



INFLUENCE OF MICRO GLASS BEADS ADDED IN A PBT MATRIX ON THE MECHANICAL PROPERTIES OF COMPOSITES

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ABSTRACT

This paper presents the influence of adding materials (micros glass spheres) in a matrix of PBT on several mechanical properties: elasticity modulus, stress at break, elongation at break, energy at break.

The mechanical properties of these composites depend on the glass beads concentration. The addition of polybutylen terephthalate with glass beads increases the values of the elasticity modulus, but reduces quite drastically the elongation at break. Using the SEM investigation, the authors pointed out the particular aspects of fracture surfaces: a ductile process at sample margins and a brittle one in the middle of the composite.

KEYWORDS: PBT, glass beads, composite, elasticity modulus, stress at break, elongation at break, energy at break

1. Introduction

It is a basic problem with the tests that the result will vary with the test piece geometry and the test conditions and it may not be easy to extrapolate to different conditions [7-9].

Even if there are many standards related to short-term tensile testing, they endeavor to quantify a number of specific characteristics which relate to the strength and deformation of a material. Knowledge of these characteristics can supply the designers with the potential performances of a material and a reliable basis of comparing materials [8, 19].

The term 'short term mechanical tests' is used as a convenience to describe mechanical properties where the effects of long times and cycling are ignored. This group of tests includes hardness, tensile, compression, shear, flexing, impact and tear. The material properties require to be rated for generating design data, for quality controlling, for predicting their durability and, unfortunately but necessarily for investigating failures. The polymers have a complex behavior thus, more than any material, they have to be evaluated in a useful way by particular or adequately adapted methods [8].

Polymeric materials are non-linear and their stress-strain characteristic is not linear and hence their modulus is not a constant [1, 2, 8, 9].

The use of PBT as an engineering material is a consequence of a balance of good properties rather than of a few outstanding ones. It does not possess the toughness of polycarbonate (PC), the abrasion resistance of an aliphatic polyamide, the heat resistance of a polysulphone, polyphenylene sulphide (PPS) or polyketone, the low water absorption of a modified poly(p-phenylene oxide) (PPO).

However, PBT, when it is suitably modified by, for example, glass fiber or fire retardants, can contribute to produce very useful compounds.

The particular characteristics of PBT, as pointed out by the suppliers [9, 26, 27], include:

- high softening temperatures (especially for composites with glass or carbon fibers, challenging the use of PC and modified PPOs);
- high rigidity, exceeded only by PPS among the engineering thermoplastics;
- good electrical insulation properties for an engineering thermoplastic as compared to PC, modified PPOs, PPS and the polyether imides;
- low friction and good abrasion resistance;
- good impact strength at low temperatures and excellent creep rupture strength;
- low water absorption and good chemical resistance, including resistance to stress cracking;

- good dimensional stability, a consequence of the low water absorption but also because of a low coefficient of thermal expansion;

- good moldability (easy flow and rapid setting).

A large number of PBT grades is available, including unreinforced, glass- and carbon-fiber reinforced, mineral filler reinforced, impact modified, elastomer modified, flame retardant and various combinations of the foregoing [9, 15, 16, 24, 27, 28].

2. Glass beads as adding material in a polymeric matrix

C type glass is adequate for using in chemically aggressive environments, especially acids. This outstanding chemical resistance is a consequence of its composition, typically as following: at least 60%

SiO₂, Li and Na oxides, Yn and Ca oxides and also rare earth oxides with small amounts of Al₂O₃, B₂O₃, Fe₂O₃, TiO₂, MnO and SnO₂ [17, 18].

Adding this type of reinforcing material influences the technological properties [5, 6, 10, 25] the mechanical ones [3, 4, 11-13, 22] and the tribological ones [14, 20]. In 2010, Akiyama et al. [2] reported a modifying tendency of the mechanical properties of the composites with ceramic particles (average diameter of 150 μm) a little greater than the glass beads introduced in PBT for this study and more ragged as compared to almost spherical shape of the glass beads (Fig. 5). Adding 60% of ceramic particles in PBT makes the elastic modulus to increase to 7500 MPa, 2.5 times greater than pure PBT, but the tensile at break decreases with 10...12% and Vickers hardness has a double value.

