1.216 ± 0.001
	28025	2.2 ± 0.4	6.7 ± 3.3	1.166 ± 0.004
	28150	2.0 ± 0.3	5.0 ± 1.1	1.189 ± 0.009
	19150	2.1 ± 0.1	2.1 ± 0.7	1.205 ± 0.007
	15006	2.9 ± 0.2	2.1 ± 0.7	1.193 ± 0.009

4. Conclusion

Rheological and mechanical properties of highly filled biocomposites based on ethylene-vinyl acetate copolymer were studied. The main purpose of such materials is using as superconcentrates in the process of manufacturing products from biocomposites. That is why the mechanical characteristics are important only for comparing the composites with each other and estimating the adhesion of the matrix polymer with the filler. It was concluded that the most durable composites are the ones based on EVA 15006, but because of the lowest MFI, they have restrictions on the processing methods. The most optimal combination of characteristics (tensile strength, elongation at break and MFI) are found in the composites based on EVA 28025, which indicates the prospect of using this EVA trademark for manufacturing of superconcentrates.

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