ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 2. 2015

Low-velocity Impact Behaviour of Carbon Fibre Reinforced Methyl Methacrylate Nanocomposites

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http://dx.doi.org/10.5755/j01.mm.21.2.7075

Received 10 May 2014; accepted 22 June 2014

In this study, the carbon fibre reinforced methyl methacrylate resin composite (CF/MMA) toecaps for safety shoes were manufactured to change impact behaviour by incorporation of nanofillers. Different types of nanofillers such as nanotubes (inorganic halloysite, multiwalled carbon nanotubes) and unmodified and organically modified nanoclays (natural bentonite and montmorillonites) were dispersed inMMA composition. The low-velocity impact test with drop-weight machine was performed with respect to the nanofiller nature and carbon fibre stacking sequence. It was found that the most influence on the stiffness and impact damage of the CF/MMA nanocomposite toecaps show organic and inorganic nanotubes or unmodified nanoclay (bentonite). Effective amounts of these nanofillers improve the low velocity impact response in 16 % – 20 %. Although the influence of nanofillerson CF/MMA composites energy absorption capability at impact energy level of 90 J is negligible, however, theireffect on thesizeof the composite toecaps damage areais considerable.

Keywords: carbon fibre methyl methacrylate composite toecap, nanofiller, drop-weight impact, energy absorption, impact damages.

1. INTRODUCTION

A common workplace injury and significant source of morbidity and disability are crush injuries to the foot. Therefore, it is recommend the use of safety shoes to help protect against these occupational hazards. Generally, for the foot and leg protection from crush injuries safety shoes have protective reinforcements. A protective toecap, installed in the front part of safety shoes, protects the toes against injuries, such as items that might fall down or similar things [1]. Usually, steel is still the most common material used for protective toecaps. Steel protective toecaps are extremely hard and difficult to damage, but heavy weight of such toecaps may increase the worker's fatigue [1, 2]. Moreover, steel toecaps are subjected to corrosion and are unsuitable for certain applications due to the electrical conductivity. The best way to overcome these drawbacks without sacrificing safety is to employ fibre reinforced polymer composite (FRPC) as toecaps material [2, 3]. FRPC have both high specific stiffness and strength; therefore, are widely used in lightweight structures subjected to the static and dynamic loads.

Different resins and fabric are used for the achievement necessary strength and safety of toecap for safety shoes [3 – 5]. The glass fibre reinforced ester based composites [3], epoxy prepregs [5] are often offered for the composite toecaps manufacturing. However, epoxy prepregs have relatively high production cost, shorts shelf life and a heat cure is necessary. While polyester resins generally have low adhesion properties, high moisture absorption capability, and are prone to water degradation.

Generally, FRPC toecaps show relatively poor absorbing energy behaviour primarily due to the brittle nature of the polymer matrix. Therefore, researchers have been looking for methods to improve impact properties of FRPC. In recent years, an extensive attention has been paid to the nanofillers as FRPC impact modifiers. There are a lot of investigations on the impact properties of fibre reinforced polymers based on nanoparticles filled epoxy [6, 7], or phenolic [8] resins. Many nanofillers such as nanoclays [9], halloysite [10] and carbon nanotubes (CNT) [6 – 8] are incorporated in to the polymer matrix in order to enhance composite resistance to the impact. Frequently high improvements of properties can be obtained even at small nanofiller loadings. Nevertheless, it is difficult to control the agglomeration or dispersion of nanofiller particles and interaction between filler and polymer matrix.

A few investigations of nanofillers influence on the properties of the thermoset methyl methacrylate resins were found, also. Generally, these resins are self-cure and have moderate strength [11]. Due to the biocompatibility, nontoxicity and non-carcinogenicity methyl methacrylate polymers (PMMA) have been used as biomaterials in dentistry and in orthopaedic surgery as bone cements for the stabilization of metallic femoral hip endoprotheses or for other orthopaedic devices [11, 12]. Influence of MWCNT functionality and loading on mechanical and thermal properties of PMMA/MWCNT bone cements was investigated in [13]. In this case, improvement in mechanical properties of nanocomposite was attributed to the MWCNTs arresting/retarding crack propagation through the cement by providing a bridging effect and hindering crack propagation. R. Gorga et al. [14] examined the influence of MWCNT on the mechanical properties of PMMA as a function of the nanotube length, concentration, and type. The largest tensile toughness improvements were obtained for PMMA/MWCNT composite at low content of MWCNT (lower 1 wt%), while no significant increases in

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the modulus was obtained due to the poor adhesion between PMMA and the nanofiller particles. Nanoclay particles incorporated in PMMA by melt blending improves overall thermal stability of composites [15]. However, there is a lack of adequate information to make a proper assessment of the resistance to impact and damages of methyl methacrylate composites used for orthopaedic devices manufacturing.

