Synthesis and Mechanical Properties of Polyurea-Based Hybrid Composites for Ballistic Individual Protection

RAZVAN PETRE[1], TEODORA ZECHERU[1], NICOLETA PETREA[1], RALUCA GINGHINA[1], SIMONA SANDU[1], MIHAELA MURESAN[1], LIVIU CRISTIAN MATACHE[1]*, ALIN CONSTANTIN SAVA[2], FLORENTINA NEATU[3]

[1]Scientific Research Center for CBRN Defense and Ecology, 225 Oltenitei Road, 041309, Bucharest, Romania

[2]Military Technical Academy Ferdinand I, 39-49 George Cosbuc Av., 050141, Bucharest, Romania

[3]National Institute of Material Physics, 077125, Magurele, Romania

During conûict situations, the combat staff is exposed to a wide variety of aggressions, such as temperature and pressure variations and dynamic impacts (from ammunition or fragments). Textiles used in the manufacture of the military uniforms and devices have always played an important role in defending the military against these hazards, and an adequate level of individual protection equipment is required. In this respect, novel fibre-reinforced polymer composite materials for military application, such as reducing blunt trauma for ballistic protection equipment, have been studied in terms of thermal and mechanical properties and ballistic protection, obtaining very good results.

Keywords: impact evaluation; mechanical testing; ballistic plate

During conflict situations, the combat staff is exposed to a wide variety of aggressions, such as temperature and pressure variations, and dynamic impacts (from ammunition or fragments). Textiles used in the manufacture of the military uniforms and devices have always played an important role in defending the military against these hazards, and an adequate level of individual protection equipment (IPE) is required [1,5].

The protective clothing can be divided in air permeable (widely used for military purposes) or air impermeable (when a polymer-based membrane or film is employed as a ûlter to prevent toxic chemicals to penetrate) [2,3], such as polyesters, polyether amides or polyurethanes [2,4].

In this respect, the present study aimed at the possibility of using some novel composites of polymers and fibre-reinforced polymer composite materials for military application: reducing blunt trauma for ballistic protection equipment. The polymer matrix is polyurea and the considered fibres are functionalized multi-wall carbon nanotubes (MWCNTs). The reinforcement of a polymeric matrix with high strength and modulus fibres using the viscoelastic displacement of the matrix under stress transfers the load to the fibre; this resulting in a high strength and a high modulus composite material [4-12].

Polyurea is a flexible aminoplast, with highly valued properties in terms of softness and flexibility, which, due to its effective energy absorption properties, is commonly used as protective coating on concrete or steel structures. Polyurea coatings combine strength with extensibility; the material being highly resistant, with low flammability and known to mitigate abrasive wear, blast and fragmentation [13-25]. From the typical application as a protective coating of concrete and steel structures, this elastomeric coating has been proven to withstand not only abrasion, but also rapid loadings like impacts, collisions or explosions [13-23].

The aim of the composite is to produce a two-phase material in which the primary phase, that determines the stiffness, is fibre-shaped and is well dispersed and bonded and protected by a secondary phase, the polymeric matrix. The fibre-reinforced polymer composite materials mechanical and physical properties are clearly determined by their constituent properties and by the micro-structural configuration. While the fibres are mainly responsible for strength and stiffness, the polymeric matrix contributes to stress transfer and provides microclimate protection.

Experimental part

Materials and methods

Polyurea (PU) and four types of polyurea-based composite materials (PUCs) have been obtained (figure 1) from components illustrated in table 1.

In the view of obtaining various concentrations of MWCNT–OH in the polyurea matrix, a 10% MWCNT-OH masterbatch has been first obtained. The MWCNT-OH has been obtained accordingly to [26] with over 95% purity and 1.65wt% OH from MWCNT supplied from Sigma-Aldrich.

The two components have been prepared, heated and mixed separately in two different recipients of the installation, dosed and heated at 60-65°C. Further on, the MWCNT-OH has been added and mixed and the polymer obtained has been pulverized in 50 μm-droplets on various layers, in different thicknesses.

In order to test the performances of the polymer materials obtained, various thicknesses of the layers have been sprayed on the support materials.

