ENHANCED MECHANICAL PROPERTIES OF POLYMER-MATRIX NANOCOMPOSITES REINFORCED BY GRAPHENE INCLUSIONS: A REVIEW

I.A. Ovid'ko[1,2,3]

[1]Department of Mathematics and Mechanics, St. Petersburg State University, St. Petersburg 198504, Russia
[2]Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61,
Vasilievskii Ostrov, St. Petersburg 199178, Russia
[3] St. Petersburg State Polytechnical University, St. Petersburg 195251, Russia

Abstract. This paper presents a short overview of recent research efforts addressing the mechanical properties of polymer-matrix nanocomposites containing graphene inclusions. A particular attention is devoted to experimental data giving evidence for enhancement of tensile strength, Young modulus and fracture toughness due to the effects of graphene inclusions in such film and bulk nanocomposites. Key factors are discussed which influence the role of graphene nanosheets and flakes in enhancement of the mechanical characteristics of graphene-polymer nanocomposites. Also, conclusions are outlined which are based on research of graphene-polymer nanocomposites with excellent mechanical properties.

This paper is written in honour of Professor Boris Ginzburg on the occasion of his 75th birthday.

1. INTRODUCTION

Graphene - a single carbon atomic sheet with hexagonal sp^2 covalently bonded crystal structure – represents a new 2D material whose outstanding mechanical, transport and thermal properties are of utmost interest from both fundamental and applied viewpoints; see, e.g., reviews [1-7]. For instance, following the experimental data [8], pristine graphene membranes are characterized by the superior strength of $\approx$ 130 GPa and Young modulus of $\approx$ 1 TPa. With these remarkable mechanical properties, graphene inclusions have a great potential to be exploited as strengthening structural elements of composites. In particular, in recent years, several research groups have fabricated polymer-matrix nanocomposites reinforced by graphene inclusions; for a review, see [9]. Such nanocomposites typically show enhanced mechanical characteristics compared to both their counterparts free from graphene and polymer-matrix nanocomposites reinforced by non-graphene inclusions.

Although studies of mechanical properties exhibited by graphene-reinforced nanocomposites are in their infancy, one can distinguish key trends in this area. In 2010, Kuilla with coworkers published a review article [9] devoted to fabrication methods for graphene-polymer nanocoposites as well as their mechanical, thermal and electrical properties. Since 2010, however, several important results on mechanical characteristics of such nanocomposites have been published, and these results have pushed the field ahead. The main aim of this paper is to give a brief overview of very recent research efforts (that have been not reflected in Ref. [9]) addressing the unique mechanical properties of polymer-matrix nanocomposites reinforced by graphene fillers.

Corresponding author: I.A. Ovid'ko, email: ovidko@nano.ipme.ru

In general, the idea to enhance mechanical characteristics of polymer materials through insertion of high-strength carbon nanoparticles is rather conventional in science and technology of polymers; see, e.g., reviews [10-14]. For instance, in recent years, this concept has been effectively exploited by Ginzburg with co-workers in enhancing mechanical and tribological properties of various polymer systems by incorporating fullerenes and other carbon nanoinclusions [15-20]. Although these and other results in the considered area are impressive [10-20], the development of strong, durable and cost-efficient polymer-matrix composite materials for current and future technologies is still an unsolved problem. In this context, search for novel materials as reinforcing fillers in polymer-matrix composites is of crucial significance. Graphene with its excellent mechanical properties serves as a good candidate for these aims. In parallel with superior strength and Young modulus, graphene inclusions have specific geometry (first of all, very large aspect and surface-to-volume ratios) and, after certain chemical modifications, specific interaction with matrix [9,21-25]. All these factors are responsible for the specific effects of graphene nanosheets on strength, Young modulus, fracture toughness and elastic properties of polymer-graphene nanocomposites. The specific effects differentiate the role of graphene inclusions as reinforcing structural elements from that of fullerenes, carbon nanotubes and other carbon nanoinclusions. More than that, with these effects, graphene inclusions can be treated as the most effective fillers in enhancing the mechanical characteristics of polymer-matrix composites [9]. The specific effects in question will be illustrated below in several scientifically and technologically important examples of graphene-reinforced polymer nanocomposites, based on publications appeared in this area in 2010-2012. In doing so, we do not pretend on exhaustive presentation of all results in the discussed field. Nevertheless, the main trends and results published in recent years will be reflected in our short review.

