

POLYMER COMPOSITES CONTAINING WASTE DUST FROM POWER PRODUCTION II. STRENGTH CHARACTERISTICS OF COMPOSITES BASED ON UPR/HIPS POLYMER SYSTEM

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Polymer composite material based on “unsaturated polyester resin/high impact polystyrene” polymer system as matrix and waste dust from power production as filler was studied. The waste was mechanically activated at dry conditions at room temperature for 30 minutes. Strength characteristics – impact, bending and compressive strength – dependance on the waste concentration was determined. The optimal results were achieved at waste concentration of 10 w.%. Morphology observations of filled systems were performed to clarify the influence of the structure on composite’s properties.

Key words: polymer system; waste dust; mechanical activation; strength characteristics; morphology

ПОЛИМЕРНИ КОМПОЗИТИ КОИ СОДРЖАТ ОТПАДНА ПРАШИНА ОД ПРОИЗВОДСТВО НА ЕНЕРГИЈА II. КАРАКТЕРИСТИКИ НА ЈАЧИНАТА НА КОМПОЗИТИТЕ БАЗИРАНИ НА ПОЛИМЕРНИОТ СИСТЕМ UPR/HIPS

Во тудот е проучуван полимерен композитен материјал на база на „незаситена полиестерска смола / високо јакосн полистирен“ како матрикс на полимерен систем и отпадна прашина од производство на енергија. Отпадот беше механички активиран на суво на собна температура за време од 30 минути. Беа одредени карактеристиките како што се јачина на удар, свиткување и компресија зависно од концентрацијата на отпадот. Оптимални резултати беа постигнати при користење на отпад од 10 мас.%. Морфолошките следења на полнитото се искористени за разјаснување на влијанието на структурата врз особините на композитот. Докажано е дека е формирана нова композиција која се карактеризира со нови додатни процеси на оние кои веќе постојат при стврдувањето како фазна сепарација и генерирањето на интерфазен слој.

Клучни зборови: полимерен систем; отпадна прашина; механичка активација; јачина; морфологија

INTRODUCTION

Previous studies have shown that it is possible to use waste dust from power industry as filler in polymer composite materials based on thermosetting polymers as unsaturated polyesters. However, it was found that the waste impacts negatively some strength characteristics of the resultant composites, most probably because of poor adhesion on the “polymer/filler” interface borderline

[1]. So the waste dust was physically modified for the purpose of improving the interface interaction between both two phases. Physical modifying was performed by mechanical treatment of waste particles that resulted in a so called mechanical activation. Such processing, according to some scientific references, causes the appearance of pores, holes or cracks on the particles’ surface, which affects the composite microstructure and properties [2].

Another way to improve the strength characteristics of composites is through polymer matrix modifying. It is well known that a large part of thermosetting polymers, like polyester and epoxy resins, have been widely used for polymer composites containing disperse and/or fibrous additives. Many of these composites have been applied as construction materials in the building, automotive and other industrial activities. Unsaturated polyester resin (UPR) has been used as a polymer matrix in compositions. The use of UPR in composite materials is limited by its brittleness and relatively high volume shrinkage [3]. These disadvantages are usually removed by filling the UPR with micro- or nanosized disperse or fibrous fillers [4,5], or by physical or chemical modification using polymer additives – thermoset or thermoplastic polymers, elastomeres, oligomeres, etc. [6–9]. Some of the most efficient polymer modifiers are thermoplastic polymers. Therefore, a modification of UPR by high-impact polystyrene (HIPS) was experimented as a possible way to increase the strength characteristics of the composite material.

This paper presents the outcomes of the strength properties investigation of an experimental material composed of UPR modified with thermoplastic additive and mechanically activated waste dust from power production.

EXPERIMENTAL

Materials

Polymer matrix. Polymer system based on Unsaturated polyester resin “Vinalkid 550 PE – R” (Orgahim, Bulgaria), with high impact polystyrene as a polymer additive, was used as matrix for the polymer composition. The resin is characterized by the following features: acid number max 30 mg KOH/g (BDS EN ISO 3682); Bruckfield viscosity (ISO 2555) 550 – 850 MPa·s; gelation time at 25 °C 6 – 8 min. It is manufactured in the form of a 63 – 66% solution of the polyester in monostyrene.