The reagents have been applied by direct continuous-layer spraying through a pressurised container at 150 bar and 65°C. Prior application, the metallic and textile support materials have been cleaned from any impurities (greases, debris, etc.) and dried. The pulverization has been performed perpendicularly on the support from 50-100 cm distance in average thickness of 0.55, 1.20, 1.75 and 2.30 mm. The materials used as support layers have been Kevlar® (prepreg) and ballistic plates.

In figure 2 are illustrated the steps pursued for the support materials (standard ballistic plates) obtainment, by simple operations and equipment.

Mechanical stress analysis

Strain, stress and Young modulus of PUC materials have been determined on an Instrom 3382 universal tensile equipment.

* email: mliviucris@yahoo.com

Composite material	Polyurea prepolymer (wt%), EUROPOL®	Polyamines (wt%), EUROPOL®	MWCNT–OH Reinforcing agent (wt%)
PU	50	50	-
PUC1	49.40	49.40	1.20
PUC2	49.50	49.50	1.00
PUC3	49.625	49.625	0.75
PUC4	49.70	49.70	0.60

Table 1
RATIOS OF THE COMPONENTS IN THE POLYMER AND POLYMER COMPOSITE MATERIALS

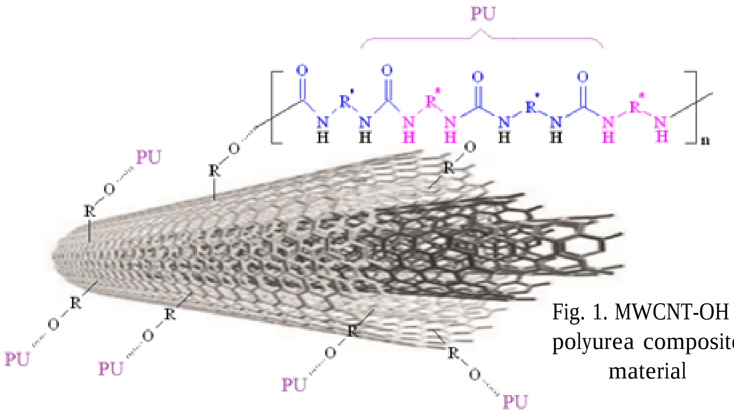

Fig. 1. MWCNT-OH - polyurea composite material


Fig. 2. Stages of the protection layers fabrication. Pulverization of PUC on support layers

Dynamic mechanical analysis

Dynamic mechanical analyses (DMA) have been performed on a TRITEC 2000 B instrument at 1 Hz frequency. The DMA data were collected from -100°C to +190°C.

Determination of ballistic protection parameters

The compositions have been characterized for their ballistic protection performances. Determination of the ballistic protection against armour piercing bullets has been performed in agreement with [27], a US standard used as reference by an important amount of countries from Europe, America and Asia.

Determinations have been performed on standard 400x400x13 mm ballistic protection plates made of Kevlar® and ceramic layers (2.98 kg) and on the same type of ballistic protection plates above which a layer of PUC has been pulverized. The latter plates obtained weighed at most 3.20 kg.

The testing equipment has been positioned in the support at a certain distance versus Magnum .44 gun barrel. The velocity measurement system, an Oehler chronograph (with a 99.7% precision), has been positioned starting from 2 m away from the gun barrel, so that the frame system, put every 0.5 m, to be perpendicular on the shooting direction.

The experimental testing program consisted in the ballistic resistance (armour piercing resistance) determination against .44 cal. Magnum bullets in standard conditions. Perforation assessment has been made visually, when it has been observed whether a hole with diameter at least equal to the ammunition calibre exists or the bullet has passed entirely through the material. Further, 7.62x51 cal. armour piercing bullets have been shot in IV level ballistic plates in four points [27], in order to assess the multi-hit ballistic impact.

Results and discussions

New materials for protection garment are under continuous research, and a dynamic impact assessment of the materials is also mandatory to be performed, due to the fact that the first-responders confront various hazards, such as suicide bombers or chemical warfare agents. Taken into account the expansion of MWCNT use in various fields, the main idea has been to assess its potential in the ballistic protection field.

Influence of carbon nanotubes concentration versus composites mechanical parameters

For each composite, five determinations have been performed (fig. 3), their average values being given in table 2.