The main goal of this work is to understand the low-weight impact induced changes in carbon fibre reinforced methyl methacrylate resin composite for shoe toecaps. The influence of various types of nanofillers on the impact behaviour and damage of the methyl methacrylate base composite was evaluated.

2. EXPERIMENTAL

2.1. Materials

Methyl methacrylate resin (MMA), 617H21-Orthocryl Sealing Resin (Otto Bock), with molar mass of 100 g/mol, viscosity of 450 mPa·s (at 20 °C), and density of 1.02 g/cm^3 was used for investigations. Tertiary aromatic amine N,N-di(2-hydroxyethyl)-p-toluidine with benzoyl peroxide (BPO), Orthocryl Resin 617P37 (Otto Bock), was applied as initiation system in the free radical polymerization. The role of the amine is to carry out the reaction in a short period at room temperature; i. e. amine accelerates the free radical decomposition of BPO. BPO was incorporated in resin composition at weight ratio MMA : BPO = 100 : 1.

Nanofillers to be used for MMA resin modification was commercially available nanotubes and clay nanoparticles. Multiwalled carbon nanotubes (MWCNT) have been gotfrom Cheap Tubes.The manufacturer specified dimensions of MWCNT are: tube length (10 – 20) µm, inside diameter (5 – 10) nm, outer diameter (30 – 50) nm [16].

Natural aluminosilicate clay – halloysite (HNT) was obtained from Imerys Tableware Limited. The manufacturer specified dimensions are: tube length (1 – 15) µm, outer diameter (10 – 150) nm.

Organically modified montmorillonites (MMT) Cloisite 15A (C15A), Cloisite 30B (C30B) and natural bentonite Nanofil 116 (N116) were kindly provided by Souther Clay Products (Gonzales, TX). MMT clays C15A and C30B were surface-treated by ion exchange reaction between Na$^+$ existing in the gallery of the nanoclay and quaternary ammonium cations. The properties of MMT are presented in [16].

2.2. Sample preparation

Defined amount of chosen nanofiller was incorporated directly in MMA resin and homogenized by sonication (Ultrasonic cleaner 8891, Cole-Parmer) 5 min at $\omega = 20$ kHz. For uniaxial tensile test a dumbbell-shaped silicone rubber mould was used to produce MMA composites test pieces with dimension of 10 mm × 7.0 mm and thickness of (1.50 ±0.25) mm.

The toecaps specimens for impact tests were obtained by hand lay-up process of 204 g/m^2 surface density twill-weaved carbon fabric with MMA resin. The composite of 12-ply of carbon fibre with different stacking sequence configurations – $[0/90]_6$, $[0/90/+45/0/90/+45]_2$, $[90]_{12}$, and $[0]_{12}$ (where +45 and 90 are symbolic notation of different orientation angles of the plies) – were manufactured. For this purpose, hand lay-up layering was carried out on the toecap-shaped mould, made from 540 kg/m^3 density polyurethane foam. Before the layering, the mould was polished and sprayed with release agent. To reduce the void content in the composite and improve the quality of the finished part, MMA resin impregnated carbon fibre composites were fabricated by vacuum bagging at pressure of 0.05 MPa for 300 s. Toecap specimens were left to cure at an ambient temperature for 72 h before being removed from the mould.

2.3. Characterization

Tensile tests were carried out at room temperature using universal testing machine H25KT with load cell of 1 N (Tinius Olsen) and a cross-head speed of 20 mm min^{-1}. The six test pieces were tested for each set of samples.

The impact resistance of composite toecaps was determined according to the industrial standards and methods for foot and leg protectors by drop-weight impact tester (EL-99, Zipor-Pegasil). In impact test, the impactor of 3 mm nose radius with mass of 25 kg was dropped. Before impact, a modelling clay cylinder of height 25 mm was positioned inside the toecap directly under the point of impact as is shown in Fig. 1. After the impact, the minimum height of clay cylinder was measured with digital indicator ID-C1025B (Mitutoyo, USA).

