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VISCOSITY OF POLYMER COMPOSITES WITH HIGH CONTENT OF METAL POWDERS PROCESSED BY INJECTION MOULDING

An important feature of injection-processed functional polymer composites is viscosity. Powder increases the viscosity of such a composite. Viscosity depends on the polymer processing properties and the shape and size of the powder particles. The injection temperature is also important. In the conducted analyses, High Impact Polystyrene (HIPS) and General Purpose Polystyrene (PS) served as the matrix for the composites. Powders with flaky and spherical particles constituted the functional phase. Powders with permanent magnetic characteristics produced from Nd-Fe-B alloys were used. In the analysis, multi-fractional (commercial) powders and selected fractions of two types of powders were used. Composites containing variable quantities of multi-fractional powders were obtained. The content of the powders was from 40 to 54% of flaky powder and up to 64% of spherical powder by volume. In addition, composites containing the selected fractions of both types of powders were prepared. The content of fractional powders was constant and it was 48% by volume. The samples were produced by injection of the composites at temperatures from 160 to 240°C.

Polystyrenes and composites with a zero shear rate have the greatest viscosity. Increasing the shear rate leads to a reduction of viscosity. The viscosity of composites with flaky powder decreases at the fastest rate. For spherical powder, the viscosity reduction rate is slower and for polystyrenes - the slowest. Slightly higher viscosity values (for the same shear rates) were obtained for general purpose polystyrene and the composites in which it served as the matrix. In composites with flaky powder, the reduction in viscosity is greater if the powder content is higher. For composites with spherical powder, an increase of the shear rate results in constant reduction of their viscosity. The viscosity of composites (with a constant content of fractional powders) decreases along with an increase of the size of its particles.

An attempt was also made to explain the phenomenon of the faster reduction of viscosity of composites with flaky powder compared to composites with spherical powder through proposing a model describing the emergence of easy-slip surface. In addition, as the temperatures of the injected composites increase, their viscosities decrease.

Keywords: functional polymer composite, injection, viscosity, functional powder

LEPKOŚĆ POLIMEROWYCH KOMPOZYTÓW O WYSOKIM NAPEŁNIENIU PROSZKAMI METALOWYMI PRZETWARZANYCH WTRYSKIWIANIEM

Istotnym zagadnieniem w przypadku funkcjonalnych kompozytów polimerowych jest ich lepkość. Zależy ona od rodzaju polimeru stanowiącego jego osnowę, zawartości proszku wprowadzonego do polimeru, kształtu i wielkości cząstek proszku oraz parametrów wtryskiwania. Proszek nadaje kompozytowi pożądane cechy, których polimer nie posiada. Powoduje jednak zwiększenie lepkości kompozytu. Do przeprowadzenia badań wytypowano proszki o cząstkach wyraźnie różniących się kształtem. Były to cząstki płatkowe i kuliste. Funkcjonalnie są to proszki o cechach magnetycznie twardych, wytwarzane ze stopu Nd-Fe-B. Na osnowę kompozytów wytypowano polistyreny w dwóch odmianach; wysokoudarowy (HIPS) i niskoudarowy (PS). W pracy stosowano napelnienia proszkami w ilości od 40 do 54% dla proszku o cząstkach płatkowych i od 40 do 64% dla proszku o cząstkach kulistych.

Z otrzymanych wyników badań można wnioskować, że największą lepkość osiągają polistyreny oraz kompozyty przy tzw. zerowej szybkości ścinania. Zwiększanie szybkości ścinania powoduje zmniejszanie się lepkości. Jest ono największe dla kompozytów zawierających proszek o cząstkach płatkowych, mniejsze dla kompozytów z proszkiem o cząstkach kulistych, a najmniejsze dla polistyrenów. Nieco wyższe wartości lepkości przy jednakowych szybkościach ścinania uzyskano dla kompozytów na osnowie z polistyrenu niskoudarowego. Wzrost zawartości proszków w kompozytach prowadzi do zwiększania ich lepkości. Dla szybkości ścinania największej, jaką zastosowano, znacznie większą lepkością charakteryzowały się kompozyty z proszkiem o cząstkach kulistych niż z proszkiem o cząstkach płatkowych. Stosowanie coraz większych cząstek proszków, przy stałej wielkości napelnienia, powoduje, że kompozyty osiągają coraz mniejszą lepkość w całym zakresie zmienności szybkości ścinania. Również dla coraz wyższych temperatur obserwuje się zmniejszanie lepkości kompozytów.