Material	Tensile stress al maximum load (MPa)	Tensile strain at maximum load (%)	Young's modulus (MPa)
PU	7.53	145.61	70.90
PUC1	8.64	156.50	30.30
PUC2	8.63	150.05	30.55
PUC3	8.23	150.26	30.32
PUC4	8.41	143.71	30.39

Table 2
PUCs MECHANICAL PROPERTIES

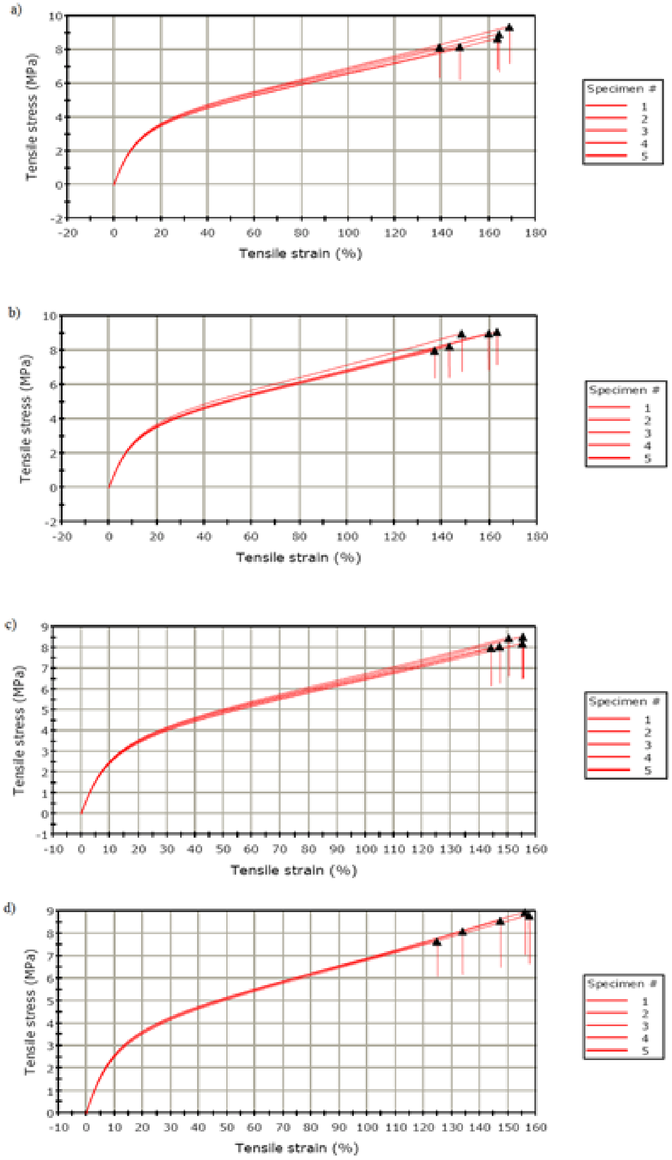

Fig. 3. Tensile strain vs. stress for PUCs: a) PUC1; b) PUC2; c) PUC3; d) PUC4.

In the case of the non-reinforced PU, at the beginning the material appeared stiff, with a quasistatic elastic modulus of 70.90 MPa. During deformation, however, the material has shown less resistance to further straining, indicating certain damaging effects and/or plastic flow. The tensile stress of the MWCNT-OH-based nanocomposites is above that of PU. This is in good agreement with the literature data [18], which indicate that an intrinsic self-reinforcing process, due to its morphology, takes place in the case of PU.

The reaction between the isocyanate and the hydroxyl groups (R-OH) correspondent to functionalized MWCNT conducts to a strong bond (through the intermediary of a polyurethane-type chemical bond) between the reinforcing agent and the polymer matrix, which contributes to the improvement of composite mechanical properties.

Dynamic-mechanical analyses

In figure 4 are given the results obtained from DMA. The recorded graphs emphasized the elastomeric character of the MWCNT-OH-reinforced composites. Measurements of transitions determinations due to molecular movements and free volume changes have been performed in order to evaluate the PUCs behaviour at various temperatures.

Viscoelastic behaviour, material response against effort versus temperature and/or strain frequency have been evaluated, and from the graphs analysis it has been established that the glass transition temperature is between -10 and -5 °C.