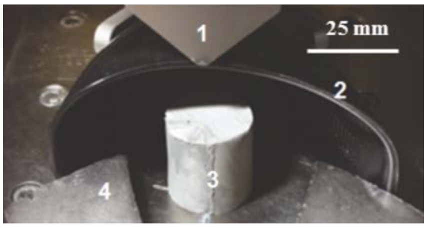


Fig. 1. Toecap testing module: nose of impactor (1), toe cap (2), modelling clay (3), holder (4)

Additionally, for the time histories of impact forces and absorbed impact energies recording during the low-velocity impact test, the resistive force exerted by the specimen on the impactor was measured by a load cell as a function of time. To characterize the impact resistance of composites software calculated important parameters drawn from basic force-time information were used.

The force $F(t)$ during the impact load depends on the drop-weight m and velocity v, while initial drop-weight falling velocity v_0 depends on the free fall acceleration g and downfall height H:

$$v_0 = \sqrt{2gH}\ . \tag{1}$$

Impactor speed v and displacement s as the time functions are determined by integrating the impact force:

$$v(t) = v_0 - \left(\frac{1}{m}\right)\int_0^t F(t)\, dt\ , \tag{2}$$

$$s(t) = \int_0^t \left(v_0 - \left(\frac{1}{m}\right)\int_0^t F(t)\, dt \right) dt\ . \tag{3}$$

After the impact, the impactor speed gradually decreases as the composite absorbs the energy. Absorbed impact energy of the impactor E_{imp} is equal to:

$$E_{imp} = \frac{1}{2} m \nu^2 . \quad (4)$$

The absorbed energy E_{ab} as the time function can be determined according to:

$$E_{ab}(t) = \frac{m \nu_0^2}{2} - \frac{1}{2} m \left(\nu_0 - \left(\frac{1}{m} \right) \int_0^t F(t)\, dt \right)^2 . \quad (5)$$

3. RESULTS AND DISCUSSION

3.1. Mechanical properties of MMA nanocomposites

Nanofillers application as structural reinforcements of polymer composites depends on the ability to transfer load from matrix to nanotubes or nanoparticles [17, 18]. Dependence of tensile properties of MMA nanocomposites upon nanofiller loading are presented in Fig. 2. As can be seen, the tensile properties changes depend on the nanofiller nature. The load transfer ability of MWCTN is negligible; therefore, adding 0.4 wt% of MWCTN results only in 16 % and 12 % improvements in the nanocomposite elastic modulus and tensile strength, respectively. It may be hypothesized that load transfer to MWCTN is limited because the nanotubes are slipping within the bundles [19]. On the other hand, HNTs markedly increase MMA resin elastic modulus (75 %), but their influence on the tensile strength is similar to that of MWCTN. It is known that nanoparticle/matrix interfacial adhesion does not noticeable affect the elastic modulus, but mainly depends on the nanofiller loading [19].

Study of MMT nature and content on the mechanical properties of MMA resin shows that unmodified N116 has significant higher influence on the polymer matrix stiffness and strength than that of organically modified MMT (Fig. 2, a, b). The increase of N116 loading up to 2 wt% results on the MMA compositestrength and Young's modulus increase (in 30 % and 60 %, respectively). Higher content of N116 decreases stiffness of nanocompositeup to unmodified MMA resin. Irrespectively, hydrophobic C15A or hydrophilic C30B nanofiller is used, MMA tensile strength decreases as nanofiller content increases. Notwithstanding, (1 – 2) wt% of C30B improves the elastic modulus of MMA resin markedly (in 30 % – 40 %).

As can be seen from Fig. 2, c, MWCNTs significantly increase deformability of MMA matrix, because large aspect ratio of carbon nanotubes would cause complex matrix filler interaction during nanotube bridging, breaking and pull-out. It probably promotes the local plastic deformation of matrix [21] and consequently greatly influences on the all MMA nanocomposite deformation ability. On the other hand, only a marginal increase in the deformability as a result of the HNT loading is observed. The deformation at break also increases N116 and C30B nanoparticles, while C15A decreases the deformability of nanocomposite in all loading cases. At higher investigated nanofillers content nanoparticles agglomeration can occur that acts as stress concentrator and reduces the strength and deformability of MMA nanocomposites.