Podjęto również próbę wyjaśnienia zjawiska szybszego zmniejszania się lepkości kompozytów z proszkiem płatkowym w stosunku do kompozytów z proszkiem kulistym, a tym bardziej polistyrenów poprzez zaproponowanie modelu opisującego sposób tworzenia się powierzchni łatwego poślizgu mających znaczący wpływ na te zmiany.

Słowa kluczowe: kompozyt polimerowy, wtryskiwanie, lepkość, proszek funkcjonalny

INTRODUCTION

One of the most important issues related to injection-processed functional polymer composites, especially those characterized by high powder content, is their viscosity. It affects their suitability as material for the production of moulded pieces, especially those with more developed shapes. The production method of such composites by injection is the same as the method of processing commonly used thermoplastic polymers. In functional composites, in which the polymer plays an auxiliary role by making the injection possible and then ensuring that the shape is preserved, the utility properties of the filling material are the most important. A considerable advantage of the injection technique is the possibility of producing elements in long production series because such a technique can be easily automated and therefore it is widely used in mass production. The properties of moulded pieces produced from injection-processed functional composites depend on the type of polymer matrix and the quantity of powder compared to the moulded piece's volume. In many cases, the properties are better if the powder content is higher. Such dependency occurs, among others, on magnetodielectric materials, which include materials with permanent magnetic characteristics as well as dielectromagnetic materials which are magnetically soft materials.

The presented paper discusses the issues related to the formation of dielectromagnets. Their matrix is polystyrene and the functional phase - Fe-Nd-B alloy powders. Particular emphasis was placed on analyzing the impact of the shape and size of the magnetic powder particles and powder content on the viscosity of such composite materials.

SELECTION OF FUNCTIONAL POWDER AS FILLER FOR COMPOSITES

Metal and metal alloy powders are produced by different methods. In each production method, powders with characteristic shapes and different sizes are obtained.

For the analyses, the powders whose particles are most different i.e. spherical powder and flaky powder, were selected.

Flaky powders are most commonly produced by grinding a thin tape obtained through rapid cooling of the liquid alloy sprayed on a cooled base. On the other hand, spherical powder is produced by spraying a liquid metal with a strong jet of inert gas.

In the study, type Nd-Fe-B alloy powders with permanent magnetic characteristics, which are used in the production of magnets, were used. The images of both types of powders are presented in Figure 1.

The conducted analysis of granulometric composition has shown that flaky powder is a coarse-grained powder with particle sizes reaching up to 250 μm and flake thickness of up to approx. 35 μm . The spherical

powder contains a large number of small particles and the largest ones do not exceed 100 μm .

