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The Influence of Nanofillers on the Mechanical Properties of Carbon Fibre Reinforced Methyl Methacrylate Composite

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The influence of different types of nanofillers – carbon nanotubes (CNT) and organically modified nanoclay – on the flexural properties and nail penetration resistance of carbon fiber reinforced methyl methacrylate (MMA) composite have been investigated. An ultrasonic mixing was used to distribute various content of nanofillers (0.7 wt.% – 3.0 wt.%) in MMA resin. Scanning electron microscopy and X-ray diffraction analyses confirmed formation of intercalated MMA clay nanocomposites. Two different stacking sequences, $[0/90]_3$ or $[0/90/45]_2$, and two types of carbon fibre, with or without epoxy binder, were used for composites preparation. The composites with stacking sequence of $[0/90]_3$ show higher resistance to the mechanical loading. Epoxy binder increases fibre adhesion interaction with MMA resin, however, almost does not influences on the fibre reinforced composite strength properties.

The results demonstrated that only low content (up to 1 wt.%) of organically modified nanoclay Cloisite 10A increases the carbon fibre reinforced composites resistance to flexure and nail penetration. The low content of CNT also increases flexural stress and modulus, but decreases resistance to the nail penetration.

Keywords: methyl methacrylate, carbon nanotubes, nanoclay, carbon fibre reinforced composite.

1. INTRODUCTION

Materials used for orthopedic applications, such as external bone fixation devices, must have high modulus and strength, long-term dimensional stability, high fatigue, and abrasion resistance. Consequently, for these purposes usually are used metals, tough plastics, and fibre (glass, carbon, graphite, aramid, etc,) reinforced polymer-matrix composites [1 – 2].

Fiber reinforced polymers have been finding wide use in orthopedic technology for many years due to high strength, but lightweight and shape-retaining yet thin, easy to clean, and hygienic. Besides, the impact, flexural and other mechanical properties are important parameters for fibre reinforced polymer matrix to be employed in such areas. Especially, these properties are important in footwear for professional use [3 – 5].

Many commercial and construction situations present the danger of sharp object penetration through sole of the footwear worn by the workers. A most common example is the presence of nails around constructions sites. This dangerous but relatively unavoidable situation results in large number of injuries to workers. Therefore, many developments have been directed to creating protective footwear. However, main part of these developments has failed due to needs to balance a high degree of protection with comfort and wearability, since the sole must remain flexible. Therefore, fiber reinforced composites find wide application for footwear components [6 – 8].

Pure not reinforced resins normally have poor impact resistance at room temperature and are brittle, which limit their use for orthopedic needs [9]. Therefore, in recent years extensive attention has been given to nanofillers as reinforcements of fiber reinforced polymer composites. Many nanofillers such as nanoclays, carbon nanotubes (CNT), and carbon nano fibers (CNFs) have been incorporated in to polymer matrix in order to enhance mechanical and physical properties [10 – 27]. There are a lot of investigations on the properties of fiber reinforced polymers based on nanoclay, CNT or CNFs filled epoxy [12 – 18], or phenolic [19 – 21] resins. While no investigations of nanofillers influence on the properties of the thermoset methyl methacrylate polymers.

Materials used for medical applications to replace or restore damaged function should be biocompatible, non-toxic and non-carcinogenic. Methyl methacrylate (MMA) polymers have been widely used as biomaterials in dentistry (denture construction, repair and relining, temporary crown and bridge materials), and in orthopaedic surgery as bone cements for the stabilization of metallic femoral hip endoprostheses or for other orthopaedic devices [22]. Usually, MMA polymers are obtained by free radical polymerization using tertiary aromatic amines together with benzoyl peroxide as an effective initiation system [23]. It significantly influences such important properties as molecular weight, mechanical strength, shade and colour stability, and biocompatibility.

Traditionally, for polymeric nanocomposites thermoplastic poly(methyl methacrylate) (PMMA) has been used. Studies on the PMMA have shown that nanoclay particles incorporated by melt blending improves overall thermal stability of composite [24 – 26]. The

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preparation of exfoliated PMMA/clay nanocomposites by *in situ* polymerization improves its tensile strength and tensile modulus [27].