2. GENERAL ASPECTS

In general, there are several key factors crucially influencing the role of nanoparticles as reinforcing fillers in polymer-matrix nanocomposites. In short, the factors/conditions allowing one to effectively improve both the strength and elastic properties of host polymers are as follows [9,21-25]:

(i) Reinforcing inclusions should have high mechanical characteristics such as strength and Young modulus.

(ii) Geometry of reinforcing inclusions should be characterized by high aspect ratio and high surface area.

(iii) Reinforcing inclusions should be homogeneously dispersed, and their agglomeration should be prevented.

(iv) Strong binding between inclusions and polymer matrix should exist.

In addition, from a practical viewpoint, fabrication of polymer-matrix nanocomposites is desired to be a cost-efficient procedure.

It is a formidable challenge to simultaneously meet the conditions (i)-(iv), in parallel with cost efficiency. Therefore, fabrication of nanocomposites with enhanced mechanical characteristics represents the subject of intense research efforts in nanoscience and nanotechnology.

Graphene with its superior values of strength $\approx$ 130 GPa [8] and Young modulus $Y \approx$ 1 TPa [8] serves as a very promising reinforcing material for polymer-matrix nanocomposites. First of all, production of graphene (at cost of $\approx$ 5 EUR/kg [25]) is cheap compared to that of carbon nanotubes having similar mechanical characteristics. Besides, 2D geometry of graphene nanosheets is responsible for maximum value of its surface-to-volume ratio and can provide very high aspect ratios. These high geometric parameters are favorable for enhancement of mechanical properties of graphene-reinforced nanocomposites. The conditions (iii) and (iv) can be fulfilled by several technological methods reviewed by Kuilla with coworkers [9]. In particular, although pristine graphene nanosheets tend to agglomerate, their oxidation and/or chemical functionalization effectively provide both homogeneous dispersion of graphene inclusions and strong binding between such inclusions and polymer matrix [9].

Thus, use of graphene inclusions in fabrication of polymer-matrix nanocomposites is typically cost-efficient, and the condition (i) is almost automatically valid for graphene exhibiting excellent mechanical properties. In these circumstances, the conditions/factors (ii)-(iv) are crucial for development of graphene-polymer nanocomposites with enhanced mechanical characteristics. In next section, we will discuss recent examples of such nanocomposites with special attention being devoted to sensitivity of their mechanical properties to the conditions/factors (ii)-(iv).

3. GRAPHENE-POLYMER NANOCOMPOSITES WITH ENHANCED MECHANICAL CHARACTERISTICS

Polymer-matrix nanocomposites with graphene flakes (consisting of several atomic layers) have been fabricated, and their mechanical properties have been examined in the experiment [25]. The key focuses of this research were placed on geometric aspects - the factor (ii) - of the reinforcement effect caused by graphene inclusions in nanocomposites with polyvinylalcohol (PVA) matrix. More precisely, May with co-workers have produced nanocomposites of two types: the namely nanocomposites containing "short" and "long" graphene flakes characterized by two typical aspect ratios ≈ 1000 and ≈ 2000, respectively [25]. In doing so, the mean dimensions of "short" flakes were as follows: length ≈ 1.1 μm, width ≈ 0.56 μm, and thickness ≈ 1 nm. "Long" graphene flakes dispersed in PVA-graphene nanocomposites had the following mean dimensions: length ≈ 2.3 μm, width ≈ 1.3 μm, and thickness ≈ 1.2 nm. May with co-workers found that "short" graphene flakes enhance strength of nanocomposites in a moderate way, in which case the reinforcement effect on the Young modulus Y is specified by the derivative $dY/dV \approx 170$ GPa, where V is the volume fraction of graphene flakes. In contrast, the effect of larger flakes is significant with the reinforcement characterized by $dY/dV \approx 680$ GPa. On the basis of these experimental data, it was concluded that the reinforcement of PVA by graphene inclusions dramatically depends on their geometry and is well pronounced at their aspect ratio = 2000 or more [25].