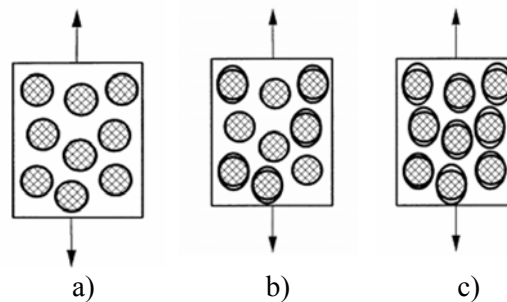


Fig. 1. Damaging models of the interface in composites with spherical particles [21]

Medadd and Fisa [21] have proposed a damaging model of the interface when samples were loaded with tensile forces (Fig. 1) that proved to be suitable to explain the PBT + glass beads composite behavior in a qualitative way. Break at traction of a composite with spherical particles depends very much on the chemical and mechanical nature of the interfaces between the polymer and the hard particles:

a) the resistance interface is not damaged under loading and the break is initially developed in the composite matrix;

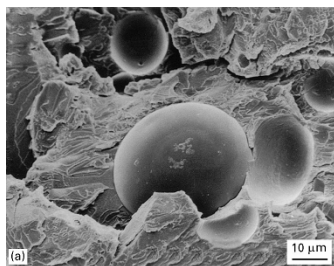
b) an interface partially damaged, usually dependent on the elasticity modulus, the volume fraction of the adding material without damaged

interfaces and the complementary volume fraction of the adding material that is characterized by a damaged interface (the ratio between these two interface categories being very hard to be estimated);

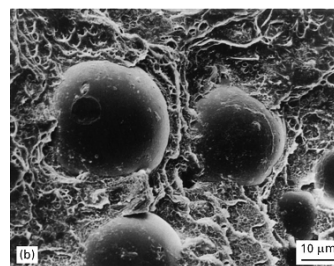
c) a wick defective interface that is easy to be destroyed when applying the load.

The difficulty is that the sample made of such a composite is loaded, all the above-described processes could occur, with different contribution to the final fracture.

Several research works reported that even if the glass beads bearing different treatment, the mechanical properties do not have significant modifications (Fig. 1.7) [21].



a) untreated



b) treated by silan (SiH₄)

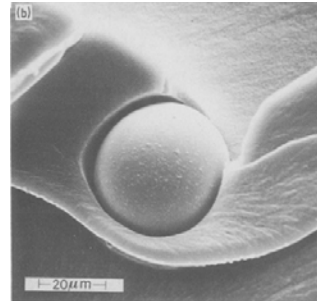
Fig. 2. Aspects of tensile fracture surface for a PS+10% GB composite [M12]

Dekkers and Heikens [12, 13] noticed that, for polymeric composites, the band forming mechanism at traction is fundamentally different, depending on the treatment applied to glass beads. After analyzing

the stresses, they concluded that the generation of the bands had occurred in the zones characterized by maximum values for the main shear stress and by maximum values of the strain energy (Fig. 3).



a). a good adherence between matrix and glass beads, using γ -aminopropil silan



b). without adherence between glass bead and the polymer matrix, as obtained with silicon oil

Fig. 3. Tensile fracture zones of the PC + GB composite [13]

3. Testing methodology materials

The samples were obtained by extruding the mixtures of granulated PBT and glass beads (Fig. 5), in three mass concentrations (Table 1), at ICEFS Savinesti, Romania. The polymer had been dried up at a temperature of 100°C within two hours. There were obtained bone samples with the geometry and dimensions given in Figure 4 and a thermal treatment was applied to the bone samples, as recommended by the producer [27].

The initial distance between the gauge marks on the central part of the test specimen was of 115 mm,

the rate of separation of the grips of the testing machine during test 5 mm/min (the speed of testing) and the it was calculated the tensile Stress (engineering), that is the tensile force per unit area of the original cross section within the gauge length, carried by the specimen at any given moment.

The here-presented results include data for at least 5 tensile tests and the average value for each mechanical characteristic was calculated and there also were presented the scattering intervals for each one. Stress was calculated with reference to the initial values of the cross section thus, there are given the engineering stress-strain curves for each material.