Ballistic protection behaviour

Many materials behave differently under static loads or dynamic loading conditions, which imply high strain rates, such as ammunition impact. Under dynamic conditions, steel and ceramics experience strain rates that turn their response from ductile to brittle. This results in a growing need for protection improvement against such dynamic impact.

The best results have been obtained for the 2.3 mm-layer of PUC3, both in terms of protection and costs, the ballistic tests being focused on this materials' thickness. The results obtained are shown in figure 5, figure 6 and table 3.

The analysis of the results obtained concluded that the ballistic protection plates layered by PUC3 have not been penetrated, offering a III A protection level against .44 Magnum Semi Jacketed Hollow Point (SJHP) ammunition, with a 15.6 g-specified mass at a velocity ~430 m/s, in agreement with [27], while the standard ballistic plate is perforated when submitted to single hit.

Furthermore, when submitted to multi-hit, and shooting 7.62 x 51 cal. armour piercing bullets, with an average

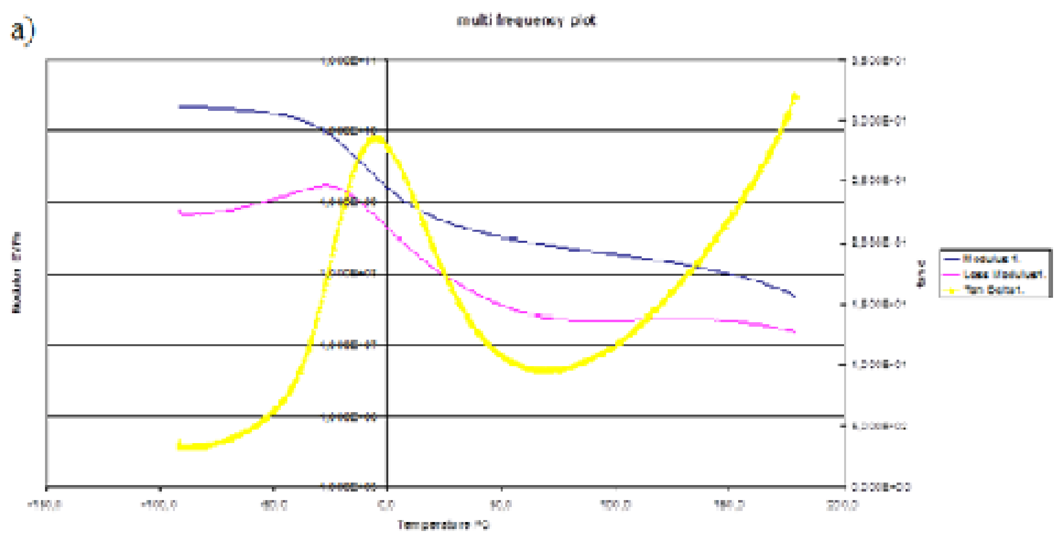

Fig. 4. DMA results for PUCs: a) PUC1

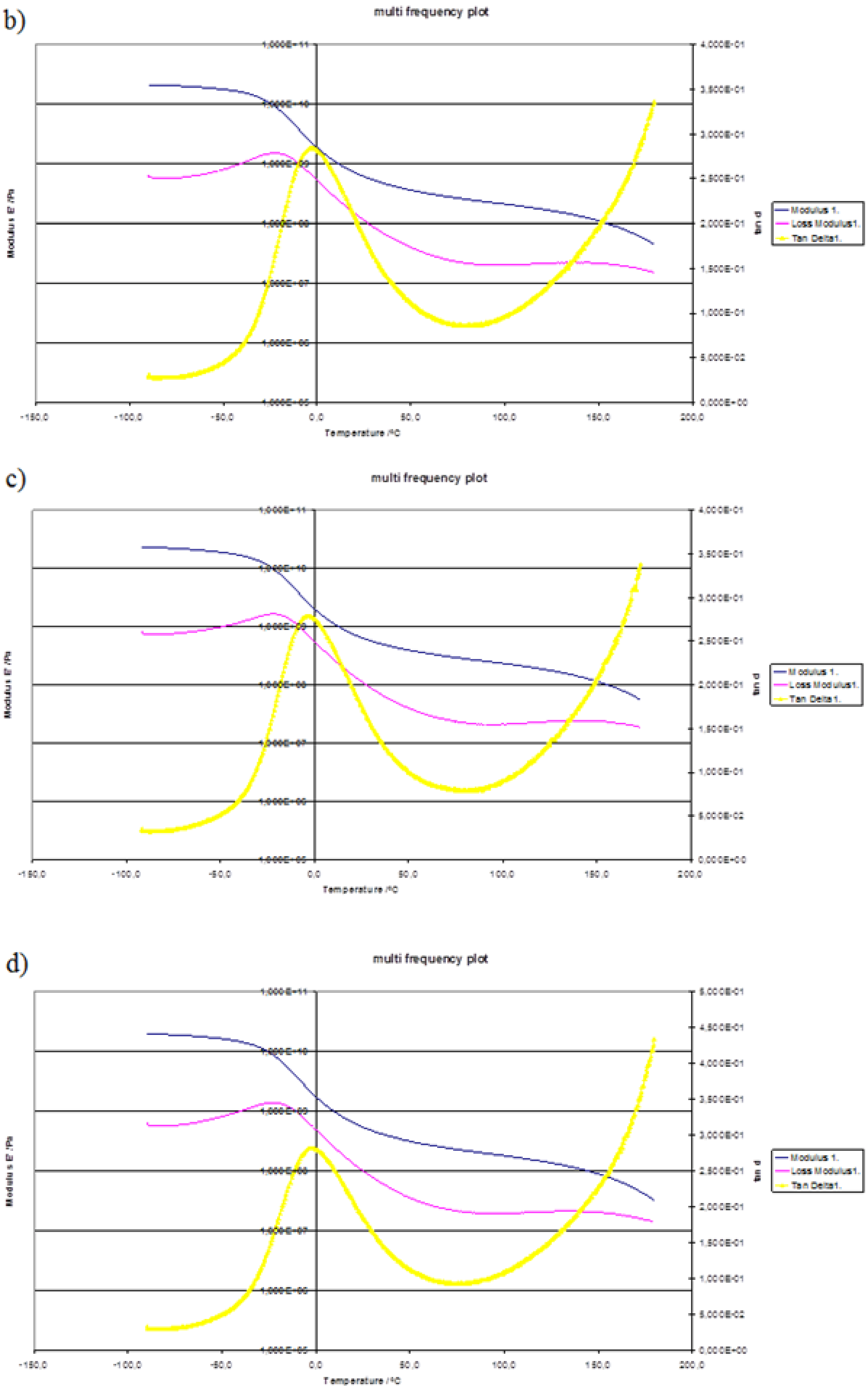

