Mesocomposites Based on the Polymethylmethacrylate Matrix

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This article describes the formation of a composite coating in a polymer matrix on an aluminum alloy. It is a PMMA coating (polymethylmethacrylate) with the addition of TiO$_2$ particles. Working with these particles requires not only safety but also a suitable preparation process to obtain particles of suitable size, their subsequent homogeneous distribution in the coating (particles of this size are influenced by electrostatically attractive forces and have a strong tendency to aggregate). The first part describes the material used, sample preparation and coating process, surface roughness measurement, SEM and EDS analysis of selected samples. The aim of the research is to find out whether it is possible to use dipping and brushing techniques when coating Al-Si alloys with polymeric materials. Consequently, what can be achieved is the roughness of the surface of the coated part compared to the uncoated surface (at different particle concentrations in the spin) and the distribution of TiO$_2$ particles on the surface of the sample.

Keywords: Mesoparticles, coating, TiO$_2$, PMMA, surface roughness

1 Introduction

Composite materials nowadays, thanks to their excellent properties, are widely used and constantly evolving. The composite material consists of a matrix, in our case PMMA, and a reinforcement (TiO$_2$). A suitable combination of matrix and reinforcement to achieve better properties of the composite as a whole, rather than simply adding together the properties of the individual components. This property of the composite is called synergism. It is important to choose the appropriate size of the reinforcement particles, as they can affect the resulting properties of the composite. Furthermore, it is necessary to realize that it is not necessary to make the whole component of the composite, but it is often sufficient to modify the surface, for example a mold which, due to a suitable coating, will obtain the desired surface properties (temperature resistance, wear reduction, hardness increase, etc.) also reduce costs [1].

The designer of composite materials aims basically to achieve a compromise. Addition of high-modulus but fragile particles. Polymer matrix leads to a light, rigid composite which may indeed possess a certain resilience, but at a cost in terms of manufacture. Loading a thermo-plastic polymer with very rigid particles (or dispersoids) will increase the modulus, but it will also reduce the shock resistance. Dispersing rubber inclusions in a hard, transparent but fragile matrix will confer a better shock resistance to it, but the price to pay is often a loss of transparency. The great difference when using very small particles, or at least, particles with one nanoscale dimension, is that one may thereby overcome the need for this kind of compromise." [13]

Trend of today brings new knowledge about composite materials. And their wide range of applications. Rapid development and technology methods enable creation materials with excellent properties. The breakthrough moment was the introduction nanocomposites.

A particle filled into the composite was choosed titanium dioxide particles. They were prepared by means of planetary ball mill, by so called wet milling. „There are three main methods for the preparation of CNT-ceramic nanocomposite powders. One is mechanical milling. It usually involves long times that could damage the particles. Wet-milling is preferred but often requires the addition of organic additives to stabilize both the nanotubes and the ceramic powder." [10]

The use of polymeric materials as a matrix for nanocomposite materials becomes a frequent case. This is mainly due to their features and availability. It is important to take care of the size of the nanoparticles used and their amount in the matrix, because that strongly affects the resulting nanocomposite.[4]

There is no need to make whole parts from the nanocomposite, we get into the phase when we use the surface properties of nanocomposites and at the same time the component is made from of the standard material, we achieve this by using the coating method, ie coating nanocomposite material to various components to improve properties surface [1].

The aim of the research is to determine if the coatings will affect the surface’s condition and its properties. I focus on selecting the appropriate preparation of sample technology, examining the particle distribution in the coating and the effect of the coating on the roughness of the surface. The examination of surface properties with surface-treated material is performed and microscopic surface samples are examined using SEM / EDS analysis.

2 Preparation of materials, coating and surface roughness measurement

The material to which the composite coating was applied is the aluminum alloy used in the automotive industry, specifically as a tire mold. For the chemical composition of silicon used, see Table 1.

Matrix material was selected as PMMA (organic glass). It is an amorphous polar plastic characterized by excellent mechanical properties. It is resistant to UV radiation and weathering. The melting point is 160 °C, the modulus of elasticity can reach up to 3200 MPa.
Tab. 1 Chemical composition of Al-Si

| Element | Si   | Fe   | Cu   | Mn   | Mg   | Cr   | Ni   | Zn   | Ti   |
|---------|------|------|------|------|------|------|------|------|------|
|         | 89.400 | 8.514 | 0.627 | 0.0048 | 0.508 | 0.550 | 0.030 | 0.087 | 0.023 | 0.098 |

Titanium dioxide TiO$_2$, characterized by high hardness, resistance to mechanical wear, UV resistance and antistatic properties, was cast as a reinforcement by a planetary ball mill from previous research [2], [3].

As a backing material, the tire production mold was used directly, which was cut to a suitable sample size.

PMMA was dissolved in chloroform (CHCl$_3$). 287 g of chloroform and 45 g of PMMA were used for the basic solution. For coating, the stock solution was further diluted in two concentrations of 1:10 and 1:3 (weight ratio of stock solution and pure chloroform).

The PMMA + CHCl$_3$ and TiO$_2$ mass concentrations were chosen (identical for both concentrations of PMMA + CHCl$_3$):

- 0%
- 0.01%
- 0.1%
- 1%

The TiO$_2$ powder is very agglomerated and, prior to being mixed with the solution, it is placed in an ultrasonic treatment plant for a few minutes, where it is broken down and disintegrated by agglomeration. It was then added to the solution and thoroughly mixed.