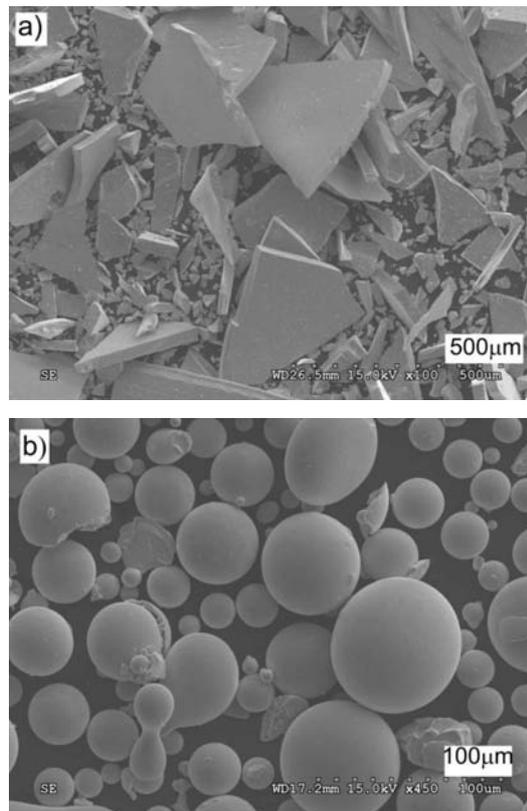


Fig. 1. Image of powder with flaky (a) and spherical (b) particles

Rys. 1. Obraz proszku o płatkowym (a) i kulistym (b) kształcie cząstek

Viscosity analyses were conducted for composites containing multi-fractional (commercial) powders as well as composites with fractionated powders. For this purpose, the individual fractions were separated from the multi-fractional powders by the sieving method. Sieves with meshes of 0.028, 0.071, 0.1, 0.20 and 0.25 mm were used. This way, the fractions with the smallest particles, whose size was less than the smallest mesh size, as well as the fractions with the largest particles were separated. In addition, for flaky powder, the fraction with an average particle size of 0.085 mm was selected. The selected fractions for both types of powders are presented in Table 1.

TABLE 1. Fractions of flaky and spherical powder selected for viscosity analyses of composites

TABELA 1. Frakcje proszku płatkowego i kulistego wytypowane do przeprowadzenia badań lepkości kompozytów

Fraction mm	Flaky powder	Spherical powder	Average size of particles in the fraction, mm
< 0.028	×	×	0.014
0.071÷0.100	×	×	0.085
0.200÷0.250	×	—	0.225

SELECTION OF THERMOPLASTIC POLYMER FOR MATRIX OF COMPOSITES

An important characteristic of thermoplastic polymers is their viscosity, which is a decisive factor in terms of their suitability for injecting them. Thermoplastic polymers are built from long macroparticles, and their length and degree of kinking determine their viscosity [1- 5].

The production process of functional composites uses polymers with great suitability for injecting. This issue is very important because the powder, which is introduced into such a polymer, considerably increases the viscosity of such a composite. An upper threshold content of functional powder in the composite exists, which, if exceeded, causes the composite to lose its capability of being injected, which makes it impossible to use this method.

After analyzing various properties of thermoplastic polymers, we selected polystyrene as the matrix for the composites.

An important advantage of polystyrene is the fact that it can be easily shaped into products, it has good resistance to chemical agents, it is resistant to atmospheric elements, it has great dielectric properties and it has sufficient mechanical properties. Polystyrene is a hydrophobic polymer, thanks to which it is resistant to the interaction of atmospheric elements, in particular water and water vapor in the air. Polystyrene's small density, ranging from 1.03 to 1.06 g/cm³, as well as low price make it a very attractive material for mass production.

The softening temperature of polystyrene depends on the molecular weight as well as the addition of plasticizers. For commonly used polystyrenes, it is from 80 to 120°C, and its thermal depolymerization occurs only at a temperature exceeding 300°C.

Two types of polystyrene: High Impact Polystyrene and General Purpose Polystyrene were used in production of the composites. In the literature, High Impact Polystyrene is often referred to as HIPS and General Purpose Polystyrene - as PS. In the paper, the polystyrenes manufactured by Firma Chemiczna Dwory SA were used [6].

PREPARATION OF GRANULATE

The composites were prepared by the solvent method, and toluene was used as a solvent. Firstly, the polystyrene solutions in toluene were prepared. For this purpose, a specified quantity of toluene was poured into a specified quantity of polystyrene. After it completely dissolved, the powder was poured in and the content was mixed to form a homogeneous mass. This mass was spread onto a flat surface in the form of a thin layer. After the solvent evaporated, a flexible plate was created, which was then mechanically processed into granules.