The role of homogeneous dispersion in enhancement of the mechanical properties of grapheme-polymer nanocomposites – the factor (iii) – was examined in the experiment [22]. Zhao with co-workers fabricated graphene-reinforced PVA nanocomposite films and tested their mechanical characteristics as functions of graphene loading characterized by volume fraction V occupied by graphene inclusions [22]. (In general, graphene loading in a nanocomposite can be also specified by its weight fraction W.) The experimentally revealed dependences of tensile strength and elongation-to-break (EB) on graphene loading are non-linear ones. So, the tensile strength dramatically increases from 17 to 42 MPa when V grows from 0% (corresponding to pure PVA film) to 1.8%. In doing so, graphene-PVA nanocomposite exhibits increase in the tensile strength by 150%. With further growth in V from 1.8 to 3%, the tensile strength increases rather weakly from 42 to 43 MPa. At the same time, EB of the nanocomposite shows an opposite trend to the tensile strength. That is, EB dramatically decreases from 220 down to 98% when V grows from 0 to 1.8%. With further growth in V from 1.8 to 3%, EB decreases in a moderate way from 98 down to around 70%.

Also, Zhang with co-workers experimentally examined the effects of graphene inclusions on Young modulus of graphene-PVA nanocomposite [22]. It was found that, in parallel with increase in graphene loading V in the graphene-PVA nanocomposite from 0 to 3%, the Young modulus Y of the nanocomposite shows a remarkable growth, as compared to pure PVA. In doing so, when V increases from 0% (corresponding to pure PVA film) up to 1.8%, value of Y rapidly increases by around 10 times from 0.10 to 1.04 GPa. Then, when V increases from 1.8 to 3%, the Young modulus Y shows a comparatively moderate growth from 1.04 to around 1.25 GPa.

Zhao with co-workers [22] discussed the physical origin of the non-monotonous character exhibited by the experimentally revealed dependences of tensile strength, EB and Young modulus of the graphene-PVA nanocomposite on graphene loading V. Following their explanation, the non-monotonous character is related to evolution from the homogeneous dispersion of graphene inclusions to spatially inhomogeneous dispersion during increase in V. More precisely, when V increases from 0% to some critical value (close to 1.8% in the discussed case), graphene nanosheets are homogeneously dispersed within nanocomposite specimens and thus provide fast, near-linear change of its mechanical characteristics (tensile strength, EB, Young modulus) with rising V. In the situation where V is larger than its critical value, the distances between neighboring graphene sheets is so small that the Van der Waals interaction between such sheets force them to join. In this situation, with rising V, the graphene sheets tend to match by their ends, overlap in their parts or even restack by planes. As a result, dispersion of the graphene nanosheets becomes spatially inhomogeneous in the graphene-PVA nanocomposite, and its mechanical characteristics change weakly with rising V, as compared to the graphene-PVA nanocomposite with homogeneously dispersed graphene inclusions. The fact is that the discussed overlapping and restacking processes weakly change the sum area of contacts between polymer chains and graphene surfaces, in which case any

rise in _V_ just slightly influences tensile stress, EB and Young modulus of graphene-PVA nanocomposite. This aspect is crucial in understanding the specific features of the factor (iii), that is, the role of homogeneous\inhomogeneous dispersion of graphene nanosheets in enhancement of the mechanical properties of graphene-polymer nanocomposites.

Xu with co-workers [24] have developed an approach to fabrication of hyperbranched polymer (HP) and graphene-HP nanocomposites through in situ grafting method. Using this method, graphene-HP nanocomposites were fabricated with HP having two degrees of branching, the namely HP with low and high degrees of branching (synthesized by cationic polymerization of 3-methyl-3-oxetanemethanol at 50 °C and 0 °C, respectively). In the nanocomposites, strong binding between chemically functionalized graphene oxide inclusions and polymer matrix was provided. The higher level of branching correlates with stronger binding. Graphene inclusions were homogeneously dispersed in nanocomposite specimens whose tensile strength and EB were tested. Thus, the experiment [24] was focused on the effects of factors (iii) and (iv) on the mechanical characteristics of graphene-polymer nanocomposites.

Results of the experiment [24] are briefly as follows. The nanocomposites show an increase in strength and Young modulus at expense of some decrease in plasticity, as compared to the pure host polymer. So, the pure polymer is characterized by tensile strength of 12.5 MPa and EB = 140 %. At the same time, graphene-HP nanocomposite at a low degree of branching shows an increased value of tensile strength = 22 MPa and a decreased value of EB =120%. The discussed trend – an increase in tensile strength and a decrease in EB – enhances in the case of graphene-HP nanocomposite at a high degree of branching. Such a nanocomposite is characterized by tensile strength = 27 MPa and a decreased value of EB =110%. The experimental data [24] confirm the important roles of factors (iii) and (iv) in graphene-induced enhancement of tensile strength of graphene-polymer nanocomposites.