HIPS (Neftohim, Bulgaria) was used as a 40 w.% solution in styrene. From previous investigations of the polymer system UP/HIPS, the optimal quantity of HIPS was determined as 10 w% from UPR weight [10].

Filler. Waste dust collected by electro filters of the thermal power station Maritza – Iztok (Bulgaria) was used as filler of the polyester resin. The filler was first dried in electrically heated thermal

chamber at 80 °C for 24 hours to remove absorbed moisture, prior to its use in the polymer composite. Then it was fractioned and the fraction 125 – 250 µm of the grains was used in the composite.

The waste concentration was experimentally determined previously to be up to 20 wt.%. Amounts greater than 20 wt.% brings two negative effects that can cause deterioration of the properties as follows:

- sharp increase in the composition viscosity;
- sedimentation of the filler and thereby anisotropy of the mechanical and strength properties.

Filler particles have been mechanically pretreated in a ball crusher with agate balls, in dry conditions, at room temperature for 15, 30, 45, 60, 120 and 180 minutes. During the milling process the surface particles energy increases constantly, but in a certain moment the geometric factor of activity (the specific surface) starts to exert influence. From this moment the specific surface decreases, and hence this corresponds to the optimal milling time. In the concrete case the optimal results were obtained at milling time of 30 minutes. After the mechanical activation, the waste was fractioned again to clarify possible changes in particles' size distribution.

Specimens

Standard specimens were used to assess the impact of the filler quantity on the strength characteristics of the polymer systems. The quantities of the polyester and the polymer additive were mixed well with a high-speed rotational mixer under mixing conditions defined by previous studies: rotation speed of the mixer's rotor – 700 min⁻¹, duration of mixing – 10 min [8]. Then the waste was added into the composition and thoroughly mixed until homogeneous mixture was obtained. Cyclohexanonperoxide in the form of a 50 % solution in dioctylphtalat (activation disintegration energy 121.4 kJ·mol⁻¹, content of the active oxygen – 9.1%) as an initiator and cobalt naphthenate as an accelerator were used for the curing of the polyester. The concentration of the initiator and accelerator was 2 w.% of the polyester's mass. Both the initiator and accelerator were added consecutively to the mixture by mixing for 15 – 20 s for each addition. The specimens were cast in polypropylene moulds of a size specified in the standard, cured at room temperature for 24 h, and then thermally processed for 2 h at 80 °C.

Testing methods

Determination of waste dust chemical composition. Following the mechanical treatment, the waste was processed thermally by three consequent treatments for the purpose of investigating the possible chemical changes. At the first stage, at 110 °C, moisture was removed. At the second stage all organic components were burnt at 600 °C and, at the third stage at 800 °C – the crystal hydrate water and gases resulting from matter decomposition were eliminated. The residuum was subjected to classical silicate and atomic absorption analyses, described in [1]. Since the weight losses of the waste did not exceed 4 wt. % and were related mainly with the detachment of physically connected water and non-burnt coal, thermogravimetric measurements were not needed.

Strength characteristics measurements.

The strength characteristics of impact strength, compressive strength and bending strength were determined as follows:

– *compressive strength* (MPa), (BDS EN ISO 604:2004), was determined on a ZD 10/90 test device at a motion speed of the plates 0,2 mm/s and measurement accuracy of $\pm 1\%$;

– *bending strength* (MPa) (BDS EN ISO 178:2002), was determined on a “Schopper” test device at a uniform loading speed and measurement accuracy of 1% (span – 40 mm);

– *impact strength* (kJ/m^2), (BDS EN ISO 179-2:2003), was determined according to Sharpi (pendulum power of 1.0 J, span of 40 mm), on standard unnotched specimens.

Every value is taken as an average of values for 10 measured specimens.