The analysis of the rheological properties was carried out for both polystyrene types and the

composites made from them. They contained multi-fractional flaky powders by volume of 40, 48 and 54%, and spherical powders of 40, 48, 54 and 64%. It should be noted that the maximum content of flaky powder in the composite was up to 54% and spherical powder - 64% by vol. [10]. Exceeding these amounts will create composites whose viscosity will be so high that they will lose their capability of being injected. The composites with fractionated powders were also analyzed. The content of fractionated powders in the composites was constant and it was 48% by volume. It was the maximum content of powders with the smallest particles in the composites.

ANALYSIS OF RHEOLOGICAL PROPERTIES OF COMPOSITES

The composites were subjected to rheological analyses in the Polymer Institute of West Pomeranian University of Technology in Szczecin. A computerized rotary rheometer ARES, developed by the Rheometric Scientific, was used. It is a CR-type rheometer, in which the shear rate is the parameter that can be set, and the instrument reads the shear stress which is converted by the computer into the corresponding viscosity.

All viscosity measurements of the composites were taken at temperatures of 160, 200 and 240°C, which are similar to the injection temperatures recommended by the polystyrene manufacturer.

RESULTS OF MEASUREMENTS

Selected results of the measurements are presented in Figures 2- 5.

Figure 2a presents the dependency between the viscosity and shear rate for high impact polystyrene and composites with a 48% content of flaky powder and spherical powder, and Figure 2b presents similar dependencies for general purpose polystyrene and composites made on its basis.

For all the materials, the highest viscosity is recorded for polystyrenes and composites at the beginning of the measurement i.e. when the shear rate is near zero. In the literature, this lowest shear rate is referred to as "zero shear rate" [7].

When comparing the flow curves for polystyrene, slightly slower viscosities were recorded for general purpose polystyrene. This results from its greater suitability for flowing, which is expressed by the melt flow index (MFI). For general purpose polystyrene, it is 11 g/10 min, and for high impact polystyrene it is smaller and amounts to 8 g/10 min.

With a "zero shear rate", composites with flaky powder have the greatest viscosity, composites with spherical powder have a smaller viscosity, and polystyrenes have the smallest viscosity. As the shear rate increases, the viscosity of all the materials decreases, while such a decrease is smallest for the polymer and

the largest for the composite with flaky powder. After exceeding certain shear rate values, which are different for individual materials, the viscosities of the composites are smaller than those of polystyrenes. The greatest reduction of viscosity occurred for composites containing flaky powder.

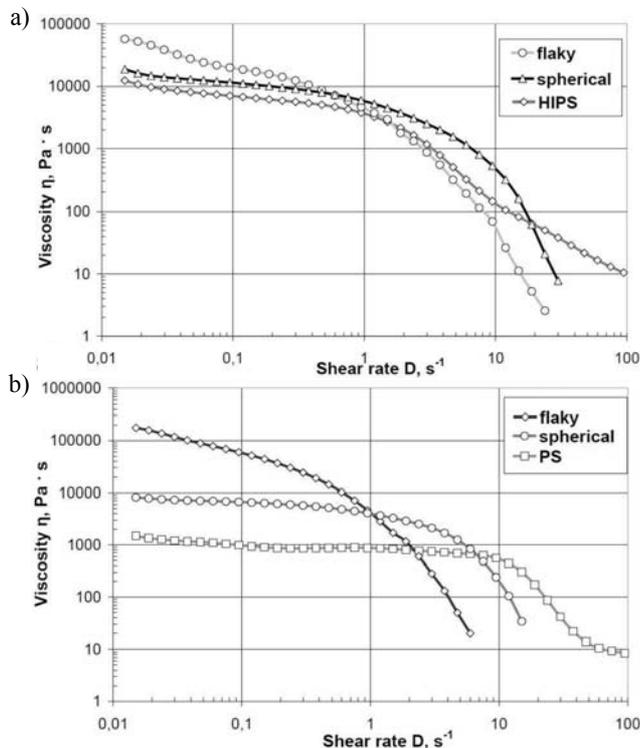


Fig. 2. Flow curves at temperature of 200 °C of composites with HIPS matrix (a) and PS matrix (b) containing multi-fractional flaky or spherical powder content of 48%

