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Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.5937/zasmat2203363V

Zastita Materijala 63 (3)
363 - 368 (2022)

Theoretical experimental aspects of composition with polymeric matrix reinforced with polymer particles

ABSTRACT

The development of composite materials and related design and production methods is one of the most important advances in the history of materials. They can be accurately modeled to respond to the requirements of the most specific applications. Many composites show, in addition to high mechanical properties, also high resistance to corrosion at high temperatures, to oxidation and wear. These unique features give design possibilities that are not achieved with any of the traditional monolithic materials. Many technological processes of composites are best suited for the production of large and complex structures, which has allowed their compaction and realization in the form of "one body", thus reducing production costs. The case of the composite with polymeric matrix reinforced with polymer particles is also interesting. PS and HDPE are two of the most used plastics in the world with a production scale of billions of tons. Less than 10% of this production is recycled. One use for recycled plastics, especially HDPE, is to melt into profiles that resemble beams, hence the term plastic beams. These products are used as building materials in many applications. One drawback of some plastic beam products is their tendency to slip.

Keywords: *composite materials, polymeric matrix, mechanical properties, PS and HDPE, plastic beams, building materials*

1. CLASSES AND CHARACTERISTICS OF COMPOSITE MATERIALS

There is no universally accepted definition of what a composite material is. For the purpose of this paper, we will call a composite a material composed of two or more distinct phases, joined together.

Figure 1 shows the main types of reinforcements used in composite materials: continuous and one-way oriented fibers, discontinuous fibers, whisker (elongated monocrystalline structures), particles and multiple forms of fiber-produced architectures textiles, such as fabrics and nets. More and more designers are using hybrid composites, which combine different types of amplifiers to get greater efficiency and reduce cost [1].

Composites are very heterogeneous materials. This means that the properties of a composite differ significantly from one point of the material to another, depending on that component of the material on which the point under study coincides. Unlike composites, monolithic ceramics and metal alloys are usually considered to be approximately homogeneous materials.

The main criterion that determines the status of composite materials is the solubility of the materials used. The basic thermodynamics of the mixture determines the state of solubility of each mixture. The initial demand is indicated by the Gibbs free energy change of the mixture and is determined by:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0$$

Where ΔH_{mix} is the change in enthalpy and ΔS_{mix} is the change in entropy during mixing. In order to occour the mixing at the molecule level, the change in Gibbs free energy must be less than 0

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Paper received: 12. 04. 2022.
Paper accepted: 05. 05 .2022.
Paper is available on the website: www.idk.org.rs/journal

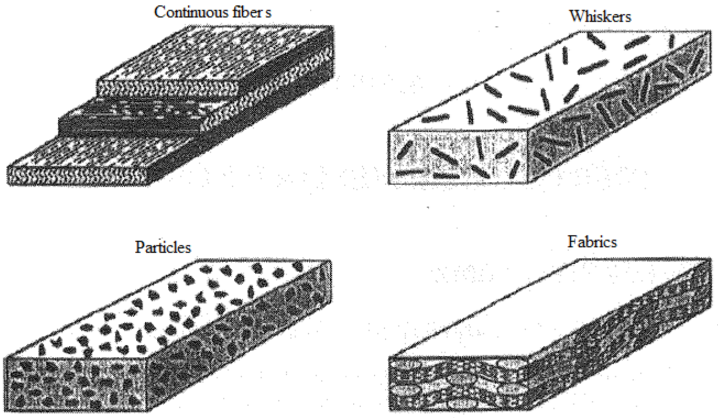

Figure 1. Reinforcement types

Slika 1. Vrste armature

2. REINFORCMENTS AND MATRIXES

There are some important aspects that need to be discussed before presenting the properties of composite ingredients. The traditional materials used in engineering applications are mainly metal alloys for most of which there are industrial and official specifications (norms). The condition is very different for composite. Most amplifiers and matrices are specific materials for which there are no industry standards. This is similar to the current status of ceramics. The situation is further complicated by the fact that there are many testing methods in use to evaluate the mechanical and physical properties of reinforcement materials and matrices. The data presented below represent a selection of information from many sources, mainly from manufacturers' articles and publications. The property values presented in this section should be considered approximate or orienting [2].

2.1. Reinforcments

The four main types of amplifiers used in composites are continuous fibers, discontinuous fibers, whiskers, and particles (Figure 1). Continuous and oriented fibers represent the most fruitful form of reinforcement and are widely used especially in high-tech applications. Most important among them today are two- and three-dimensional fabrics and nets. However the material presented will focus on particulate amplifiers.