Gorga R. [28] investigated the influence of multi-walled carbon nanotubes (MWNT) on the mechanical properties of PMMA as a function of the nanotube orientation, length, concentration, and type. In this study the largest improvements (the increase in 170 %) obtained in the case of tensile toughness for the MWNT/PMMA sample with 1 wt.% of MWNT. No significant increases in modulus or yield strength were obtained at lower loadings which consistent with the very poor adhesion between PMMA and the MWNT. The electrical properties of PMMA and double wall carbon nanotubes (DWCNT) nanocomposites have been investigated in [29]. It was found that the electrical conductivity property of the PMMA changes from insulating state to semiconducting state with incorporation of DWCNT.

The aim of the present work is to describe the process-structure-property relationship of carbon fibre reinforced non-toxic methyl methacrylate composites suitable for manufacturing of orthopedic footwear nail penetration resistant inserts.

2. MATERIALS AND METHODS

2.1. Materials

For investigations carbon fibre reinforced MMA matrix composites were produced. Two types of twill-weave carbon fiber with and without epoxy (EP) binder with surface density of 204 g/m^2 from R&G Faserverbundwerkstoffe GmbH were used.

Methyl methacrylate resin (617H21-Orthocryl Sealing Resin, Otto Bock) with molar mass of 100 g/mol, viscosity of 450 mPa·s (at 20 °C temperature), and density of 1.02 g/cm^3 was applied for wet lay-up of carbon fabric. Tertiary aromatic amine N,N-di(2-hydroxyethyl)-p-toluidine with benzoyl peroxide (BPO), Orthocryl Resin 617P37 (supplier Otto Bock), was used as initiation system in the free radical polymerization. The role of the amine is to carry out the reaction in a short period of time at room temperature, i. e. it accelerates the free radical decomposition of BPO. It is generally agreed that a benzoyl free radical is formed when benzoyl peroxide reacts with the tertiary aromatic amine accelerator N,N-di(2-hydroxyethyl)-p-toluidine, and that this benzoyl free radical initiates polymerization of MMA monomers [30]. MMA with BPO was mixed at weight ratio of 100 : 1 (N,N-di(2-hydroxyethyl)-p-toluidine is incorporated in MMA resin composition).

Multiwalled carbon nanotubes (CNT) from Cheap Tubes, Inc. were used with purity verified as 95 %. These nanotubes were prepared by the method of catalytic vapor deposition. The manufacturer specified dimensions are: tube length $L = 10\ \mu\text{m} - 20\ \mu\text{m}$, inside diameter $d_i = 5\ \text{nm} - 10\ \text{nm}$, outer diameter $d_0 = 30\ \text{nm} - 50\ \text{nm}$. The pristine nanotubes were lightly ground by pestle and mortar prior to use without surface modification at any time during processing.

The organically modified montmorillonite clay Cloisite 10A (C10A) was kindly provided by Souther Clay Products (Gonzales, TX). C10A was commercially modified by dimethyl, benzyl, hydrogenated tallow, quaternary ammonium.

2.2. Carbon fibre reinforced MMA polymer composite preparation

The C10A nanoclay or CNT were incorporated directly in MMA resin by sonication (Ultrasonic cleaner 8891, Cole-Parmer) for 5 min. The composites were formed by wet lay-up process of carbon fabric with MMA resin. For investigation four different composites based on carbon fiber reinforcement (with and without EP binder), and two different stacking sequences were used. The stacking sequence of the carbon fibres was 6-ply composites with $[0/90/45]_2$ and $[0/90]_3$ plates, where the „0”, „45”, „90” are symbolic notation of the plies different orientation angles. The thickness of the composite plates was 2 mm.

