

# Effect of sedimentation on the final hardness of polymeric particle composites

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## Abstract

VALÁŠEK P., MÜLLER M., PROSHLYAKOV A., 2012. **Effect of sedimentation on the final hardness of polymeric particle composites.** Res. Agr. Eng., 58: 92–98.

In present days composite materials are the indispensable part of many branches. They make a foray into the branch of agricultural production, where they are getting to intensive development of systems utilized e.g. at soil processing. Composites can be defined as materials which synergically combine properties of matrix and filler. One of possibilities of polymeric particle composites preparation is the application of suitable filler together with some types of epoxy resins. This application extends the usable properties of resins. For the exact definition of these materials use it is necessary to map their behaviour. In the paper the problems are described, which concern the composite hardness changes as a consequence of the filler particle sedimentation in the course of the resin curing. The composite matrix was the two-component epoxy resin and the filler were chips of materials cutting process. The use of waste filler suggests itself the ecological possibility of recycling, which should be preferred in consideration to the environment friendliness.

**Keywords:** epoxy resin; hardness; X-ray analysis; waste

In view of their properties the polymeric particle composites found their use in branches of agricultural production, too. Especially the reduced soil adhesion and reduction of frictional resistance connected with it belong among these properties. The corrosion elimination is another indisputable advantage. It influences qualitative and quantitative indicators in agricultural manufacturing agrocomplex. Securing of sufficient wear resistance and of outside influences is the important condition. From the wear theory it is evident that the filler content and type are very important. The paper deals with the significant assumption of the polymeric particle composite systems in view of the potential filler sedimentation.

Research of the above mentioned problems is the first precondition for the successful application of polymeric particle composites. At practical application it is necessary to work on the adhesive bonding principles and main factors connected with it. The mechanical preparation of applied surfaces belongs among these factors. The optimal parameters of the surface preparation are presented e.g. by Müller in his works (MÜLLER et al. 2006, 2007, 2009; HERÁK et al. 2009). Under the term “composite materials” we understand heterogeneous materials composed of two or more phases. Single phases can be divided into the continuous one – matrix and into the strengthening one – filler. According to the matrix

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Supported by the Internal Grant Agency of the Czech University of Life Sciences Prague, Czech Republic, Projects No. 31140/1312/3118 and 31120/1312/3116.

type we divide composites in polymeric, metallic, ceramic, carbon and glass. In the experiments carried out the two-component epoxy resin Epoxy 1200/324 (DCH-Sincolor, Pilsen, Czech Republic) was used as matrix. The epoxy resin character enables their filling with organic fillers, which can influence the range of composites mechanical properties. Under the term “article filler” we mean non-fibrous particles, whose dimensions are not too different in all directions. These particles are above all in the shape of sphere, cube, tetrahedron, lamella or similar (MACHEK, SODOMKA 2008). The improvement of some mechanical properties is the aim of the filler use. Hardness and abrasive wear resistance belong among properties (VOCEL, DUFEK 1976). By the addition of filler the composite resulting price can be minimized. In the experiments carried out the filler function was hold by chips from material cutting, which fall under the group 12 01 01 according to the waste classification in the Czech Republic, i.e. waste from milling and cutting process, which shows neither dangerous properties mentioned in supplement No. 2, nor components mentioned in supplement No. 5 of the Act No. 185/2001 Coll. The use of waste as filler does not increase indisputably the price of the final composite, and as mentioned in MÜLLER and VALÁŠEK (2010) such filler improves some mechanical properties (hardness, abrasive wear resistance). SAPATHY and BIJWE (2002) in their experiment with resins filled with corundum particles of size 40–100  $\mu\text{m}$  found out that the corundum inclusion caused the abrasive wear resistance and tensile strength increase. At that they found out the evident correlation between wear resistance and hardness. The primary purpose of polymeric particle composites is bonding. From this follows the necessity of wear resistance and hardness increase. So the similar correlation between wear resistance and hardness is probable. On the ground of this assumption the hardness in different points of the tested samples was examined, so that the relation between hardness, used filler type and content in matrix in different composite points in direction from sediment to non-sediment parts could be determined.