3.2. Impact behaviour of CF/MMA composite toecaps

Preliminary investigations of the impact resistance of 12-ply unidirectional CF/MMA composites toecaps showed only fibre delamination and matrix crack at 40.7 J – 60 J impacts energy. However, splitting between fibres and matrix, fibre fracture and perforation were dominant modes around part of impact at markedly higher impact energy level. Thus, for investigations of the impact behaviour of CF/MMA composite toecaps impact energy level of 90 J was chosen.

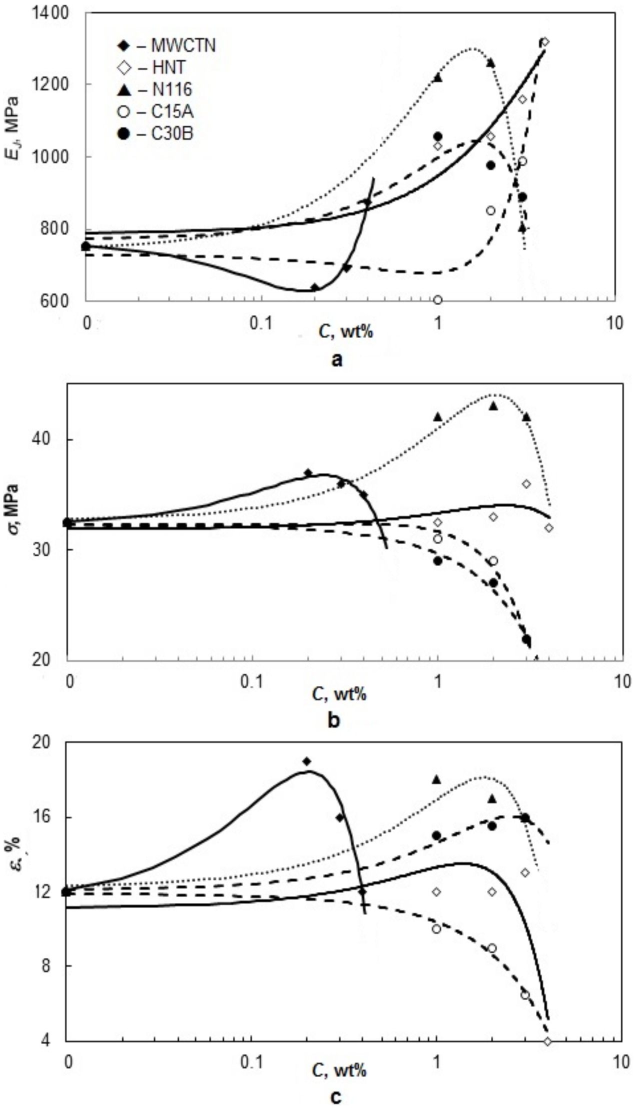


Fig. 2. Dependence of MMA nanocomposites Young's modulus (a), tensile strength (b) and deformation at break (c) upon content of various nanoparticles

In order to obtain optimum stacking sequence of composite toecaps, 90 J impact test was performed using specimens with four different fibres stacking sequence and stacking angle. The investigations showed thatthe impact resistance of 12-ply unidirectional CF/MMA composites with $[0]_{12}$ and $[90]_{12}$ orientations show 16 % – 22 % lower interior height than that of CF/MMA composites with stacking sequences of $[0/90]_6$ and $[0/90/+45/0/90/+45]_2$. Therefore, for further investigations $[0/90]_6$ stacking sequence was chosen.

The effective nanofillers loadings, at which maximal improvement in the mechanical properties of MMA nanocomposite was reached (see Fig. 2), were selected for determination of the nanofiller nature influence on the impact resistance of carbon fibre reinforced MMA composites. As can be seen from Fig. 3a, the interior height clearance after impact of the toecaps made from CF/MMA nanocomposites with 3 wt% of N116 and HNT increases in ~20 % and ~16 %, respectively, compared to the toecap from the composite without nanofiller. Such changes of the impact resistance might be attributed to the intrinsic matrix toughening provided by these nanofillers [23]. CF/MMA nanocomposite with 3 wt% of C30B shows the same impact resistance as was obtained in the case of unmodified one. On the other hand, the toecaps from CF/MMA/C15A nanocomposite havethe lowest interior height values. Due to C15A ability to increase MMA matrix stiffness, the interior height isin 11 % lower than that without filler.