Morphology observations. Optical microscopy was used to study the composite morphology – observations were made using optical microscope PZD (Poland) at magnification 90 and 110 \times .

RESULTS AND DISCUSSION

Waste dust characterization

It is obvious from the data presented in Table 1 that the mechanical treatment influences the particles size toward larger size distribution. Waste fractional analysis showed that the amount of largest size particles ($>500 \mu\text{m}$) decreases and the

amount of smallest ones ($<45 \mu\text{m}$) increases. Size distribution of medium size particles (between 125 and 500 μm) becomes more uniform as the amount of fraction 125 ÷ 250 μm decreases and that of 250 ÷ 500 μm increases.

Table 1

Fraction distribution of waste before and after mechanical activation.

№	Particles fraction, μm	Content, wt. %	
		Unactivated	Mechanically activated
1	>500	3.61	1.85
2	500 – 250	22.87	31.49
3	250 – 125	45.38	34.64
4	125 – 63	21.03	21.35
5	63 – 45	4.46	4.92
6	<45	2.35	5.74
$\Sigma =$		99.70	99.99

The XRD analysis revealed the presence of the following phases (vol.%): quartz (35.68); $\text{CaAl}_2\text{Si}_2\text{O}_8$ (28.03); mullite – $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (25.95); magnetite – Fe_3O_4 (7.06); cristobalite (3.27) (Fig. 1).

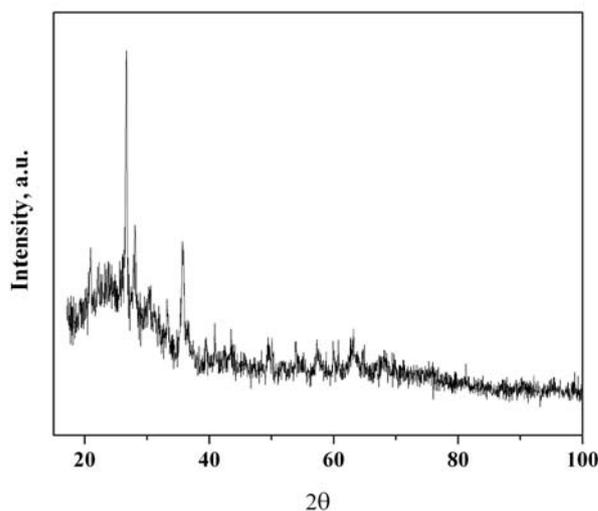


Fig. 1. XRD pattern of waste dust

Chemical composition. Previous chemical analysis of waste showed that it is composed by mixture of oxides – more than 50% is SiO_2 , and there is some Al_2O_3 , ferrous oxide and other oxides. The mixture also contains heavy metals oxides and alkaline oxides in traces. The unique volatile oxide is SO_3 [1]. Chemical analysis of the

waste after mechanical processing did not reveal changes in its composition.

Strength characteristics of composite material

Data obtained by strength characteristics measurements for polymer composites based on pure UPR and polymer system UPR/HIPS demonstrate the influence of the polymer additive on the material's strength characteristics.

Impact strength (σ_i). Considering the impact strength, the positive effect of HIPS is clearly expressed – the values for the composites based on the UPR/HIPS polymer system are higher than the ones for pure UPR-composites in the entire waste concentration range (Fig. 2). The main contributor to this effect is the polymer additive, which was corroborated by our previous investigations: it was found that amounts of HIPS up to 10 w.% increase the shock resistance of UPR significantly [10].

The waste amount affects the impact strength values for both studied composite materials. There is slightly increasing trend for the pure UPR-based composite. Values for the UPR/HIPS based composites are higher for every concentration of waste dust, but there is a maximum on the graph between 10 and 15 w% waste.