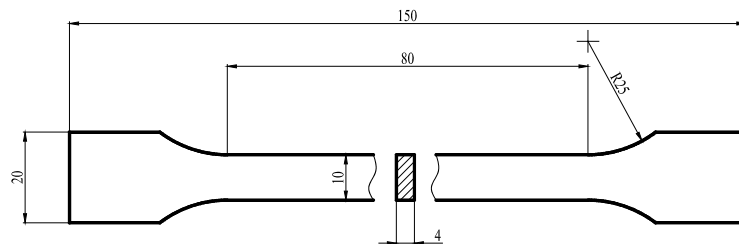


Fig. 4. Bone sample Type 1A ISO 527-2

Table 1. Materials tested

Material symbol	Composition (%wt)	
PBT	neat polymer, grade Crastin 6130 NC010 [10]	
GB10	10% GB	glass bead + 1.5...2% PA + 1% black carbon, for technological reason
GB20	20% GB	
GB30	30% GB	

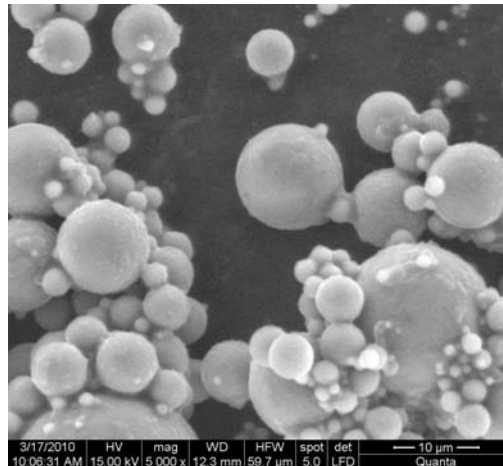


Fig. 5. Glass beads before being mixed with PBT

The traction tests were done with the help of the universal testing machine TESTOMETRIC M350-5AT, having a force cell of 5kN, as recommended by EN ISO 527-2 [25], in the Laboratory of Polymeric Materials Research (Faculty of Mechanical Engineering, "Dunarea de Jos" University of Galati).

The values for the mechanical properties were calculated as the average of five tests that the authors consider to have no anomalous features and in accordance with the literature [9, 24, 27, 28].

4. Experimental results

For PBT, the stress-strain curves (Fig. 7a) have the same aspect as presented in [4, 5, 16, 24]; it was noticed a typical creep zone for the thermoplastic polymers, as this polymer could be included in the class of tough materials with a yield stress lower than the failure stress [8]. The composites have the shape of the stress-strain curves typical for brittle materials (Fig. 7b, c and d).

The authors applied Einstein's model for having a dependency of the mechanical properties on the mass concentration of glass beads,

$$E_c = E_m (1 + V_f), \quad (1)$$

where E_m is the elasticity modulus of the matrix and V_f is the volumic fraction of the adding material. For the composite with 10% GB, the value of the

elasticity modulus as experimentally determined is greater with 10.8% as compared to the value given by Eq. (1) and for the composite with 20% GB, the experimentally obtained value is greater with 21.3% as compared to the theoretical value given by the same model of mixture. The elasticity modulus and the density for glass beads were taken from literature [13, 21]: $E_f = 70000$ MPa, $\rho_f = 1.6$ g/cm³.

Analyzing Fig. 3.4, the following remarks may be made:

- the elasticity modulus of these composites with PBT matrix increases almost linearly with the massic concentration of GB;

- stress at break for the composite with 10% GB is just 10% higher than the polymer but the composites with 10% GB and 20% GB have lower values, 85% and 63%, respectively from the values exhibits by the polymer (Fig. 6b);