Rys. 2. Krzywe płynięcia w temperaturze 200°C kompozytów na podstawie polistyrenu HIPS (a) oraz polistyrenu PS (b) zawierających wielofrakcyjny proszek płatkowy bądź kulisty w ilości 48%

On the other hand, Figure 3 presents the impact of shear rate on the viscosity of composites containing various quantities of flaky powders (Fig. 3a) and spherical powders (Fig. 3b).

With a zero shear rate, composites with the highest powder content have the greatest viscosity. If flaky powder is used as a filler, the viscosity of the composite, decreases at the fastest rate - probably particle disaggregation is a reason. After exceeding a certain shear rate, the viscosity of such a composite is smaller than that of composites with a smaller powder content. Consequently, for the highest shear rate used in the analysis, the composite with the smallest powder content has the greatest viscosity and the composite with the highest powder content has the smallest. A change in viscosity as a function of increasing shear rate is slightly different for composites with spherical powder. In this case, the reduction of the viscosity of certain composites is almost the same for all the materials. Consequently, both for the highest and for the smallest shear rate, the composite with highest powder density has the greatest viscosity.

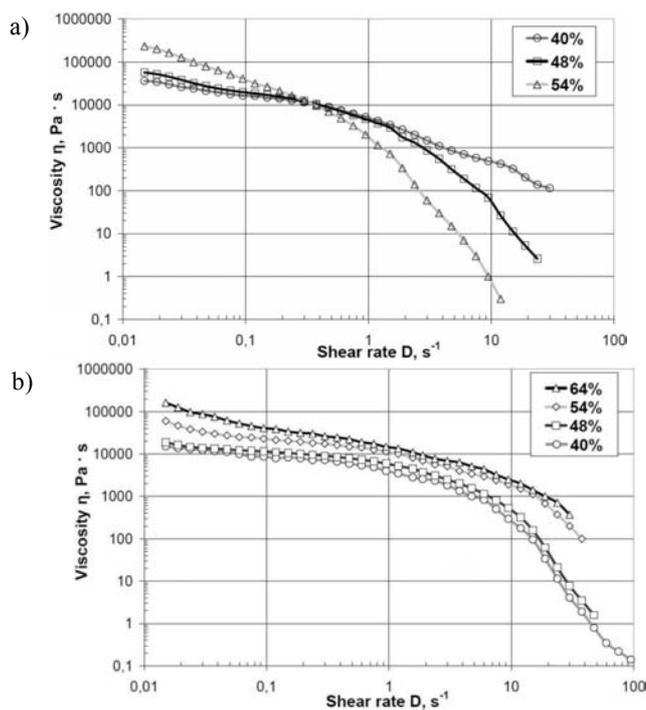


Fig. 3. Flow curves at temperature of 200°C of composites with HIPS matrix containing various quantities of multi-fractional flaky (a) and spherical (b) powders

Rys. 3. Krzywe płynięcia w temperaturze 200°C kompozytów na podstawie z polistyrenu HIPS zawierających różne ilości wielofrakcyjnych proszków płatkowych (a) i kulistych (b)

Figure 4 presents changes in viscosity depending on the shear rate of composites containing flaky (Fig. 4a) and spherical (Fig. 4b) powder, for different temperatures.