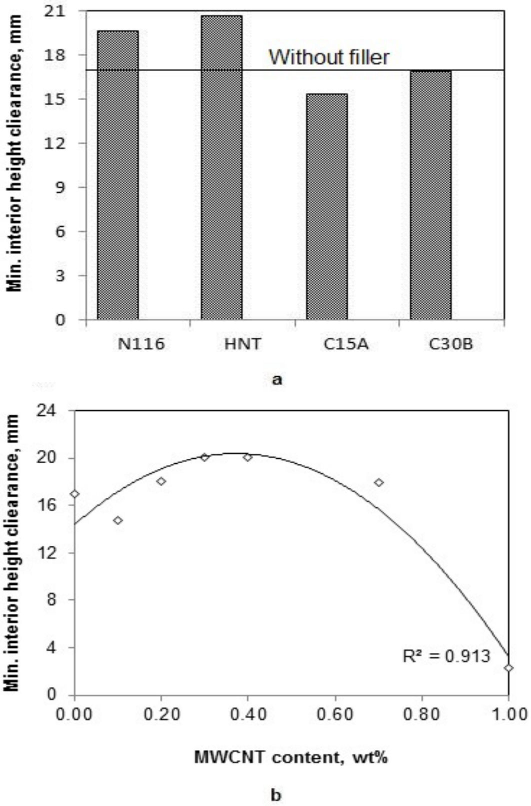


Fig. 3. Dependence of minimum interior height clearance of CF/MMA composite toecaps upon nanofiller nature: 3 wt% MMTs and HNT (a), MWCNT (b) (sequence $[0/90]_6$)

From Fig. 3, b, is evident that only low content (not higher than 0.4 wt%) of MWCNT improves impact properties of toecaps and minimum height clearance increases in 18 % (from 17 mm up to 20.1 mm). The carbon nanotubes discourage delamination and crack propagation in matrix through crack arrest, resulting in the reduction of the delamination area [8]. However, as the content of MWCNT increases up to 0.7 wt% the minimum interior height clearance of toecap after impact decreases more than 7.5 times (from 17 mm down to 2.2 mm). The decrease of impact resistance at higher nanofiller loading can be attributed to the MWCNT influence on the MMA resin curing.

The contact force-displacement curve of CF/MMA composite toecap is given in Fig. 4. The impact graph can be characterized by two impact force parameters – F_{max} and F_{crit} (Fig. 4). Impact on the composite produces the characteristic response of an initial rise in load until a first drop occurs at F_{crit}, which is defined as the critical force for delamination [23]. The delamination process is accompanied by reduction of the force increase ratedue to the decrease in the bending stiffness of the laminate, as a result of the internal delamination damage. Reloading phase of the specimen to the maximum point F_{max} may occur if enough residual potential energy is stored in the impactor [23].