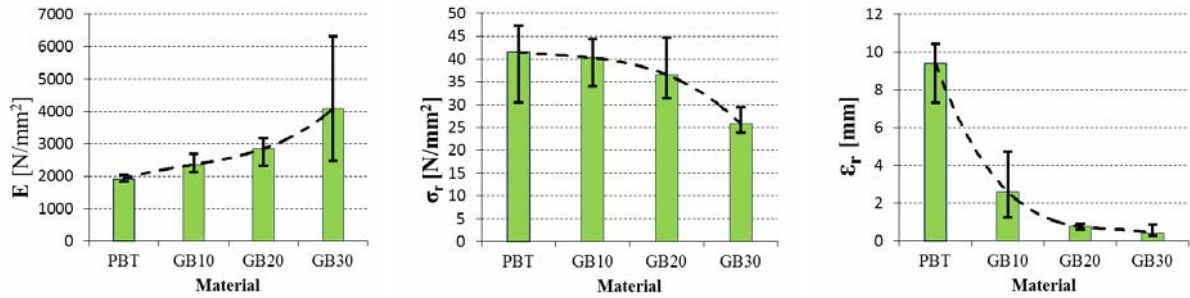
- elongation at break decreases with ~72% for PBT + 10% GB and with ~92% for the composite PBT + 20% GB, as compared to the value obtained for PBT.

The composites have reduced elongation at break (Table 2 and Fig. 6c) and none of the samples not presented the typical bottle neck shape characterizing the polymer.

There is a clear tendency of decreasing the value for the strength limit only for the composite with 20% and 30% GB, respectively.

Table 2. Average values of several mechanical properties for the tested materials

Characteristic	Material			
	PBT	GB10	GB20	GB30
Elasticity modulus, E [N/mm ²]	1923.458	2358.356	2848.581	4087.458
Stress at break, σ_r [N/mm ²]	41.571	40.265	36.543	25.795
Elongation at break, ϵ_r [mm]	9.404	2.609	0.763	0.411
Energy at break, [N·m]	17.665	2.207	0.701	0.294

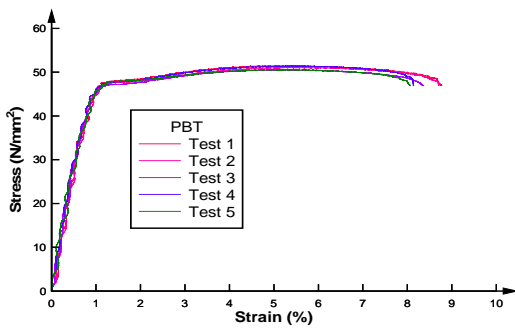


a) Elasticity modulus

b) stress at break

c) elongation at break

Fig. 6. Average values and scattering ranges for the discussed mechanical characteristics of the tested materials

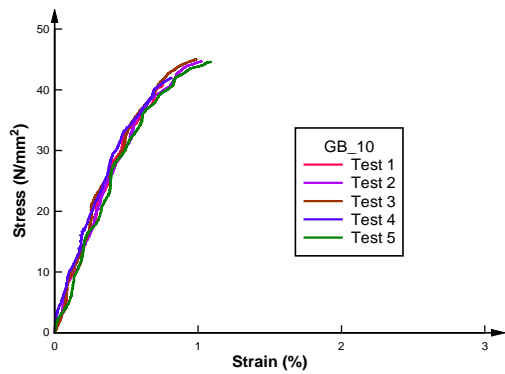


a) curves stress-strain

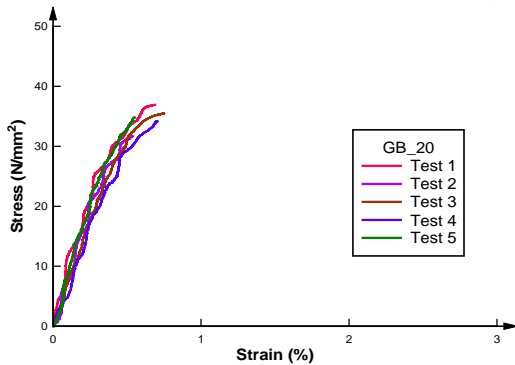


a) set of five samples, after being tested

Fig. 7. Stress-strain curve (left) for PBT and tested samples (right)