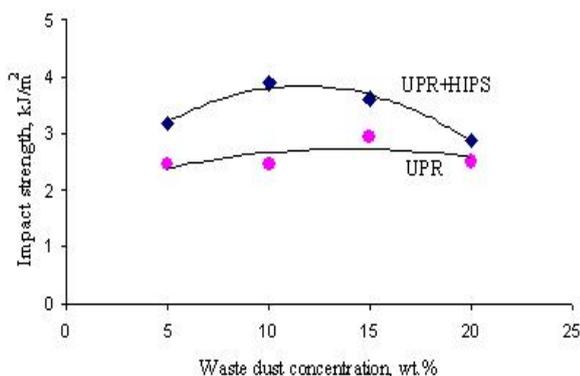


Fig. 2. Dependence of impact strength on waste dust concentration for both kinds of polymeric composites

Bending strength (σ_b). Fig. 3 shows that values of bending strength for UPR/HIPS composites are higher than those for composites based on pure UPR in a large range of the waste concentration.

However, the increase in filler amount of >20 mass. % causes deterioration in bending strength for both types of composites. The trend is more expressed for UPR based composites.

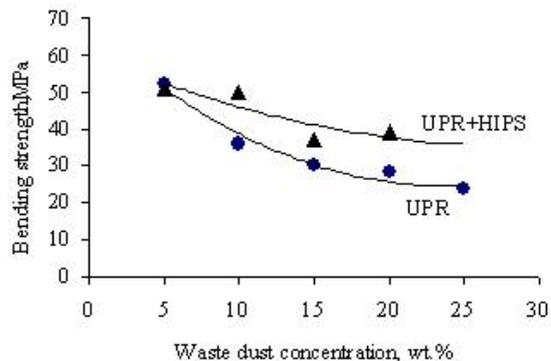


Fig. 3. Changing of composites bending strength with waste concentration increase

Compressive strength (σ_c). In contrast to bending strength and impact strength, the compressive strength values for pure UPR-based composites are higher than values for UPR/HIPS-based composites for filler amounts of up to 15 w.% (Fig. 4). Similarly, the compressive strength decrease is more expressed for pure UPR-based composites.

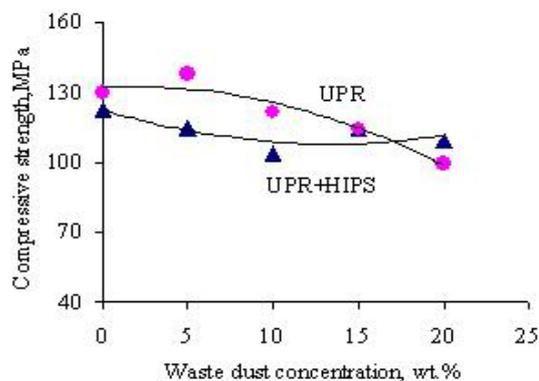


Fig. 4. Compressive strength of polymer composites vs. waste dust concentration

Lower strength characteristics at higher waste amounts probably result from some processes of filler sedimentation at concentrations of more than 10 w%. This negative effect of sedimentation processes causes some gradient in the composites and anisotropy of properties.

The changes of the three studied characteristics σ_i , σ_b и σ_c with increasing waste amount are similar for both composites and can be described by second order polynomial analytical dependence (Table 2).

Table 2

Analytical equations describing changing of strength characteristics σ depending on waste dust concentration C for two studied polymer composites

Characteristic	Equation	
	UPR	UPR + HIPS
Impact strength	$\sigma_i = 0.0009C^2 - 0.0203C + 2.6957$	$\sigma_i = -0.0143C^2 + 0.3345C + 1.8825$
Bending strength	$\sigma_c = 0.0779C^2 - 3.6394C + 67.218$	$\sigma_b = 0.03C^2 - 1.73C + 60.25$
Compressive strength	$\sigma_c = -0.153C^2 + 1.023C + 131.39$	$\sigma_c = -0.153C^2 + 1.023C + 131.39$

Composites morphology and colloidal-chemical peculiarities

The optical micrographs revealed that the composites are heterogeneous multiphase materials. For the UPR/HIPS based composite (Fig. 5), the multiphase structure is a result of two simultaneous processes: the chemical process of UPR solidification and a phase separation process, caused by thermodynamic incompatibility of UPR and HIPS [12]. As a result, a two-phase disperse system arises: with UPR as a disperse media and HIPS as a disperse phase. An inter phase layer is generated on the phase separation border between the two phases whereby the strength characteristics of the polymer system largely depend on its thickness, structure and properties.