## MATERIAL AND METHODS

At the curing process the uneven filler distribution in matrix occurs (VALÁŠEK, MÜLLER 2010). For the possible composite properties examination in various solid parts the measuring of hardness, density and phases image analysis were carried out using sub-parts of dimensions  $25 \times 25 \times 12.5$  mm, which are made using the saw blade partition of primary bodies of dimensions  $25 \times 25 \times 75$  mm (Fig. 1), where the figure shows the direction of the gravitational force and in this way the presupposed sedimentation direction, which represents the filler particles motion during the resins curing. The lower part of the sub-part 1 corresponds to the “sediment face” of the composite. The X-ray analysis was realized using the cylindrical sample of 10 mm diameter and 25 mm height. The samples lower size made the X-raying easier and enabled the better and complete X-ray image, which supplements the described problem. The polymeric particle composites were prepared with 12.5 and 25% vol. of filler in the matrix. The representation of the filler part by the % vol. eliminates the influence of different resin and filler densities. The resin density in uncured state was according to the producer information of  $1.15 \text{ g/cm}^3$ , while the chips density was in non-compressed state of  $1.8 \pm 0.13 \text{ g/cm}^3$ . This value was determined at  $23^\circ\text{C}$  as the ratio of the sample weight to its vol. For the test samples preparation the moulds made from silicone rubber (Lukopren 1522) were used, because they showed separation property towards the used resin. The made moulds were dried, cleaned and degreased. They showed separation property towards the used resin. Before casting the filler was homogeneously dispersed in the matrix using the ultrasound. The curing time mentioned by the producer was 24 h at the temperature of  $23^\circ\text{C}$  (at this temperature the perfect curing occurs after 7 days).

The hardness was measured on the sides of sub-parts 1–5, after that on the sections between the sub-parts (Fig. 1). For the hardness measuring the Shore D scale was used. This method uses the test

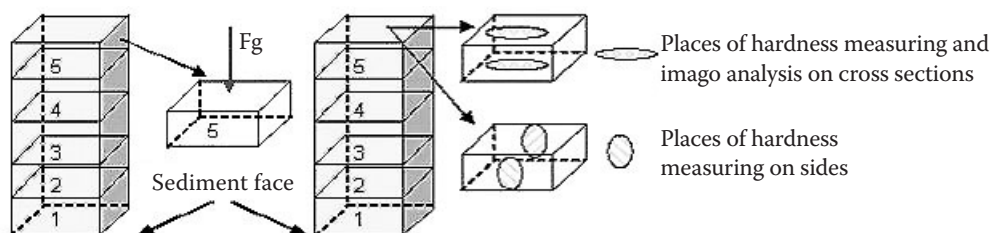


Fig. 1. Cutaway diagram

body penetrating into the tested body. The final hardness value depends on the modulus of elasticity and on the material visco-elastic properties. The hardness is read on the scale in units from 0 to 100, where zero corresponds to the full penetrating, 100 to the null one (ČSN ISO 868 2003).

Single sides of sub-parts (Fig. 1) were analysed using the stereoscopic microscope (Arsenal, Ltd., Prague, Czech Republic). The phases ratio of these sides was determined and graphically demonstrated. Next the sub-parts density was calculated.

### RESULTS AND DISCUSSION

The filler in form of chips was taken as waste from the universal Pilous bandsaw, using the cutting speed of 40 m/min. The concrete chip shape depends on the cutting conditions and above all on the cutting speed. Used chips were most similar to the spiral flat ones (TARASOVICOVA et al. 2010). To determine concrete sizes and dimensions of single particles the image analysis was carried out, using the stereomicroscope. Using the built-in camera (Artray Co., Ltd., Tokyo, Japan) and software Quick (Software Quick Photo Promicra, Ltd., Prague, Czech Republic) single particles surfaces in 2D at 3.5× magnification were measured. For the particle size description the two-dimensional plane was chosen intentionally owing to the shape unevenness. The obtained data were statistically analysed. The resulting frequency histogram from the filler surface is presented in Fig. 2. The shape and size of the particles are presented in Fig. 3.