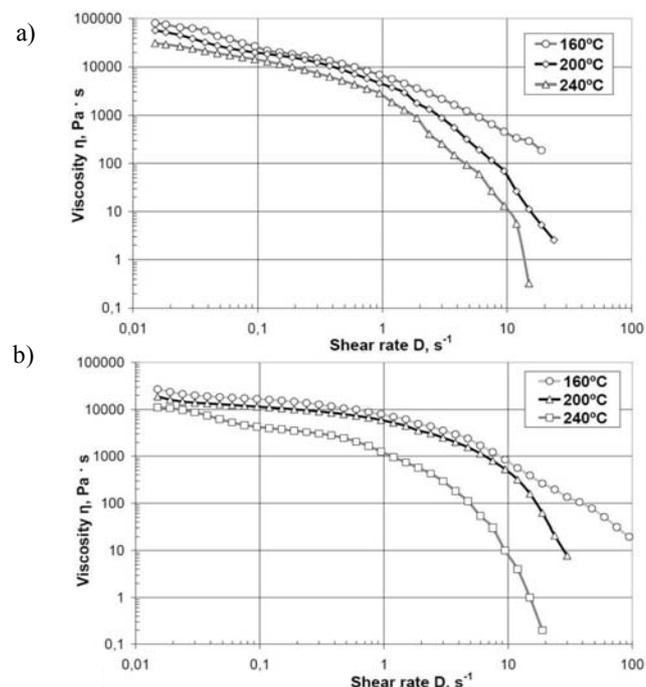


Fig. 4. Flow curves of HIPS matrix composites with 48% content of multi-fractional flaky (a) and spherical (b) powder

Rys. 4. Krzywe płynięcia kompozytów na podstawie z polistyrenu HIPS z 48% napełnieniem wielofrakcyjnym proszkiem płatkowym (a) i kulistym (b)

The analyses have shown that as the temperature of the composites increases, their viscosity considerably decreases. For the specified shear rate, the composites analyzed at a higher temperature also had a smaller viscosity. Such a conclusion is true for all composites, regardless of the shape of the filling particles.

The next figure (Fig. 5) presents the results of analogical tests but for composites containing fractionated powders; Figure 5a for flaky powder and Figure 5b for spherical powder, respectively.

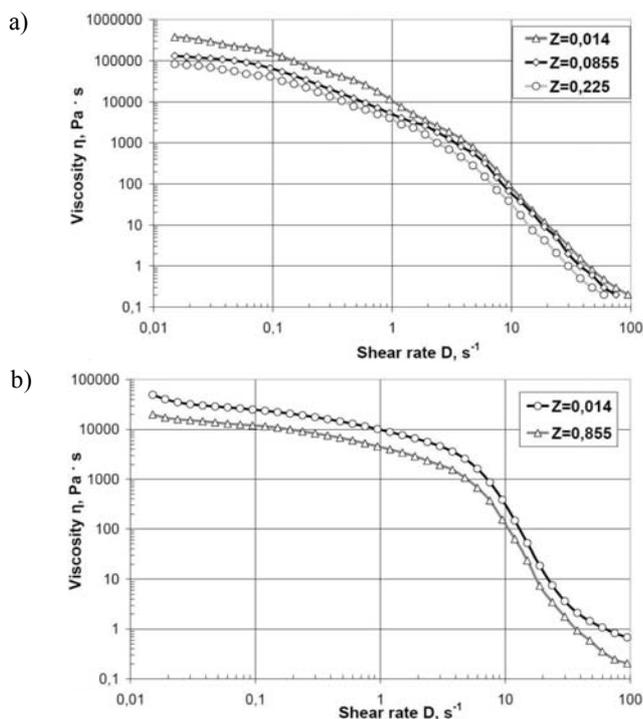


Fig. 5. Flow curves of HIPS matrix composites with 48% content of fractionated flaky (a) and spherical (b) powder

Rys. 5. Krzywe płynięcia kompozytów na osnowie z polistyrenu HIPS z 48% napełnieniem proszkami frakcjonowanym, płatkowym (a) i kulistym (b)

The obtained results of the analyses show that the size of the powder particles also changes the viscosity of the composites as a function of shear rate. With a fixed shear rate, the composites containing powders with smaller particles have a higher viscosity, and this is true regardless of the particle shape. The impact of the powder granularity on the viscosity of the composites is much smaller than the impact of the shear rate.