2.2. Polymeric matrix materials

There are two main classes of polymers used as matrix materials: thermosetting and thermoplastic. Thermosets are materials that undergo a heat treatment process during fabrication, after which they harden and cannot be reshaped. Thermoplastics, on the other hand, can be softened and reshaped repeatedly by heating them. Thermoplastics are usually divided into subclasses: amorphous, crystalline and liquid crystals. There are numerous polymers in both classes.

Polymeric matrixes are relatively weak materials, with low rigidity and visco-elastic behavior. The strength and rigidity of PMCs (polymer matrix composite) is mainly due to the fibrous phase. One of the main problems in matrix selection is the maximum working temperature, when it is known that the properties of polymers decrease significantly with increasing temperature. A measure widely used to measure the temperature relative resistance of polymers is the glass transition temperature (Tg), which is the approximate temperature at which a polymer is converted from a relatively rigid material to a viscous material. Polymers suffer significant losses in both strength and hardness when heated above their vitrification temperature. New polymers, with increasing temperature resistance, are constantly evolving, allowing them to compete with a range of metals [3].

An important factor in the selection of polymer matrices is also their sensitivity to moisture. The resin tends to absorb water, which causes dimensional changes and reduces hardness and durability at high temperatures. The rate of moisture absorption, usually measured as a percentage of weight gain, depends on the polymer and the relative humidity of the environment.

3. MECHANICAL PROPERTIES OF POLYMER MATRIX COMPOSITES

Polymers are materials with relatively low durability. To provide materials with mechanical properties suitable for structural uses, it is necessary to reinforce them with continuous or discontinuous fibers. Improvements in mechanical properties are also achieved by adding polymer particles, as presented in the HDPE/PS (high density polyethylene/polystyrene) composite. Where the resulting material has improved properties against each of the elements.

The properties of PMCs, especially strength, depend on temperature. The temperature dependence varies greatly from one polymer to another. This is also true for epoxies with different compositions, which have different vulcanization and glass transition temperatures. Some polymers, such as polyimides, retain good properties at high temperatures, which allows them to be compared to titanium [4].

4. EXPERIMENTAL PART AND RESULTS

Characteristics of the studied materials.

Sample compositions

The samples we studied are post-use polymers whose characteristics and compositions are presented in Table 1.

Table 1. Some physical properties of the homopolymers and compositions of the mixtures studied

Tabela 1. Neka fizička svojstva homopolimera i sastavi proučavanih smeša

Polymer	Mold Flow Index (g/10 min)	Density (g/cm^3)	Mixture (% volume)					
			I	II	III	IV	V	VI
HDPE	0.3	0.963	50	60	70	75	100	0
PS	1.53	1.003	50	40	30	25	0	100

Sample characteristics

Samples for mechanical tests were produced according to ASTM D638 standard in pre-heated stamps. The mixtures were prepared from lightly ground fractions into pieces of the order of mm^2, through a squeezer with a Brabender screw at T = 180°C and a rotational speed of 20 rpm, injected by a machine Negri and Bossi NB 55 at T = 220°C. Testing of the winning samples was conducted at the laboratories of Rutgers the State University of New Jersey.

Description of realized evidence

The Instron model 1122 dynamometer with a head speed of 5 mm/min based on ASTM D638 was used to determine the traction properties of the samples, while the IZOD impact tests were performed on the basis of ASTM D256 in a Dynatup model pendulum model POE 2000 at T=30°C and T = 23°C.

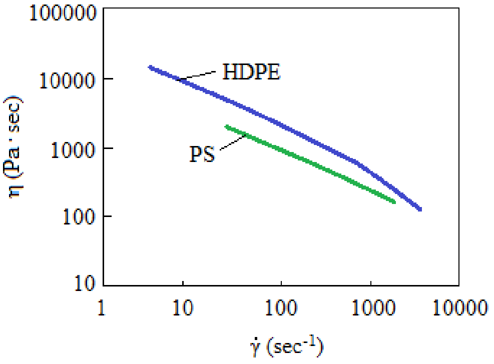

Fig. 2. Viscosity of homopolymers versus creep ratio in 190°C

Slika 2. Viskoznost homopolimera u odnosu na odnos puzanja na 190°C

The results represent the arithmetic mean of 10 measurements. Figure 2 represent viscosity versus creep ratio in 190 ^{0}C.