On each of composites of 12.5 and 25% filler content a run of experiments was carried out with the aim to determine the composite density and hard-

ness, better to say of the sub-parts. The experimentally determined density in direction from the “sediment face” of the composite decreased as it is presented in Fig. 4, which states the mean values of determined density in coordinates density – sub-part of the body (distance from the sediment face in mm). In Fig. 4 two decreasing curves are presented (meeting the test bodies of 12.5 and 25% filler content), which represent the composite 1–5 subparts density (Fig. 1). The horizontal broken lines correspond to the primary test bodies density before the cutting into sub-parts, when the composite specific density of the 12.5% filler content reached the value of  $1.24 \pm 0.05 \text{ g/cm}^3$  and of the 25% filler content value of  $1.29 \pm 0.03 \text{ g/cm}^3$ . The specific density of composite sub-parts (1–5, Fig. 1) decreased from  $1.60 \pm 0.02$  to  $1.10 \pm 0.01 \text{ g/cm}^3$ , at the composite of 12.5% filler content and from  $1.73 \pm 0.04$  to  $1.14 \pm 0.01 \text{ g/cm}^3$  at the composite of 25% filler content. This fact confirmed the theoretically expected density decrease in the direction from the sediment face. At the composite of 12.5% filler content from the third sub-part (i.e. 45 mm from the sediment face) the density is practically constant, while the density decrease at the composite of 25% filler content is more balanced in the whole course. The filler is dispersed in the matrix more regularly. It is evident from the X-ray images.

Analogously as the density the composite hardness should be dependent on the filler content in the matrix. As it is evident from Figs 5 and 6, in the direction from the sediment face the hardness decrease occurs. The broken line represents the measuring carried out on the sub-parts surfaces, where the hardness of the sub-part 1 corresponds to the value 0 on the  $x$ -axis, value 1 on the  $x$ -axis