AN ATTEMPT TO EXPLAIN THE PHENOMENON

The high viscosity of polymers results from the length of macro-particles and degree of their kinking [1-5]. After heating the polymer, relaxation of the individual chains takes place. If the temperature is high enough, it is easier for them to unkink and the polymer is able to flow. In the initial stage of viscosity measurement, the individual chains stretch and lay

parallel to one another according to the direction of shear stress. Such an arrangement of chains makes it easier for them to move vis-a-vis one another on easy-slip surfaces, resulting in a reduction of viscosity. This is a correct phenomenon and is characteristic for pseudoplastic liquids [7- 9].

In the composites containing powder fillers, whose bond to the polymer is weak, the easy-slip surfaces run on the surface of the particles. The analysis of the obtained results allowed us to propose a model for the emergence of easy-slip surfaces. Figure 6 presents such a model for composites containing flaky powder, and Figure 7 - the model for composites with spherical powder [10].

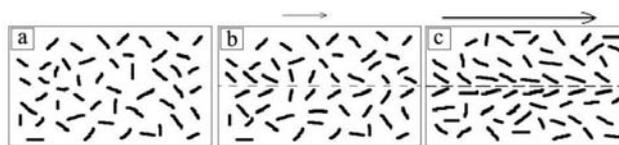


Fig. 6. Chart describing emergence of easy-slip surface for composites with flaky powder

Rys. 6. Schemat tworzenia się powierzchni łatwego poślizgu dla kompozytów z proszkiem płatkowym

Before the beginning of viscosity analysis, the arrangement of the flakes in the composite is random (Fig. 6a). The application of shear stress to the upper surface of the analyzed material results in flexible deformation of the polymer thus causing slight rotation of the flakes (Fig. 6b). An increase of shear stress, which results in plastic deformation of polystyrene, causes the flakes to arrange themselves in a parallel manner according to the direction of deformation. This way, easy-slip surfaces are created (Fig. 6c).

Similar phenomenon occurs for composites containing spherical powder (Fig. 7). In the figure, the fragments of adjacent composite layers designated as A and B separated by an easy-slip surface are indicated.

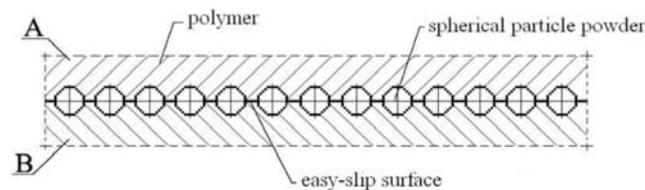


Fig. 7. Chart describing emergence of easy-slip surface for composites with spherical powder

Rys. 7. Schemat tworzenia się powierzchni łatwego poślizgu dla kompozytów z proszkiem kulistym

Easy-slip surfaces created in the composite containing spherical powder are more developed than similar surfaces for the composite with flaky powder. The moving polymer must additionally undergo local deformations. For this reason, after achieving an adequately high shear rate, the viscosity of the composite with spherical powder is greater than that of the composite with flaky powder.

Weak cohesion between the filler and shielding is an important characteristic of composites with metal powders. One could suppose that if it were strong, the viscosity of such composites would be considerably higher. In such a situation, it would be more difficult to inject and the maximum content of functional powders in the composites would certainly be lower.

CONCLUSIONS

The conducted analyses allowed us to formulate the following conclusions:

1. The viscosity of functional polymer composites depends on all factors which pertain to their production. These include: type of polymer used as the composite matrix, content, shape and size of the powder particles, injection temperature and probably disaggregation of the particles and traces of toluene.
2. A maximum density level for the composites exists, which, if exceeded, will result in such an increase of viscosity that they will lose their capability of being injected.
3. Composites with the so-called “zero shear rate” have greatest viscosity.
4. Increasing the shear rate results in a reduction of viscosity of the composites.

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