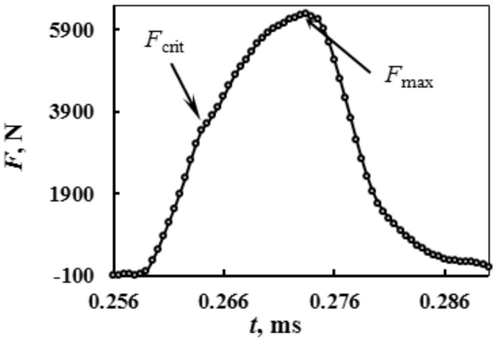


Fig. 4. Force-time curve of composite toecap at E_{imp} = 90 J

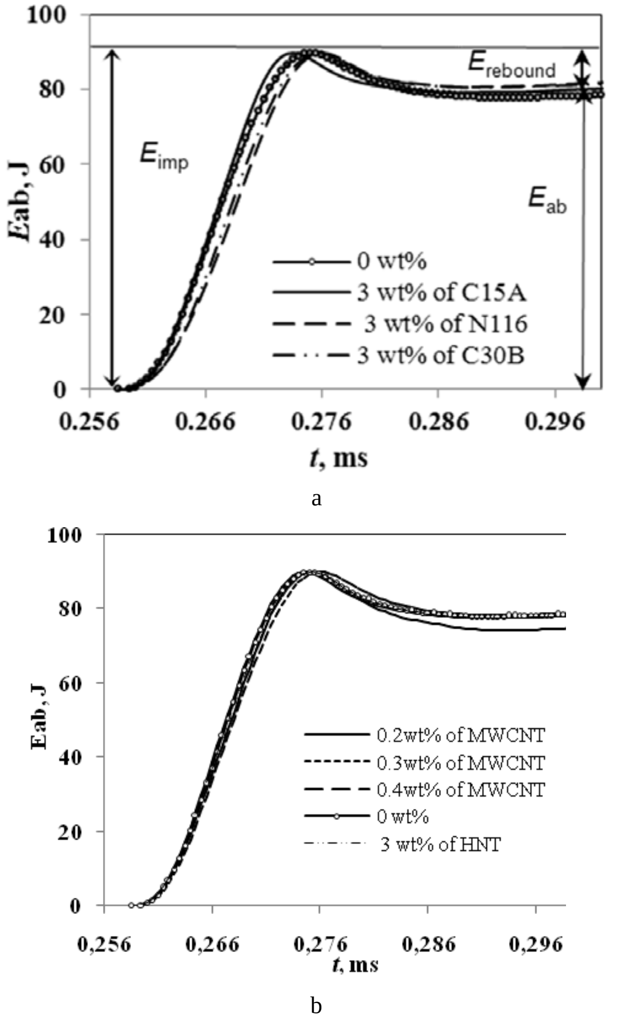
The averaged F_{crit} and F_{max} values for all impacted CF/MMA composite toecaps upon nanofiller nature are presented in the Table 1. From listed data it is clear that the toecaps manufactured from MMTs modified CF/MMA nanocomposites show 13 % – 20 % lower F_{crit} values, i. e. fibre delamination and matrix cracking in composite began earlierthan in the case of unmodified CF/MMA composite or CF/MMA/MWCNT and CF/MMA/HNT nanocomposites. Independently of nanotubes nature, the F_{crit} values of composites toecaps are close to that of unmodified CF/MMA composite.

Table 1. The impact parameters of various CF/MMA nanocomposite toecaps

Nanofiller type	Nanofiller content, wt%	Maximal forceF_{max}, N	Critical forceF_{crit}, N	Absorption energy E_{ab}, J
Without filler	0	6278	3420	81.78
MWCNT	0.2	6802	3556	78.61
	0.3	6764	3072	82.13
	0.4	6811	3567	81.63
HNT	3	6675	3402	81.80
C15A	3	6726	2868	83.35
C30B	3	6447	2784	83.79
N116	3	8035	2996	84.25

All nanofiller modified CF/MMA nanocomposites show F_{max} values higher than that of unmodified CF/MMA composite. It means that higher force is needed to initiate nanocomposite failure. Comparable evaluation of nanofiller influence shows that the highest increase in F_{max} value from 6278 N up to 8035 N (*ca*. 30 %) is observed in the case of 3 wt% of N116. It is related to the high MMA nanocomposite stiffness, because usually the lower stiffness of composites, the lower F_{max} values are obtained [14]. Higher in 10 % F_{max} values are also observed in the case of MWCNT. However, no direct relation between MWCNT content and $F_{\max}$ values was found (Table 1). On the other hand, although HNTs significantly increase MMA matrix stiffness, but their influence on $F_{\max}$ of CF/MMA composite is negligible.

During the impact when impactor do not penetrate the specimen, the total impact energy introduced to a composite (E_{imp}) is divided in two parts: elastic energy E_{el} and absorbed energy (E_{ab}). E_{ab} is the energy absorbed by the composite through the impactand E_{el} is the energy transferred to the impactor that bounced back from the composite [23].The influence of nanofiller loadings on the nanocomposite toecaps energy-time responses is presented in Fig. 5. In all investigated cases E_{el} was detected.