Fig. 4. DMA results for PUCs: b) PUC2; c) PUC3; d) PUC4.

Table 3
COMPARATIVE DATA ON THE RESULTS OBTAINED FOR STANDARD BALLISTIC PLATES AND PUC-LAYERED

No.	Ballistic plate	Ammunition	Distance (m)	Average velocity (m/s)	Results obtained
1	standard	.44 SJHP Magnum	5	430	perforation
2	PUC1-0.55 layered	.44 SJHP Magnum	5	430	perforation
3	PUC1-1.20 layered	.44 SJHP Magnum	5	431	perforation
4	PUC1-1.75 layered	.44 SJHP Magnum	5	430	perforation
5	PUC1-2.30 layered	.44 SJHP Magnum	5	429	slight perforation
6	PUC2-0.55 layered	.44 SJHP Magnum	5	430	perforation
7	PUC2-1.20 layered	.44 SJHP Magnum	5	431	perforation
8	PUC2-1.75 layered	.44 SJHP Magnum	5	430	perforation
9	PUC2-2.30 layered	.44 SJHP Magnum	5	430	slight perforation
10	PUC3-0.55 layered	.44 SJHP Magnum	5	430	perforation
11	PUC3-1.20 layered	.44 SJHP Magnum	5	431	perforation
12	PUC3-1.75 layered	.44 SJHP Magnum	5	430	slight perforation
13	PUC3-2.30 layered	.44 SJHP Magnum	5	430	no penetration
14	PUC4-0.55 layered	.44 SJHP Magnum	5	430	perforation
15	PUC4-1.20 layered	.44 SJHP Magnum	5	431	slight perforation
16	PUC4-1.75 layered	.44 SJHP Magnum	5	429	no penetration
17	PUC4-2.30 layered	.44 SJHP Magnum	5	430	no penetration