The study of morphological aspects was carried out through samples that were destroyed, cryogenically broken and the fracture surfaces, after being coated with gold, were observed by means of SEM (scanning electron microscopy) model Zeiss 982 GEMINI FEMSE +.

5 .INTERPRETATION AND DISCUSSION OF EXPERIMENTAL RESULTS

Interpretation and discussion of test morphology

Table 2. shows the melt flow index and experimental density and calculated at 190°C by the law of addition.

Table 2. Melt flow index and experimental density calculated at 190°C by addition law

Tabela 2. Indeks tečenja rastopa i eksperimentalna gustina izračunati na 190°C po zakonu adicije

Mixture	Mold Flow Index(g/10 min)		Density (g/cm^3)
	Experimental	Calculated	
Mixture 1	1.19	1.57	0.9234
Mixture 2	1.31	2.04	0.9261
Mixture 3	1.81	2.01	0.9261

In our case, taking into account especially the complicated composition of the mixture, we did not aim to fully study the rheological characteristics of these materials, but simply to check whether such mixtures may present melting properties, which may prevent machinability by conventional machinery.

In Table 2 the experimental values of the melting flow index are compared with the values calculated using the law of addition. Experimental values are lower than the calculated values, which suggests that there are weak interactions between the components, due to the same chemical structure of the coupling components. This leads us to the conclusion that the workability of the mixtures is not a particular problem.

Density - in Table 2 are presented the density values of mixture 1, 2 and 3, which are about 0.5% higher than the calculated values based on the average weights of the contributions of different components, assuming that the degree of crystallization of crystallizable polymers are not affected by melting. Thus we can conclude that the mixtures have a compact structure [5].

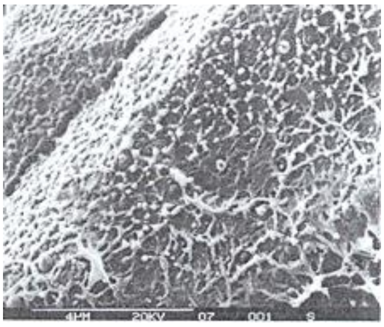

Fig. 3. Micrograph obtained with MSE of cold broken surface at HDPE / PS mixture = 60/40 (magnification 300 x)

Slika 3. Mikrofotografija dobijena sa MSE hladno izlomljene površine u HDPE / PS mešavini = 60/40 (uvećanje 300 x)

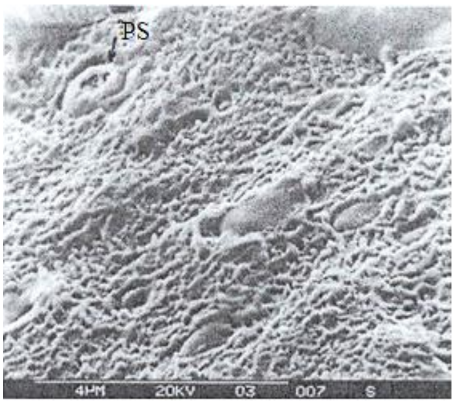

Fig. 4. Micrograph obtained by SEM of cold fractured surface of mixture HDPE/PS = 70/30 (magnification 300 x)

Slika 4. SEM mikrografija dobijena sa hladno polomljene površine mešavine HDPE/PS = 70/30 (uvećanje 300 x)

The morphologies of the fractured surfaces of mixture 1, 2, 3 and 4 are shown in Figures 3, 4, 5 and 6. The morphology of mixture 1, not shown here, appears as single-phase material, which means that the two components are indistinguishable in such composition.

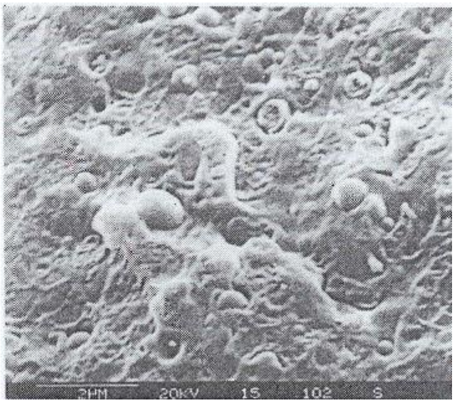

Fig. 5. Micrograph obtained by SEM of cold fractured surface of mixture HDPE/PS = 75/25 (magnification 300 x)