Inside the so formed polymer matrix are included waste particles (Fig. 6).

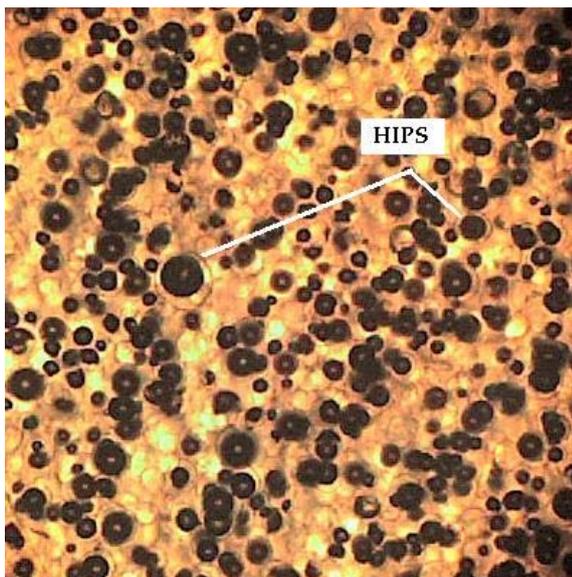


Fig. 5. Optical microscopy graph of polymer system UPR/HIPS (10 wt.% HIPS, 700 min⁻¹, 10 min), magnification 90×

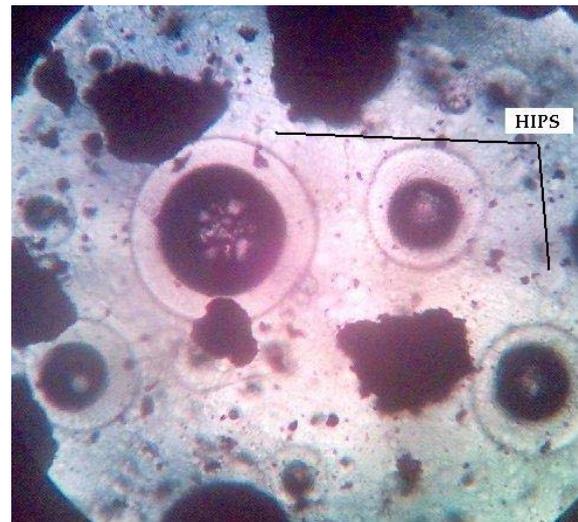


Fig. 6. Optical microscopy graph of filled with waste particles UPR/HIPS polymer system (magnification 110×

According to Lipatov, in polymer systems containing filler a new composition is formed due to the new processes added to the already existing ones of curing – the processes of phase separation and inter-phase layer generation. This composition results from the difference in adsorption interaction between the polymer system components and the filler surface, as well as the impact of filler particles on resin curing. A close analysis of these inter-phase layers indicates the presence of a complicated multi-phase structure, resulting from selective adsorption of one of the polymer system components. This adsorption is determined by the differences in components surface tensions [13]. Composition gradient is thus formed which is retained at a considerable distance from the solid surface close to the particles surface. This gradient causes structural micro-heterogeneity at molecular level which in turn impacts the overall system properties.

CONCLUSION

– The polymer composites under investigation were based on the polymer system UP/HIPS, and are in fact a multiphase disperse system in which polyester resin serves as disperse medium, and HIPS and the particles of the mechanically activated waste serve as dispersed phase. The morphology and composites' properties depend on the phase separation and selective adsorption processes which occur at the border between the polymer phase and solid surface.

– Inclusions of polymer additives increase the impact and bending strengths, and decrease the compression strength.

– Mechanical activation of waste does not impact its chemical composition, but changes the particles size distribution to lower homogeneity.

– Increase in the waste amount causes a drop in the values of bending and compressive strength. This effect is marked at waste concentrations of over 10 w.%, wherein there is filler particles sedimentation which results in composition and properties gradient.

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