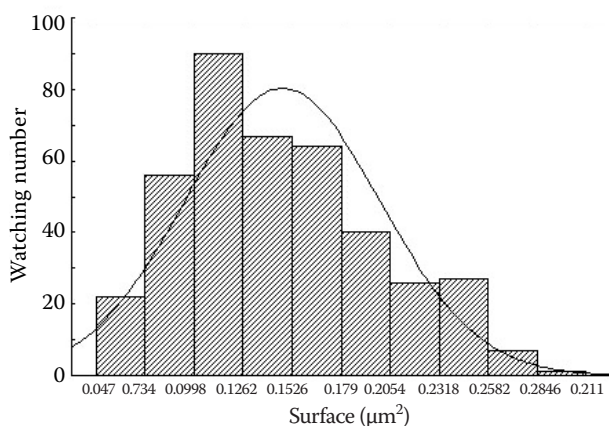


Fig. 2. Frequency diagram of the filler surface

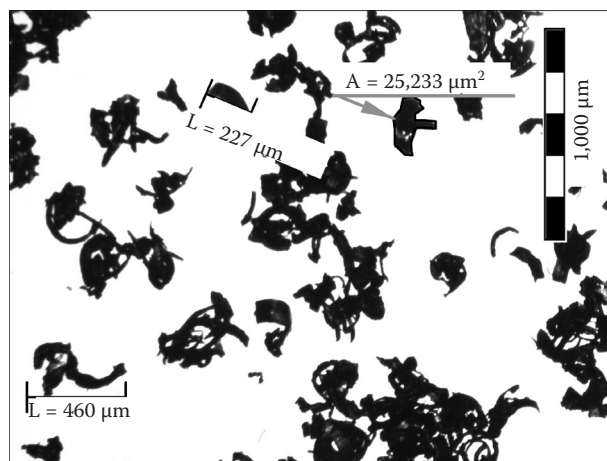


Fig. 3. The shape and size of the particles

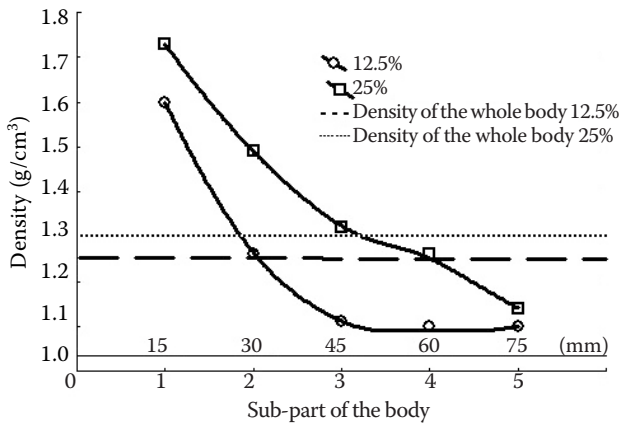


Fig. 4. Specific density of the bodies sub-parts

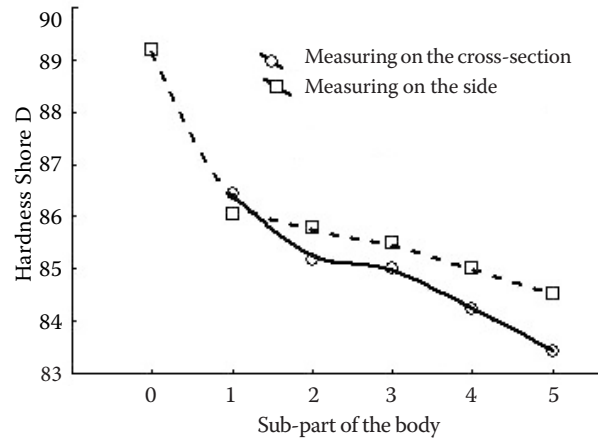


Fig. 5. Hardness of bodies sub-parts (12.5%)

corresponds to the measurement between sub-parts 1 and 2, so in the distance of 15 mm from the sediment face. In the same way it was measured up to the upper surface of the sub-part 5 (value 5 on the *x*-axis). The full curve presents the hardness values measured on the sub-parts sides, where the value on the *x*-axis corresponds to the number of the sub-part (Fig. 1).

From the mentioned hardness values the precondition was confirmed that at the composite of 25% filler content the filler distribution was more equal – the hardness varied from  $89.32 \pm 1.6$  to  $84.55 \pm 0.95$ . At the composite of 12.5% filler content the hardness values varied from  $88.72 \pm 1.8$  to  $84.51 \pm 0.84$ . The hardness on the composite surfaces was smaller than on the cross-sections. This confirms the fact that in the composite surface layer the resin is more contained than the filler. The filler distribution in the matrix is presented by the image analysis of single phases, demonstrated in Figs 7 and 8 using the stereoscopic microscope at 3.5× magnification.

The upper images respond to the surface centre of the lower surface of sub-part 1. Next images respond always to the cross-sections of following pictures (1/2, 2/3, 3/4) in Fig. 1. The measuring of phase parts was carried out on surfaces of each cross-section, but only the first four images in direction from the sediment face are shown in Figs 7 and 8. In the Fig. 2 or more precisely 3 phases can be seen, namely: filler (grey), matrix (black) and air blebs [at the black-and-white print the blebs are not differentiable from the filler – their occurrence would be visible from the cross-section 2/3 and to the upper (non-sediment)] part of the body their

share increases. At the composite of 25% filler content the mentioned filler distribution evenness can be seen in the whole body compared to the composite of 12.5% filler content. Single phases shares are presented in Figs 9 and 10, where only the filler and air blebs communal percentage is demonstrated. The sum of demonstrated phases and matrix is equal to 100%.

Cylindrical samples of 10 mm diameter and 25 mm height were X-rayed using scintillator for illustrative representation of filler distribution. After the low-energy X-ray bundle goes through the sample it is caught by the scintillator, from which a part of arising optical radiation is directed by the macroobjective into the water-cooled camera with detector of  $4008 \times 2648$  pixel resolution. The lamp PXS5-927 (Crytur, Ltd., Turnov, Czech Republic) was used at experiments. The filler distribution following from the grey level image analysis is graphically demonstrated in Figs 11 and 12.