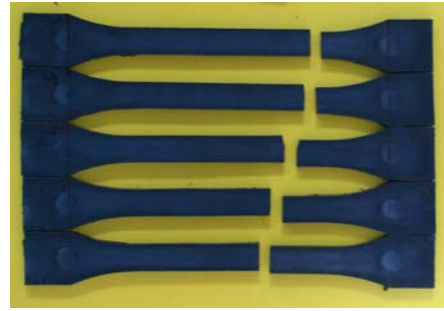
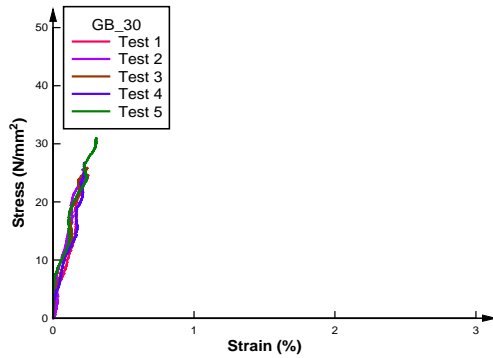


a) PBT + 10% GB



b) PBT + 20% GB





c) PBT + 30% GB

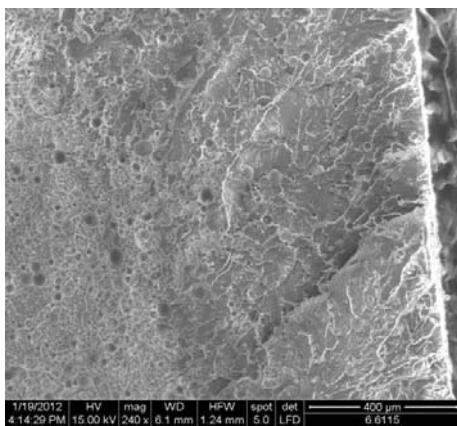
Fig. 8. The stress-strain curves for the PBT+GB composite (left) and the sets of samples after break (right)

Table 2. Data upon the mathematical models attached to the experimental data

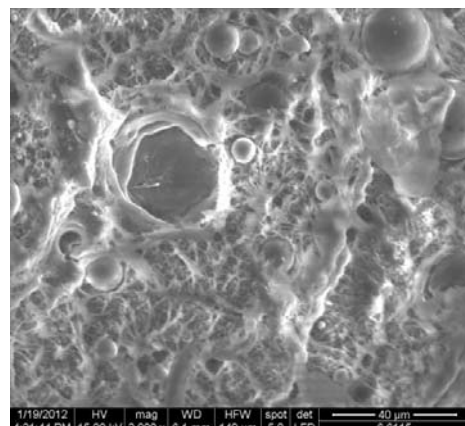
Material symbol	Relation	Correlation coefficient	Standard error about the line
PBT	$y = -0.741 + 50.492x + 57.331x^2 - 124.096x^3 + 89.270x^4 - 34.749x^5 + 8.185x^6 - 1.201x^7 + 0.107x^8 - 0.005x^9 + 0.0001x^{10}$	0.999	0.376
	$y = \frac{a \cdot b + c \cdot x^d}{b + x^d}$ (Fig. 4) a=2.886, b=0.1674, c=50.597, d=2.255	0.996	0.667
GB10	$y = -0.356 + 82.171x - 36.466x^2$	0.999	0.304
GB20	$y = -0.871 + 93.729x - 57.723x^2$	0.999	0.396
GB30	$y = 1.513x + 119.147 - 88.929x^2$	0.993	0.701

SEM images show that the damaging process of the interface has an intermittent nature (Fig. 8b reveals a bigger glass bead that was discontinuously detached from the matrix). For the tested composites, the 1% PA, even small, could influence the interface resistance, having a greater ductility and adherence to

the glass beads as compared to PBT. Analyzing the SEM images from a small scale to larger ones, one may notice the existence of two types of surface aspect. At the sample margins the fracture surface has a ductile nature but towards the center of the sample the aspect becomes brittle (Figs. 7 and 8).