2.2. Flexural tests

The flexural properties of fibre reinforced composites were determined by three-point bending test in accordance with LST EN ISO 178, using a universal testing machine (Tinius Olsen, Redhill, England) with a load cell of 5 kN at a constant speed of 1 mm/min. Six samples (4 × 80 × 10 mm^3) were cut from composite sheets. The flexural strength, σ_f was calculated following the relationship:

$$\sigma_f = 3Fl/2bd^2, \qquad (1)$$

where F is the maximum load, l is the distance between supports, b is the width of the specimen, d is the height of the specimen.

The flexural modulus, E_f was calculated using equation:

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}}, \qquad (2)$$

where σ_{f1} and σ_{f2} are the flexural stress, measured at deflection s_1 and s_2, respectively.

The flexural strain was calculated using following equation:

$$\varepsilon_f = \frac{6sh}{l^2}, \qquad (3)$$

where s is deflection, h is the thickness.

2.3. Nail penetration resistance

It is relevant to examine the effect of layered structures resistance to penetration and layer damage [31]. In this study the force required to penetrate the composite sheet was determined in accordance with LST EN 12568, using universal testing machine (Tinius Olsen, Redhill, England). The nail with diameter of 4.50 mm and with truncated end was used in the test (Fig. 1).

The three test pieces of dimensions 30 mm × 30 mm were cut from the composite sheets and tested separately. The test peace was clamped between two plates (see Figure 1), with its edge being at least 15 mm away from the tip of nail. The nail was deflected into the sample at a constant speed of (10 ±3) mm/min until the point has penetrated completely. The test result is required maximum force to penetrate the composite sheet.

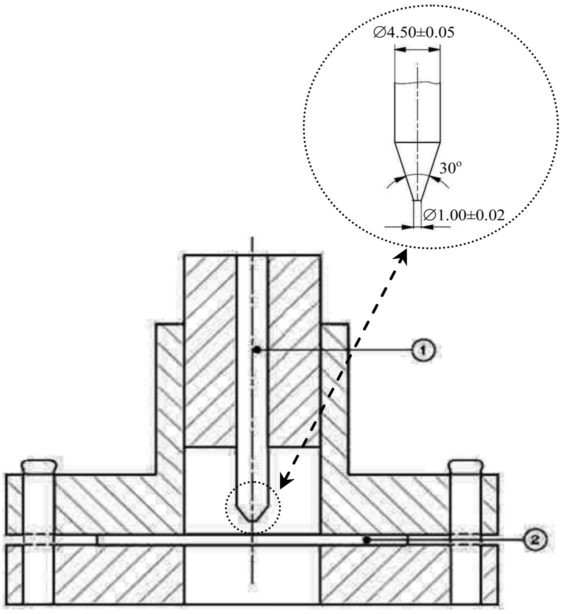

Fig. 1. Schematic example of apparatus for nail penetration resistance test: 1 – test nail, 2 – test piece

Obtained load versus penetration depth plot shows two distinct phases of failure propagation for complete penetration [32]. As can be seen from Fig. 2, the first phase, named as damage initiation phase, is observed from the moment of nail impact to the point of peak load, where the damage initiates with almost uniform deflection with some initial penetration peaks.

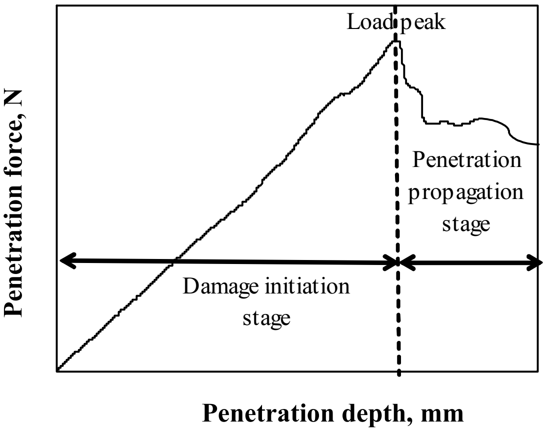

Fig. 2. Plot of penetration force versus depth in nail penetration resistance test

At the point of peak load, test piece is penetrated by nail completely and then rapid load-reduction is achieved. This phase can be identified as penetration propagation phase (Fig. 2).