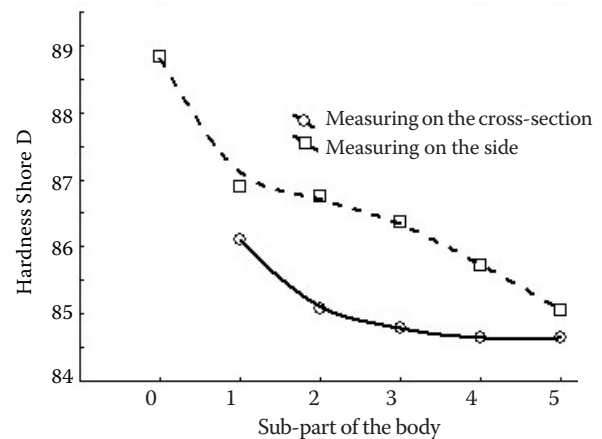


Fig. 6. Hardness of bodies sub-parts (25%)



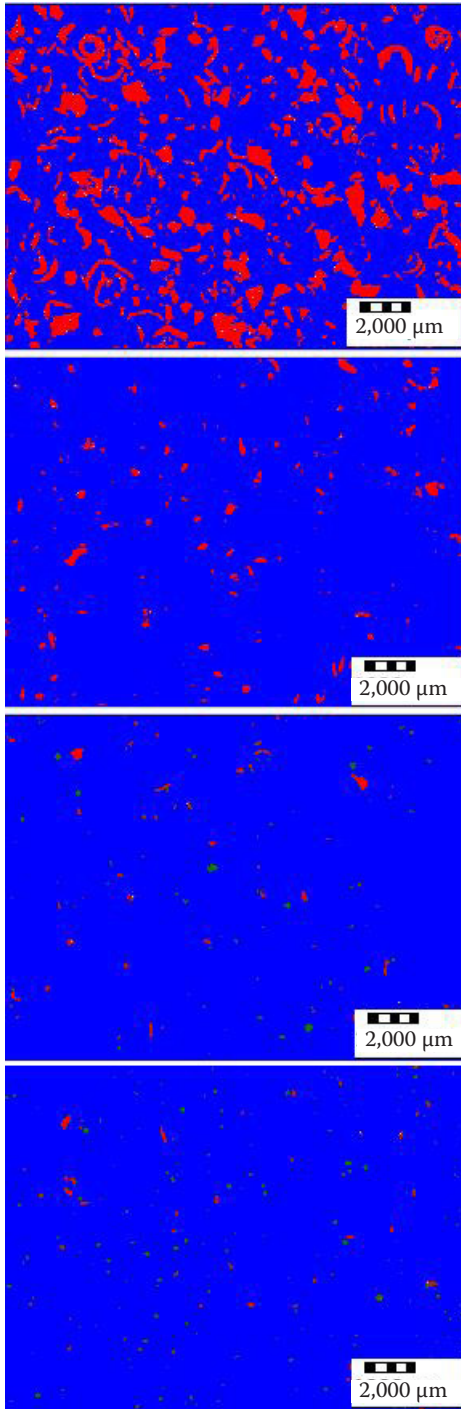


Fig. 7. Microscopic analysis of phases (12.5%)