Bao with co-workers [23] reported on their comparative study of mechanical and other properties of polymer-matrix nanocomposites of the two types, the namely PVA-matrix nanocomposites reinforced by graphene nanosheets and those containing graphite oxide (GO) particles. In fact, this research was concerned with the roles of all the factors (i)-(iv) in enhancement of mechanical properties of graphene-polymer nanocomposites. In particular,

the role of the factor (i) was examined in the context of the fact that graphene nanosheets are stronger than GO. Geometry of graphene nanosheets is specified by slightly higher aspect ratios than that of GO particles, and this aspect is concerned with the influence of the factor (ii) on mechanical characteristics of the nanocomposites under study. GO has much more functionalities than graphene, in which case GO particles are more homogeneously dispersed and have stronger binding with PVCA matrix, as compared to graphene nanoseets. In this context, the comparative study [23] deals also with the factors (iii) and (iv).

The main conclusion of the experiment [23] is in the dominant character of the factor (i). More precisely, although the factors (iii) and (iv) are much more favorable for GO particles as reinforcing fillers, and the factor (ii) is similar for both GO particles and graphene nanosheets, mechanical characteristics of graphene-PVA nanocomposites are better than those of GO-PVA nanocomposites (for details, see Table 1 in Ref. [23]). For instance, insertion of GO particles and graphene nanosheets with the same loading _V_ = 0.8% into a PVA matrix results in a 52% and 66% increase in tensile strength, respectively [23].

The discussed conclusion on the dominant character of the factor (i) in enhancement of mechanical properties of polymer-matrix nanocomposites is significant for understanding a potential of graphene in reinforcing such nanocomposites, in comparison with other fillers. In particular, the experiment [23] is indicative of the crucial role of superior mechanical characteristics of graphene in its ability to reinforce polymer-matrix nanocomposites. This statement is well consistent with experimentally documented advantages of graphene nanosheets over reinforcing fillers made of other materials; see, e.g., a review [9]. In the rest of this section, we will illustrate such advantages in the exemplary case of an epoxy polymer reinforced by partially oxiginated graphene nanosheets [21]. This case is also interesting, because it deals with a non-typical research subject. More precisely, the experiment [21] was in part focused on fracture toughness being examined rarely in this research area, as compared to tensile strength, EB and Young modulus of graphene-polymer nanocomposites.

So, partially oxiginated graphene nanosheets were dispersed in an epoxy polymer matrix, and mechanical characteristics of resultant nanocomposites with various graphene loadings were examined [21]. It was experimentally found that the mode I fracture toughness (K_{IC}), the ulti-

mate tensile strength and Young modulus of the nanocomposite with 0.125% weight fraction W of graphene inclusions are by 65%, 45%, and 50% larger than those of its graphene-free counterpart (the baseline epoxy), respectively. On the basis of fractography analysis, Rafiee with coworkers [21] attributed the experimentally documented dramatic enhancement of toughness to the role of dispersed graphene sheets as hard inclusions that deflect growing cracks and thus increase both fracture surface roughness and its energy. Besides, crack deflection due to graphene inclusions in the nanocomposites locally provide mixed-mode conditions for growing cracks, and this also hampers crack growth, as compared to pure mode I conditions.

The fracture toughness K_{IC} of the graphene-epoxy nanocomposite as a function of the graphene weight fraction W has its maximum at $W = 0.125\%$, and K_{IC} gradually decreases with further increase in W [21]. Rafiee with coworkers relate this behavior to degradation in the dispersion of graphene inclusions at $W > 0.125\%$.