2.4. Nanocomposites characterization technique

Wide angle X-ray diffraction (XRD) analysis was performed using a diffractometer DRON-6 equipped with a copper target ($\lambda = 1.54$ Å) and flat diffracted beam pyrolitic graphite monochromator. Diffraction patterns were recorded at 35 kV and 20 mA.

Scanning electron microscope (SEM) analysis was performed using the microscope Quanta 200 FEG (FEI, Netherlands) at 10 keV or 20 keV and was used for composites surface investigation.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of MMA/nanoclay composites

The wide range XRD analysis results of MMA polymer, C10A nanoclay, and MMA nanocomposite with 3 wt.% of C10A filler are shown in Fig. 3. As can be seen, the interplanar distances of organically modified clay C10A layers calculated according to Bragg's law are $d_{001} = 1.96$ nm. The MMA polymer diffractogram is characteristic for an amorphous polymer and confirms that any very small crystals are presented in the sample. The XRD pattern of MMA/C10A nanocomposites has a weak diffraction peak at 4.94° ($d_{002} = 3.58$ nm), relative to the C10A, and new peak at low angle 2.48° ($d_{001} = 3.50$ nm). These results indicate the formation of intercalated nanocomposite. It may be supposed that sonification leads to the delamination of silicate layers and intercalation by MMA macromolecules [33].

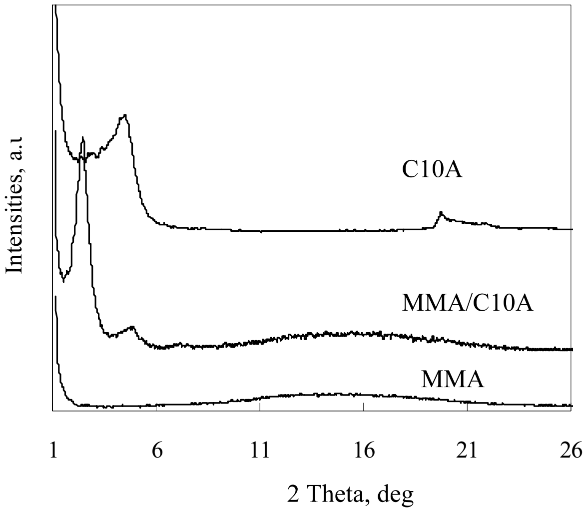

Fig. 3. X-ray diffractograms for MMA, C10A nanoclay, and MMA/C10A (97/3 wt.%) nanocomposite

SEM micrograph of the MMA nanocomposites containing 3 wt.% of C10A is presented in Fig. 4. It is seen that organoclay C10A is well dispersed within MMA and distribution of exfoliated, intercalated and not dispersed C10A particles are clearly seen. The diameters of nondispersed C10A particles are in the range of 1 μm – 3 μm.

3.2. Investigation of flexural resistance of the carbon fibre reinforced MMA composites

The differences in the materials and their structures are reflected in the different flexural properties of the final composites [34]. Table 1 presents the results of three point bending tests of carbon reinforced MMA polymer nanocomposites. As can be seen, the carbon fabric with EP binder had higher flexural properties of composite than that without binder. The flexural stress and flexural modulus with EP impregnated carbon fibre are higher in 10 % and 18 %, respectively, than that of carbon reinforced composite without fibers binder. It can be attributed to the higher adhesion interaction between MMA polymer and carbon fiber, because fibre impregnation by EP melt binder increases its adhesion capability to polar matrix [35].