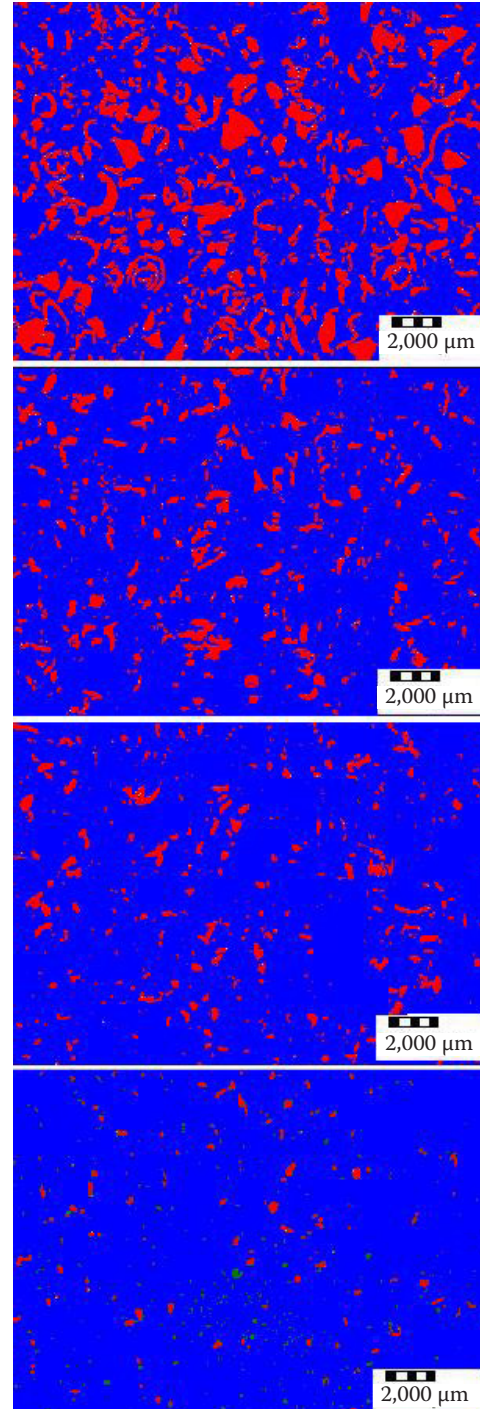


Fig. 8. Microscopic analysis of phases (25%)

### CONCLUSION

From the measured results it is evident that the gravitation force having effect in the course of resin curing on the filler particles causes the uneven distribution of the filler in the matrix. The unevenness was proved as on the different specific density of

composite sub-parts, so on the hardness values, X-ray images and image analysis of composite parts. This unevenness has also influence on mechanical properties. With higher filler content in the matrix greater homogeneity of single phases in the whole sample volume occurs. If we compare the mean specific density values of composites with

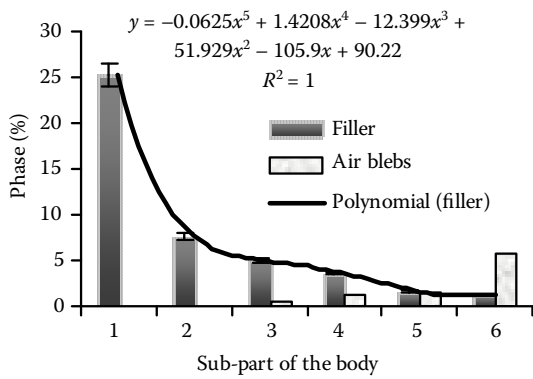


Fig. 9. Graphical representation of phases proportion – 12.5%

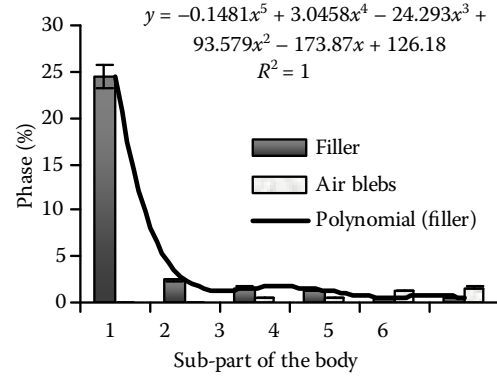


Fig. 10. Graphical representation of phases proportion – 25%

12.5% and 25% filler content in sediment faces, the difference between these values is of 0.13 g/cm<sup>3</sup> (the hardness difference is of 0.6), while in non-sediment part the difference of measured values is not so evident – the difference between specific density values is of 0.04 g/cm<sup>3</sup> (difference between hardness values is of 0.04). The highest density was measured in the sediment face of the composite

with 25% filler content, when the density was by 53% higher than the density after curing without the filler (1.13 ± 0.01 g/cm<sup>3</sup>). The lowest density was recorded in the non-sediment part of the composite with 12.5% filler content, when this value was of 2.7% lower than the density of cured resin without the filler. This was probably caused by the air blebs presence in the material. The air blebs were