Note that the 65% increase in the fracture toughness of an epoxy system due to addition of graphene inclusions at $W = 0.125\%$ is remarkable in the sense that a similar level of increase in the fracture toughness can be achieved by insertion of other inclusions, but at much higher weight fractions of these inclusions. For instance, one can increase the fracture toughness by around 60-65% through addition of SiO_2 at its $W = 14.8\%$ [26], Al_2O_3 at the volume fraction $V \approx 5\%$ [27], and TiO_2 at the volume fraction $V \approx 10\%$ [27]. Also, the 42% increase in the fracture toughness is achieved by addition of carbon nanotubes at $W \approx 0.5\%$. The discussed advantage of graphene nanosheets as toughening inclusions in polymer-based nanomposites is, in particular, attributed to their sheet geometry being more effective in crack deflection, as compared to ball-like and cylinder-like shapes of $SiO_2/Al_2O_3/TiO_2$ nanoparticles and carbon nanotubes, respectively.

Also note that, since degradation in the dispersion of graphene nanosheet inclusions at high enough values of W leads to suppression of their toughening effect, a more homogeneous dispersion of such inclusions may dramatically enhance the fracture toughness of graphene-polymer nanocomposites at $W > 0.125\%$. More generally, homogenization of dispersion of graphene inclusions at their high loadings is expected to be an effective method capable of improving mechanical characteristics of graphene-polymer nanocomposites.

4. CONCLUDING REMARKS

To summarize, the experimental data discussed in this short review are indicative of very promising role of graphene inclusions (carbon monolayer nanosheets or flakes having thickness of several atomic layers) as strengthening and toughening structural elements in polymer-matrix nanocomposites. In this rapidly growing filed, the key experimentally documented trends and experiment-based conclusions are briefly as follows:

(A) Due to the effects of graphene inclusions, several important mechanical characteristics (tensile strength, Young modulus and fracture toughness) of graphene-polymer nanocomposites significantly increase at expense of some decrease in plasticity, as compared to pure host polymers.

(B) The role of graphene inclusions in enhancement of the mechanical characteristics exhibited by graphene-polymer nanocomposites are controlled by the four main factors. These are (i) superior mechanical properties of graphene; (ii) high aspect ratio and maximum surface area of graphene nanosheet/flake inclusions; (iii) homogeneity of dispersion of graphene inclusions within polymer matrix; and (iv) strength of binding between graphene inclusions and polymer matrix.

(C) Graphene inclusions are typically more effective in enhancement of the mechanical characteristics of polymer-matrix nanocomposites, as compared to carbon nanotubes, graphite inclusions and inclusions of non-carbon materials. The factor (i) is responsible for advantages of graphene over inclusions made of graphite and non-carbon materials in use as reinforcing fillers. Graphene and carbon nanotubes have similar values of strength and Young modulus [7,8]. Therefore, the factor (i) does not provide preference of graphene over carbon nanotubes. Nevertheless, with the geometric factor (ii), 2-dimensional graphene sheets are more effective as strengthening and toughening fillers in polymer-matrix nanocomposites than 1-dimensional carbon nanotubes. In addition, use of graphene is more cost-efficient, as compared to carbon nanotubes.

(D) The factors (i)-(iv) can be regulated, controlled and enhanced in order to improve mechanical characteristics of graphene-polymer nanocomposites such nanocomposites. In doing so, one should take into account the fact that these factors may compete. For instance,

oxidation and chemical modification of graphene nanosheets are effectively exploited in enhancing both homogeneous dispersion of nanosheets and their binding with polymer matrix (the factors (iii) and (iv), respectively). At the same time, the oxidation and chemical modification processes can decrease both strength and Young modulus of graphene nanosheets (and thus suppress the factor (i)). Also, increase in sizes of graphene nanosheets can be used in enhancement of both their aspect ratio and thereby the mechanical characteristics - tensile strength and Young modulus – of polymer nanocomposites reinforced by such nanosheets (the factor (ii)). However, grain boundaries and other defects are more likely to exist in larger graphene sheets than in their small-sized counterparts [5,6]. At the same time, strength characteristics of graphene inclusions containing grain boundaries significantly degrade, as compared to superior strength of pristine graphene; see reviews [5,7]. That is, the factors (i) and (ii) can be in competition. In the context discussed, in order to enhance mechanical properties of graphene-polymer nanocomposites, the effects caused by the factors (i)-(iv) on these properties should be optimized.

(E) In order to prevent restacking of graphene nanosheets and thus enhance both their homogeneous distribution and large active surface area (being in contact with polymer matrix), it would be logical to use curved graphene nanosheets as reinforcing fillers in graphene-polymer nanocomposites. Examples of such curved graphene fillers can be a highly disclinated graphene [28] and curved polycrystalline graphene sheets [5], whose geometries evidently prevent restacking processes. This approach is worth being examined experimentally.