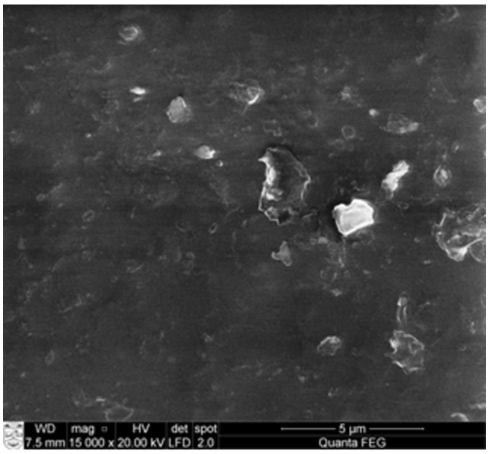

Fig. 4. SEM image of MMA polymer surface with 3 wt.% of C10A nanoclay

Fiber orientation is very important in determination of the strength of the composites [36, 37]. In this study the comparison of both stacking sequences showed that $[0/90]_3$ composite has slightly higher values of flexural properties than in the case of $[0/90/45]_2$ composite. However, this difference is not significant and is close to the coefficient of variation.

Table 1. Influence of C10A nanoclay on the flexural properties of carbon fibre reinforced MMA composites

Fibre type	Stacking sequence	C10A content, wt.%	Flexural modulus, MPa	Flexural stress, MPa
Not impregnated	$[0/90]_3$	0	25662 ±1994	495.5 ±52.9
	$[0/90/45]_2$	0	24003 ±1195	459.0 ±48.6
EP binder	$[0/90]_3$	0	30433 ±1034	545.0 ±56.0
	$[0/90/45]_2$	0	24793 ±1372	509.0 ±38.0
		1	26542 ±2599	471.2 ±55.4
		2	21112 ±1740	341.0 ±65.1
		3	18251 ±5978	235.8 ±79.8

From Table 1 can be seen that the flexural strength gradually decreases as nanoclay content increases and 3 wt.% of C10A twice decreases the flexural stress (from 509 MPa down to 236 MPa).

On the other hand, 1 wt.% of C10A increases the flexural modulus in 7 %. However, further increase of nanoclay content up to 3 wt.% decreases flexural modulus in 35 %. Such decrease at higher clay content can be attributed to the higher possibility of nanoclay agglomerates formation and the reducing of clay reinforcement efficiency. It is known [38] that particle aggregation is the primary reason of the decrease of materials strength even the modulus slightly increases.

As it can be seen from the Table 2, CNT improves flexural properties of carbon reinforced MMA nanocomposites. The flexural strength of nanocomposite incorporating 0.7 % of CNT is improved in 6 %, while flexural modulus increased in 14 %.

Table 2. Influence of CNT on the flexural properties of carbon fibre reinforced MMA polymer composite*

CNT content, wt.%	Flexural modulus, MPa	Flexural stress, MPa
0	24793 ±1372	509.0 ±38.0
0.7	30850 ±3729	542.4±48.8

*stacking sequence of $[0/90/45]_2$ and fibre impregnated with EP binder.

3.3. Resistance of carbon fibre reinforced MMA composites on nail penetration

Penetration force-depth curves for the carbon fibre reinforced MMA polymer composites are shown in Fig. 5. As can be seen, in the case of unfilled MMA polymer, the gradual increase of the penetration load is observed up to sharply downfalls at the moment that the nail penetrates into the composite sheet. As can be seen, in the case of MMA nanocomposites the force-penetration depth curves usually have several peaks until the penetration of the nail occurs. Therefore, in this case as penetration force is considered maximal value of the applied force. The repeating downfalls of the composite penetration force in the case of MMA nanocomposites may be attributed to the increase of composites brittleness.

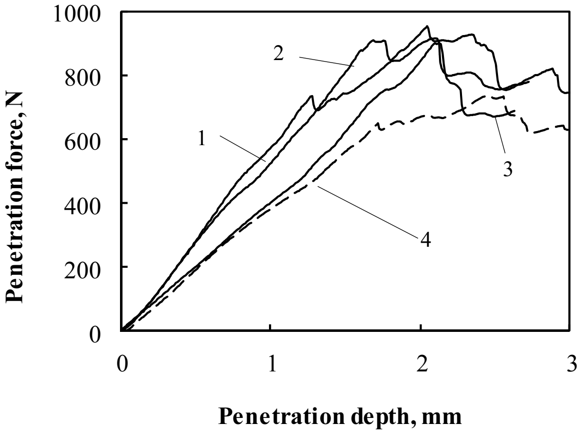

Fig. 5. Penetration curves for EP impregnated carbon fibre reinforced MMA composite of $[0/90/45]_2$ stacking sequences at different C10A nanoclay content, wt.%: 1 – 0, 2 – 1, 3 – 2, 4 – 3