Two methods were used to apply the composite coating:

- dipping (the sample is immersed in solution and brush application (the solution is applied to the sample by drawing the brush).

The resulting sample was dried at room temperature.

3 The surface roughness measurement

The surface roughness measurement was carried out on the Hommel Tester T800 according to the standard measurement method. The sample track was 4.8 mm and the TK300 sensor type. Each sample was measured five times and the arithmetic mean was calculated from the measured values. As a reference sample, a clean, uncoated sample was chosen. The measured values were Ra (mean arithmetic deviation of the profile), Rz (max. profile height) and Rt (total height of the profile).

Research provides data for the evaluation of the coated samples and their comparison with the uncoated sample. It was important to choose the kind of added reinforcement particles in the matrix. Several variants of the concentrations of the added particles were also tested in the coatings, namely titanium dioxide particles. Two variants of dilution of the coating solution and technology of its application to the underlying material were prepared.

By measuring the roughness, it has been found that the increase in the parameters to be evaluated is not entirely dependent on the TiO$_2$ concentration in the coating or on the sample coating technology. However, there is an observable increase in roughness in comparison to the uncoated sample. The largest increase in measured parameters is apparent from the resulting measurement graphs. Sample without coat is called „X“.

From Figure 1, we can see that there has been an increase in roughness relative to the roughness of the non-coated material (X). The increase was mainly due to the value of Rt. Roughness Ra values increased at a minimum. There is also a decreasing tendency of roughness with the increasing concentration of TiO$_2$ in the solution.
At higher concentrations of PMMA + CHCl₃, there was also an increase in roughness as shown in Figure 2. Here we can see partly decreasing tendencies of roughness with increasing TiO₂ concentration, but on the contrary, the highest roughness here reaches the ratio with the highest concentration of TiO₂ in solution.  

At a lower concentration of the PMMA + CHCl₃ solution applied by the brush, there was also an increase in roughness, see Figure 3. Compared to the sample in the soaked solution, the increase in roughness was not as great compared to the uncoated reference pattern.
At a higher concentration of the brush application of PMMA + CHCl₃, see Figure 4, it can be seen that the roughness is comparable to the uncoated reference sample. A sample with a TiO₂ concentration of 0.01% achieves almost twice the roughness, but it may be due to a measurement error.

4 SEM analysis

Titanium dioxide exhibits lower electrical conductivity than iron or aluminum, and it is therefore necessary to use high acceleration stress values for SEM and EDS analysis of coatings containing these particles, as has been found in previous research. Due to the large number of samples, only some samples were selected for the SEM analysis for the idea of the structure and distribution of particles in the coating layer.

Important surface information brought SEM and EDS analysis. The particle distribution in the coating was not completely regular, which could have affected previous measurements. For samples with a brush coating method, it is possible to see the texture left by brush bristles. SEM analysis revealed that titanium particles often form agglomerations. The measured particle sizes range from hundreds of nanometers. On the surface of the coating often there are inclusions in the form of dust particles, which are easily detected for their shape and size. The best coating quality was found in samples with the highest TiO₂ concentration, ie 1%, a new beneficial finding.

Fig. 4 Surface roughness of samples of PMMA + CHCl₃ concentration 1:3, brush application

Fig. 5 Sample diluted 1:10, TiO₂ concentration 0.1% and dipped
In Figure 5 we can see the agglomeration of TiO$_2$ particles. The particles are very irregular with a smooth surface and sharp edges of these titanium dioxide particles are visible. The particle size is in hundreds of nanometers. The particles are present in the coating both individually and in clusters. Particles often create these agglomerations, and it is difficult to record particle size.

For the preparation of these other coatings, I would recommend to remove the deficiencies found by SEM and EDS analysis: Using longer ground TiO$_2$ particles to reach a 100 nm dimension, coating the samples and drying them in a dust extraction hood. To reduce the occurrence of particle agglomeration, I would suggest a longer period of particle disruption using ultrasound in the production of the coating solution. I hope my work has brought the knowledge for further research on these coatings.

Figure 6 shows that a higher concentration of TiO$_2$ in the solution results in a more even distribution of the particles in the coating.

**Fig. 6 Sample diluted 1:10, TiO$_2$ concentration 1% and dipping**

**Fig. 7 Sample diluted 1:10, TiO$_2$ concentration 1% and brush applied**
In the case of a brush-coated sample, a noticeable texture of the coating can be observed, as shown in Figure 7, as in the previous case, a more even distribution of the particles at a concentration of 1% TiO$_2$ can be observed here.

5 Conclusions

The work was focused on the possibilities of preparation of the composite layer from PMMA and TiO$_2$ particles and subsequent coating of the surface of the aluminum alloy with this solution and the assessment of the influence of the coating on the roughness of the surface.

Two concentrations of PMMA + CHCl$_3$ with different concentrations of TiO$_2$ were selected for the experiment. The coating process was chosen for dipping and brush application, for their simplicity and ease of realization.

For most samples, the roughness values were increased, except for the latter, but no particle concentration, solution or coating technique was found. However, greater roughness may not have a negative effect on the resulting properties, and in some applications it is advantageous and desirable. In the brush application method, a distinctive texture of the surface is created.

From the SEM and EDS analysis, it is clear that the particles are strongly agglomerated despite the use of an ultrasonic purifier to form solutions of given concentrations. Furthermore, we can see that the best (homogeneous) particle distribution on the surface of the coated sample is reached at higher concentrations of TiO$_2$ in the solution.

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