Slika 5. SEM mikrografija dobijena sa hladno polomljene površine mešavine HDPE/PS = 75/25 (uvećanje 300 x)

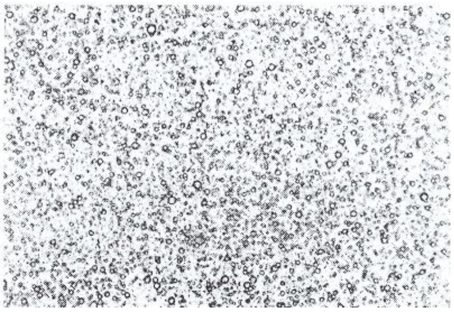

Fig. 6. Optical micrograph of HDPE/PS = 75/25 mixture in 180^{0}C (magnification 200 x)

Slika 6. Optički mikrofotografija mešavine HDPE/PS = 75/25 na 180^{0}C (uvećanje 200 x)

Mixture 2 represents HDPE matrix with plastic fractures with PS impurity not easily discernible. In the case of mixture 5 the same morphological characteristics were observed from the plastic waste. The morphology of mixture 3 (figure 7) clearly represents the PS domains which are broken down by the rough surface of typical globules. By reducing the amount of PS (figure 7) to 25% (mixture 4) this component almost tends to form a continuous phase in the HDPE matrix; PS is still distinct in the form of separate spherical particles [6].

Crystallizing Behavior-While the recrystallization process is very important in controlling morphology, i.e. also mechanical properties, it is of interest to discuss melting behavior during cooling.

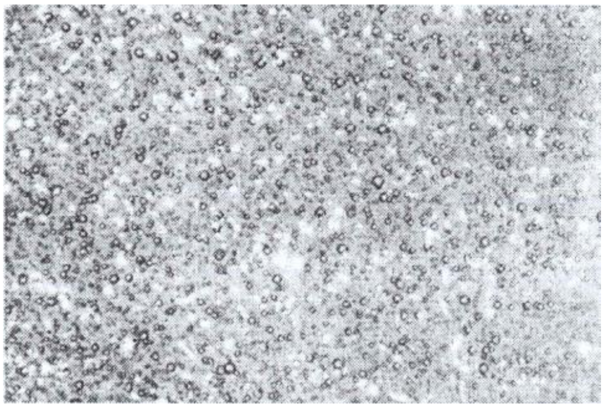

Fig. 7. Optical micrograph of HDPE / PS = 75/25 mixture at 140°C (magnification 200 x)
Slika 7. Optička mikrofotografija mešavine HDPE / PS = 75/25 na 140°C (uvećanje 200 x)

In contrast, the Tc of HDPE in the mixture is slightly higher than that of the single component and the difference deepens with increasing cooling rate. This behavior is undesirable considering the favorable effect on HDPE and PS already crystallized in the HDPE nucleation process. Thus, the HDPE matrix always crystallizes when PS are solid and PS is under its glass transition. During crystallization a reduction in volume occurs and the matrix wrinkles over the domains of the dispersed phases gluing them together very tightly. This is the main reason for the good contact between the matrix and the various polymer domains observed in the electron microscope analysis [7].

6. INTERPRETATION AND DISCUSSION OF RESULTS FOR EVALUATION OF MECHANICAL PROPERTIES

Tensile behavior - The values of the modulus of homopolymers vary by about ± 5%, while for mixtures by about ± 8%. The change data of ób and óy range from ± 12% for homopolymers to ± 18% in the case of merger values; åb results have the widest variation rate ranging from ± 20% to ± 27%.

Reducing the amount of HDPE in a joint increases the modulus and flexural strain, while ób practically does not change and åb seems to reach the maximum for mixture 3 having 70% PE. Mixture 5, prepared with the light fraction of plastic waste, shows practically the same modulus of elasticity and durability as pure homopolymers (Mixture 4); however, the samples are broken before they reach the major deformation of the mixture 4, probably due to defects created by the impurities, which are not completely removed during the flotation process. The increase of modulus E from the reduction of the percentage of HDPE is very much in the prediction of the addition rule, as shown in figure 7.