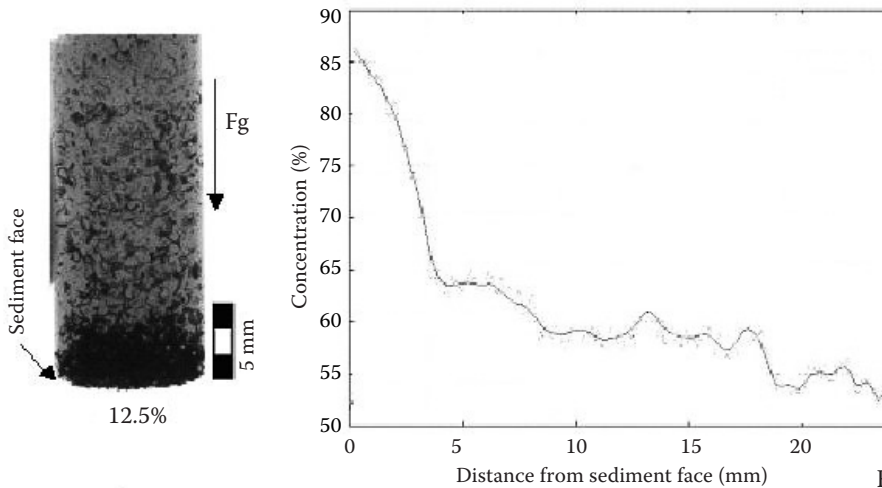


Fig. 11. X-ray sample analysis (12.5%)

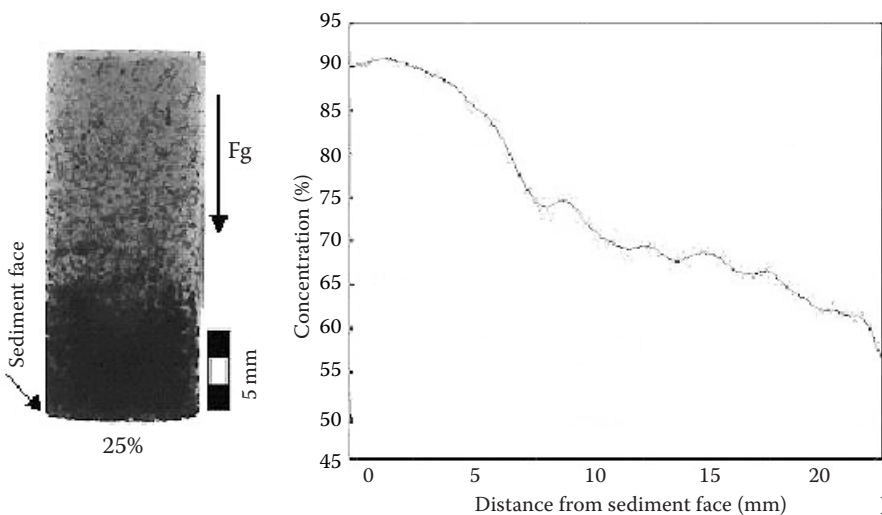


Fig. 12. X-ray sample analysis (25%)

discovered by the stereomicroscopic image analysis of phases. It is possible to expect that the sedimentation process depends on the composite shape and size. The potential application field of such systems with filler on the basis of waste is in renovation of soil processing tools, where the emphasis is put on wear resistance and hardness together with minimization of frictional forces between tool and soil. Owing to the composite material applied thickness it can be on the basis of carried out experiments expected that the sedimentation influence on the filler distribution will be negligible.

The experiments carried out confirmed the assumption of VOCEL and DUFEK (1976) and XUE QUNJI and WANG QIHUA (1997) that the filler application in epoxy resins influences the final properties considerably. The hardness of the resin itself reached the value of  $83.1 \pm 3.2$ . Composites containing filler on the basis of waste reached higher hardness in all sub-parts. So the experiments confirmed that the waste from material cutting process is usable as filler. Although the application of such fillers is limited by their properties, it offers relatively easy way of recycling, which is inexpensive and environment friendly.

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Received for publication January 13, 2011

Accepted after corrections October 7, 2011

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