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REFERENCES

[1] A.K. Geim and K.S. Novoselov // *Nature Mater.* **6** (2007) 183.

[2] A.H. Castro Nero, F. Guinea, N.M.R. Peres, K.S. Novoselov and A.K. Geim // *Rev. Mod. Phys.* **81** (2009) 109.

[3] A.A. Balandin // *Nature Mater.* **10** (2011) 569.

[4] F. Molitor, J. Guttinger, C. Stampfer, S. Droscher, A. Jacobson, T. Ihn and K. Ensslin // *J. Phys.: Condens. Matter* **23** (2011) 1.

[5] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **30** (2012) 201.

[6] L.P. Biro and P. Lambin // *New J. Phys.* **15** (2013) 035024.

[7] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **34** (2013) 1.

[8] C. Lee, X. Wei, J.W. Kysar and J. Hone // *Science* **321** (2008) 385.

[9] T. Kuilla, S. Bhadha, D. Yao, N.H. Kim, S. Bose and J.H. Lee // *Prog. Polymer. Sci.* **35** (2010) 1350.

[10] C.C. Wang, Z.X. Guo, S.K. Fu, W. Wu and D.B. Zhu // *Prog. Polymer Sci.* **29** (2004) 1079.

[11] S. Bal and S.S. Samal // *Bull. Mater. Sci.* **30** (2007) 379.

[12] K.L. Winey and R.A. Vaia // *MRS Bull.* **32** (2007) 314.

[13] P. Gajendran and R. Saraswathi // *Pure & Appl. Chem.* **80** (2008) 2377

[14] M. Rahmat and P. Hubert // *Composites Sci. Technol.* **72** (2011) 72.

[15] B.M. Ginzburg, A.O. Pozdnyakov, D.G. Tochil'nikov, Sh. Tuichiev and A.A. Shepelevskii // *Polymer Sci. A* **50** (2008) 865.

[16] D. Rashidov, U. Shoimov, Sh. Tuichiev and B.M. Ginzburg // *Russian J. Appl. Chem.* **81** (2008) 1618.

[17] B.M. Ginzburg, Sh. Tuichiev, D. Rashidov, S.K. Tabarov and P.I. Ivashchenko // *Tech. Phys. Lett.* **36** (2010) 804.

[18] B.M. Ginzburg, D.G. Tochil'nikov, A.I. Lyashkov, V.L. Ugolkov, V.K. Lavrent'ev, P.A. Shijan and V.P. Ponimatkin // *J. Macromol. Sci. B* **50** (2011) 1047.

[19] B.M. Ginzburg, D.G. Tochil'nikov, P.A. Shiyan and V.P. Ponimatkin // *Russian J Appl. Chem.* **84** (2011) 1456.

[20] B.M. Ginzburg, Sh. Tuichiev, D. Rashidov, S.K. Tabarov, T.E. Sukhanova and M.E. Vylegzhanina // *Polymer Sci. A* **54** (2013) 658.

[21] M.A. Rafiee, J. Rafiee, I. Srivastana, Z. Wang, H. Song, Z.-Z. Yu and N. Koratkar // *Small* **6** (2010) 179.

[22] X. Zhao, Q. Zhang and D. Chen // *Macromolecules* **43** (2010) 2357.

[23] C. Bao, Y. Guo, L. Song and Y. Hu // *J. Mater. Chem.* **21** (2011) 13942.

[24] Q. Xu, Y. Gong, Y. Fang, G. Jiang, Y. Wang, X. Sun and R. Wang // *Bull. Mater. Sci.* **35** (2012) 795.

[25] P. May, U. Khan, A. O'Neill and J.N. Coleman // *J. Mater. Chem.* **22** (2012) 1278]

[26] B.R.K. Blackman, A.J. Kinloch, J. Sohn Lee, A.C. Taylor, R. Agarwal, G. Schueneman and S. Sprenger // *J. Mater. Sci.* **42** (2007) 7049.

[27] B. Wetzel, P. Rosso, F. Haupert and K. Friedrich // *Eng. Fract. Mech.* **73** (2006) 2375.

[28] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **34** (2013) 12.