a

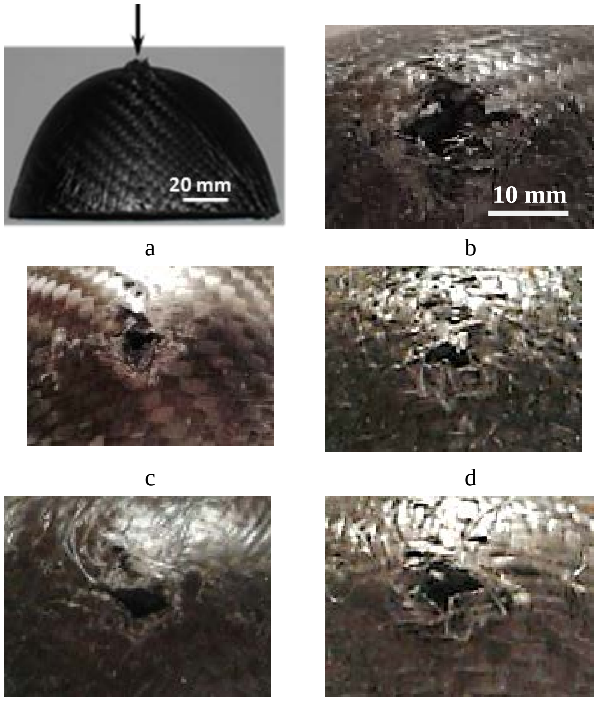
b

Fig. 5. The influence of nanofiller nature and content on the energy-time curves of CF/MMA composite toecaps at E_{imp} = 90 J: MMT (a), MWCNT and HNT (b)

Investigations show only marginal changes in CF/MMA composites energy absorption capability upon nanofiller nature. The analysis of energy absorption values of composite presented in Fig. 5 showed that the toecaps absorb approx. 90 % energy.The evaluation of data presented in Table 1 reveals that E_{ab} of CF/MMA/N116 nanocomposite toecaps is 3 % higher than that of unmodified composite. The influence of C30B and C15A nanofillers on the composites E_{ab} is even less – increase only in 1 % is observed.These results are in good correlation with the investigations of the toecaps interior height clearance after impact (Fig. 3, b).

The energy absorption capability of CF/MMA/MWCNT composite toecaps increases as nanotubes content increases. The highest E_{ab} is observed at 0.3 wt% of MWCNT as in the case of toecaps interior height clearance (Fig. 3, b). The energy absorption capability of HNT filled nanocomposite toecaps isin the same range as for unfilled CF/MMA.

Impact damage in fibre reinforced composites involves four major failure modes: matrix cracking, delamination, fibre breakage, and penetration of the impacted surface [24]. The images of CF/MMA/nanofiller composite toecaps after impact only for one fibre stacking subsequence $[0/90]_6$ are given in Fig. 6.



a b

c d

e f

Fig. 6. Damage of CF/MMA nanocomposite toecaps subjected to impact (a) upon nanofiller nature: without filler (b), 0.3 wt% of MWCNT (c), 3 wt% of N116 (d), 3 wt% of HNT (e), 3 wt% of C15A (f)

The visual analysis of CF/MMA/nanofiller composite toecaps after impact shows matrix cracking and fibre delamination at the contact place of impactor. The damage of CF/MMA nanocomposite toecapsoccursdue to the fibre breakage and pull-out at the front, where the tensile and compressive stress concentration is developed (Fig. 6, b – f). Approximately 10 mm – 15 mm diameters penetration areas in front of the toecaps can be seen. However, the damage areas of the CF/MMA/MWCNT, CF/MMA/HNT, and CF/MMA/N116 nanocomposites toecaps are less compare to that of CF/MMA composite. On the other hand, C15A almost do not influence on the penetration area decrease of nanocomposite toecaps (Fig. 6, f).

4. CONCLUSIONS

Toecaps for protective shoes were manufactured from carbon fibrereinforced polymer composites using methyl methacrylate (MMA)resin by liquid resin impregnation and vacuum bagging techniques. Before fibre impregnation, methyl methacrylate resin was modified with various organic and inorganic nanofillers that change polymer stiffness and strength properties.

The stiffness and strength of the natural bentonite (N116) modified MMA were found to be higher than in the case of other nanofillers. Halloysite (HNT) also markedly increases resin stiffness, while multiwalled carbon nanotubes (MWCNT) considerably influence on MMA resin deformability due to the nanotubes ability to promote plastic deformation during loading.

Low-velocity impact testof toecaps obtained from carbon fibre reinforced MMA resin modified with various nanofillers composites by 25 kg impactor was conducted. Various loadings of MWCNT, N116 or HNT nanofillers improve the low velocity impact response by 16 % – 20 %.The results based on load-time and energy-time histories and damages inspection allow identify various fracture and damage modes of carbon fibre reinforced composite toecaps, such as fibre breakage, matrix cracking, and delamination of impacted surface. Although nanofiller influence on CF/MMA composites energy absorption capability at impact energy level of 90 J is negligible, MWCNT, N116 or HNT limit the damage size of composite toecaps.

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