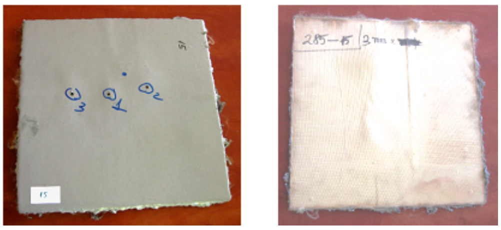

Fig. 5. Ballistic protection plate - exposed side and reverse side after shooting

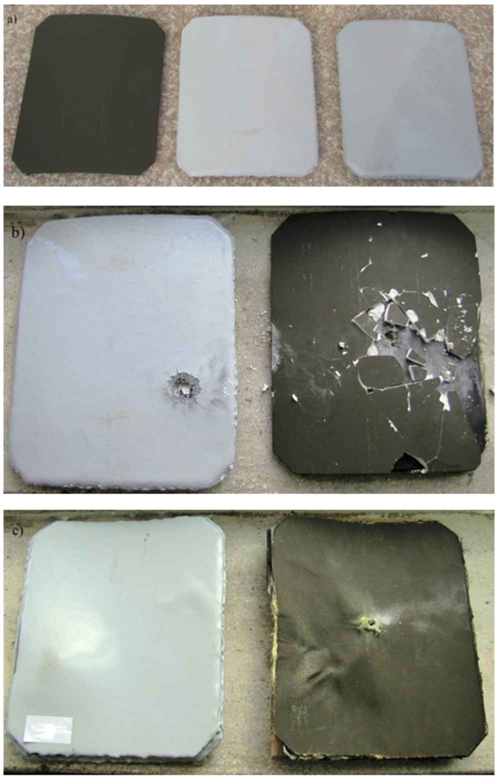

Fig. 6. a) Prior shooting: standard ballistic plate; 1.2 mm-layered PUC3-standard ballistic plate; 2.3-layered PUC3-standard ballistic plate; b) exposed side after the shot; c) reverse side after the shot

velocity of 875 m/s and 10.8 g specified mass, against a IV level ballistic plate enriched with a 2.3-layer of PUC3, after the first two shots, the plate has not been penetrated, while only the third bullet partially penetrated only the ceramic of the ballistic plate, with a minimal backface signature recorded, and the fourth perforated the ballistic plate, creating a major blunt trauma. This might be also due to microfractures occurred in the material during the previous two shots (fig. 7).

Conclusions

Natural or man-made hazards have always represented a threat to humans. Typical hazards include chemicals, collisions and terrorist attacks. Since unconventional threats appear all the time, the interest of this study has been to examine new structures of composite materials that protect better the first responders against dynamic loads.

The evaluation of MWCNT-OH-based polyurea composites has shown that inserting a 2.3 mm-layer of this material dramatically improves the ballistic properties of the protection plates.

Next to the physical, chemical and mechanical properties, the cost versus the benefits, other performances, such as: an excellent and smooth adherence to the support materials and a short drying time (< 5 min.), conduct to the conclusion that PUCs may be successfully used for the fabrication of IPEs.

Acknowledgements: The authors thank Professor Hubca and coworkers from University Politehnica of Bucharest for the analyses performed. This work has been supported by a grant of the Romanian National Authority for Scientific Research, project number PN-III-P1-1.2-PCCDI-2017-0871.