From Table 3 it is evident that the nail penetration resistance of the carbon fibre reinforced MMA composites depends on the carbon fabric stacking sequence, but fibre impregnation with EP binder eliminates influence of fabric stacking sequence. Thus, for the nanofiller content influence investigations on the penetration resistance only composite with $[0/90/45]_2$ stacking sequences and EP impregnated carbon fiber was chosen.

As it can be seen from the Table 3, the penetration force of carbon fibre reinforced MMA nanocomposites increases (in 9 %) as C10A nanoclay content increase up to 2 wt.%. Similar improvement to penetration is observed in the case of nanoclay reinforced E-glass/vinyl ester matrix laminated composites [32]. However, further increase of C10A content decreases nail penetration resistance in 14 %.

Table 3. Nail penetration resistance of carbon fibre reinforced MMA polymer composites

Fibre type	Stacking sequence	C10A content, wt.%	Penetration force, N	Penetration depth, mm
Not impregnated	$[0/90]_3$	0	969 ±135	2.3 ±0.2
	$[0/90/45]_2$	0	753 ±124	1.6 ±0.3
EP binder	$[0/90]_3$	0	822 ±77	1.7 ±0.2
	$[0/90/45]_2$	0	835 ±67	2.1 ±0.2
		1	909 ±124	2.0 ±0.3
		2	903 ±112	2.3 ±0.2
		3	722 ±50	2.5 ±0.2

The CNT influence on the nail penetration resistance of EP impregnated carbon reinforced MMA nanocomposites is shown in the Fig. 6. As it can be seen, 0.7 wt.% of nanofiller decreases composites penetration resistance from 835 N to 800 N (about 3 %).

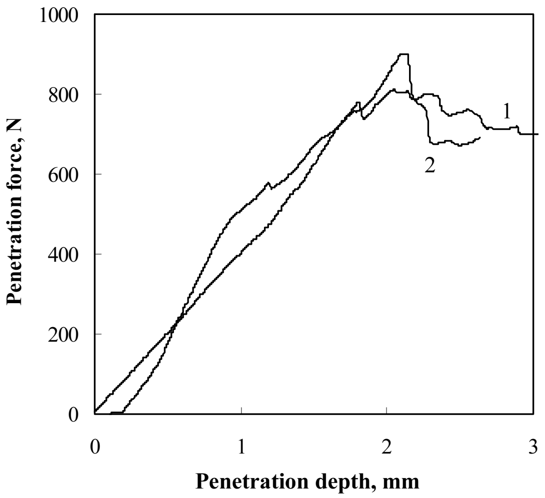

Fig. 6. Penetration curves for EP impregnated carbon fibre reinforced MMA unfilled (1) and 0.7 wt.% of CNT filled (2) composites (stacking sequences $[0/90/45]_2$)

Thus, as in the case of nanofillers influence on the epoxy and phenolic resin properties [13, 15, 17, 21], the incorporation of the nanoclay or carbon nanotubes in polymer matrix is available way to modify the strength properties of the fibre reinforced MMA composites.

4. CONCLUSIONS

The structure and properties of the carbon fibre reinforced non-toxic methyl methacrylate polymer composites were investigated. Epoxy binder increases fibre adhesion interaction with MMA resin, however, it does not influence on the strength properties of composite. However, the 6-ply carbon fibre reinforced MMA composites with stacking sequences of $[0/90]_3$ were found to show higher resistance to flexure and nail penetration.

Low content – 1 wt.% of organically modified nanoclay increases the flexural stress and modulus and nail penetration resistance of carbon fibre reinforced MMA composites. However, low content of carbon nanotubes only slightly improves the composite flexural properties, but decreases nail penetration resistance.

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