If we consider mixtures as composites, in which the matrix is HDPE and the filler is PS, we can compare our mechanical data with the Nielsen model developed for systems with polymeric amplifiers. It should be said that this approximation is almost simplified, because the difference between the HDPE module and the PS component is not as large as in the case of a polymeric matrix and an inorganic filler. (Nevertheless) We think that this approximation can be achieved by performing the following assumptions:

The matrix is composed of HDPE for all compounds and its modulus measured experimentally is (≈151 MPa).

The filler is composed of PS and its modulus measured experimentally is (≈739 MPa).

The photos obtained by MSE provide evidence that the disperse phase geometry is complex, due to the presence of elliptical and spherical domains.

Tensile module and impact resistance are very important properties in the field of reclaimed plastics applications. The increase of the torsional modulus by the addition of more rigid polymers is evident, which confirms that the stress transfer between phases is also effective in the torsional mode. The torsional modulus of mixture 5 is almost equal to the tensile modulus of mixture 2 if we consider the uncertainty of the experiment.

Although the impact properties of the mixtures usually improve with increasing HDPE content, the effect is dramatic at low temperatures, which requires special care if such application is required [8]. Impurities are the cause of low impact resistance at 30°C (220 J/m) in mixture 5 compared to mixture 2, which does not break. This suggests that more precise separations and washing steps are needed before processing the mixture.

7. CONCLUSIONS

Determining the optimal HDPE/PS mixture ratio of unused and comparing it with raw materials has been studied for the city of Tirana, with HDPE and PS materials collected and selected through the flotation method. Thanks to experience and experiments performed in the laboratories of Rutgers the State University of New Jersey, was able to determine the optimal 75/25 HDPE / PS mix ratio.

From the study of samples taken with optimal mixture ratio 75/25 HDPE / PS it resulted that:

- The rheological behavior of mixtures, the viscosity against creep stress is negative deviation (PS / HDPE) and positive deviation (HDPE / PS).
- The density is about 0.5% higher than the calculated values based on the average weights of the contributions of different components, which have a compact structure.
- The morphology of the mixture, as seen in the figures above, shows that the 75/25 ratio has a clearer phase distribution.

The behavior of the molten material during cooling, recrystallization, as a very important process in controlling morphology, was studied with scanning electron microscope. From the matrix analysis it resulted that HDPE always crystallizes when PS are solid and PS is under its glass transition [9].

Another important factor where we stopped is the mechanical behavior of the joint. Based on Nielsen, PS have amplifying effect on HDPE matrix and strain transfer at low deformations is good. The increase of the torsional modulus by the addition of more rigid polymers is noticeable, which confirms that the stress transfer between phases is also effective in the torsional mode [10].

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IZVOD

TEORIJSKO EKSPERIMENTALNI ASPEKTI KOMPOZICIJE SA POLIMERNOM MATRICOM OJAČANOM POLIMERNIM ČESTICIMA

Razvoj kompozitnih materijala i srodnih metoda projektovanja i proizvodnje jedan je od najvažnijih napredaka u istoriji materijala. Mogu se precizno modelovati da odgovore na zahteve najspecifičnijih aplikacija. Mnogi kompoziti pokazuju, pored visokih mehaničkih svojstava, i visoku otpornost na koroziju na visokim temperaturama, na oksidaciju i habanje. Ove jedinstvene karakteristike daju mogućnosti dizajna koje se ne postižu ni sa jednim od tradicionalnih monolitnih materijala. Mnogi tehnološki procesi kompozita su najpogodniji za proizvodnju velikih i složenih konstrukcija, što je omogućilo njihovo zbijanje i realizaciju u obliku „jednog tela“, čime se smanjuju troškovi proizvodnje.

Interesantan je i slučaj kompozita sa polimernom matricom ojačanom polimernim česticama. PS i HDPE su dve najkorišćenije plastike na svetu sa skalom proizvodnje od milijardi tona. Manje od 10% ove proizvodnje se reciklira. Jedna upotreba za recikliranu plastiku, posebno HDPE, je da se stapa u profile koji podsećaju na grede, otuda i termin plastične grede. Ovi proizvodi se koriste kao građevinski materijal u mnogim aplikacijama. Nedostatak nekih proizvoda od plastičnih greda je njihova sklonost klizanju.

Ključne reči: *kompozitni materijali, polimerna matrica, mehanička svojstva, PS i HDPE, plastične grede, građevinski materijali.*

Naučni rad
Rad primljen: 12. 04. 2022.
Rad prihvaćen: 05. 05. 2022.
Rad je dostupan na sajtu: www.idk.org.rs/casopis