Fig. 7. Evaluation of 2.3-layered PUC3- IV level ballistic plate shot proof

References

1.BICES COE CIED PORTAL, Chemical IEDs Current status and Trend Threat, 2016.
2.MAGALHÃES, M.J., DE MAGALHÃES, S.T., REVETT, K., JAHANKHANI, H., Cham International Conference on Global Security, Safety, and Sustainability, 2016. p. 331-341.
3.BREWER, S.A., Recent Pat. Mater. Sci., **4**, no. 1, 2011, p. 1-14.
4.ZHANG, M., ZHAI, Z., LI, M., CHENG, T., WANG, C., JIANG, D., CHEN, L., WU, Z., GUO, Z., J. Compos. Mater., **50**, no. 24, 2015, p. 3363-3372.
5.CHEN, Y., ZHANG, B., GAO, Z., CHEN, C., ZHAO, S., QIN, Y., Carbon, **82(C)**, 2015, p. 470-478.
6.LU, S.W., FENG, C.L., NIE, P., MA, K.M., J. Aeronaut. Mater., **35**, no. 2, 2015, p. 12-20.
7.KAYMAKCI, A., AYRILMIS, N., GULEC, T., TUFAN, M., J. Compos. Mater., **51**, no. 9, 2016, p. 1187-1195.
8.MAPKAR, J.A., IYER, G., COLEMAN, M.R., Appl. Surf. Sci., **255**, 2009, p. 4806-4813.
9.PENG, C., ZHANG, S., JEWELL, D., CHEN, G.Z., Progr. Nat. Sci., **18**, 2008, p. 777-788.
10.LI, J., VERGNE, M.J., MOWLES, E.D., ZHONG, W.H., HERCULES, D.M., LUKEHART, C.M., Carbon, **43**, no. 14, 2005, p. 2883-2893.
11.DAVIDSON, J.S., PORTER, J.R., DINAN, R.J., HAMMONS, M.I., CONNELL, J.D., J. Perform. Cstr. Facil., **18**, no. 2, 2004, p. 100-106.
12.PITCHAN, M.K., BHOWMIK, S., BALACHANDRAN, M., ABRAHAM, M., Composites Part A: Appl. Sci. Manufact., **90**, 2016, p. 147-160.
13.FATT HOO, M.S., QUYANG, X., DINAN, R.J., Proceedings of the 8th International Conference on Structures Under Shock and Impact, WIT Press, Crete, Greece, 2004, p. 129-138.
14.PORTER, J.R., DINAN, R.J., HAMMONS, M.I., KNOX, K.J., The AMPTIAC Quarterly 6, 2002. p. 47-52.
15.MEYERS, M.A., Dynamic Behaviour of Materials, John Wiley & Sons, Hoboken, NJ, USA, 1994.
16.BORVIK, T., LANGSETH, M., HOPPERSTAD, O.S., MALO, K.A., Int. J. Impact Engineering, **22**, no. 9-10, 1999, p. 855-886.
17.BORVIK, T., HOPPERSTAD, O.S., BERSTAD, T., LANGSETH, M., Int. J. Impact Engineering, **27,** no. 1, 2001, p. 37-64.
18.REPPEL, T., DALLY, T., WEINBERG, K., Technische Mechanik, **33**, no. 1, 2013, p. 19-33.
19.CHEN, C.C., LINZELL, D.G., J. Computer Engineering, 2014, 416049.
20.CRAWFORD, J.E., SHENGRUI, L., Enhancing Building Security Seminar, Singapore, 2005.
21.BILLAUDEAU, E., Materials, 2010.
22.CAI, D., SONG, M., Compos. Sci. Technol., **103**, 2014, p. 44-48.
23.CASALINI, R., BOGOSLOVOV, R., QADRI, S.B., ROLAND, C.M., Polymer, **53**, 2012, p. 1282-1287.
24.TOADER, G., RUSEN, E., TEODORESCU, M., DIACON, A., STANESCU, P.-O., ROTARIU, T., ROTARIU, A., J. Appl. Polym. Sci., **133**, no. 38, 2016, APP43967.
25.TOADER, G., ROTARIU, T., RUSEN, E., TARTIERE, J., EANU, S., ZECHERU, T., STANCU, I.-C., SERAFIM, A., PULPEA, B., Mat. Plast., **54**, no. 1, 2017, 22-28.
26.VULCAN, M.A., DAMIAN, C., STANESCU, P.-O., VASILE, E., PETRE, R., HUBCA, G., Mat. Plast., **54**, no. 1, 2017, p. 41-44.
27.***NIJ STANDARD 0101.06, Ballistic resistance of body armour, 2008.

Manuscript received: 01.08.2018