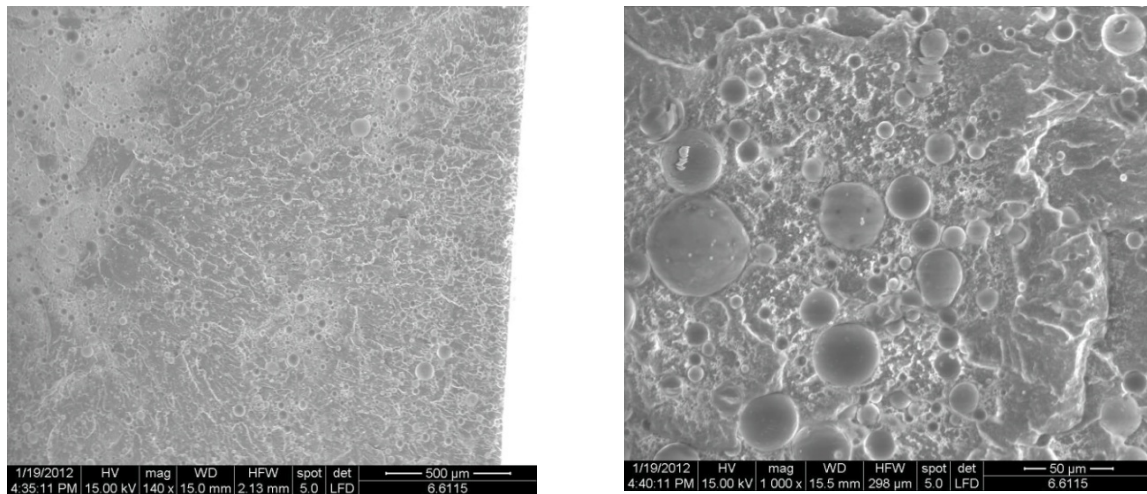


a). Ductile (at the sample margin - right) and brittle (left) aspects of the fracture section



b). Intermittent detaching of glass beads in the middle of the fracture section

Fig. 9. Typical aspects of the fracture section for samples made of the PBT + 10% GB composite



a). Zone of ductile fracture

b). Middle zone of the fracture,
with brittle aspect

Fig. 10. Typical aspects for tensile break surface of the PBT + 20% GB composite

4. Conclusions

The addition of polybutylen terephthalate with glass beads increases the values of the elasticity modulus but reduces quite drastically the elongation at break. The results obtained point out the importance of testing polymers and their composites.

The authors elaborated mathematical models for each tested material. The mathematical models could be useful in analyses with finite elements in the first step evaluation of a design.

References

- [1]. Agbossou A., Bergeret A., Benzarti K., Alberola N. - *Modelling of the viscoelastic behaviour of amorphous thermoplastic/glass beads composites based on the evaluation of the complex Poisson's ratio of the polymer matrix*, Journal of Materials Science, pp. 1963-1972, (1993).
- [2]. Akiyama, M., Yamaguchi, T., Matsumoto, K., Hokkirigawa, K. - *Polymer Composites Filled with RB Ceramics Particles as Low Friction and High Wear Resistant Filler*, Tribology online, Vol. 5, No. 1, January, pp. 19-25, (2010).
- [3]. Arencon D., Velasco J.I., Realinho V., Antunes M., Maspocho M.L. - *Essential work of fracture analysis of glass microsphere-filled polypropylene and polypropylene/poly (ethylene terephthalate-co-isophthalate) blend-matrix composites*, Polymer Testing, 26, pp. 761-769, (2007).
- [4]. Bai S.-L. - *The role of the interfacial strength in glass bead filled HDPE*, Journal of Materials Science Letters, 19, pp. 1587-1588, (2000).
- [5]. Banik K., Mennig G. - *Influence of the Injection Molding Process on the Creep Behavior of Semicrystalline PBT During Aging Below its Glass Transition Temperature*, Mechanics of Time-Dependent Materials, 9, pp. 247-257, 2006.
- [6]. Bessmertnyi V.S., Krokhin V.P., Lyashko A.A., Drizhd N.A., Shekhovtsova Zh. E. - *Production of Glass Microspheres Using the Plasma-Spraying Method*, Glass and Ceramics, vol.58, nos.7-8, (2001).
- [7]. Brandrup, J., Immergut, E.H. & Grulke E.A. - *Polymer Handbook*, 4th Edition, Wiley-Interscience, England, (2003).

- [8]. Brown, R., - *Handbook of Polymer Testing - Short-Term Mechanical Tests*, Rapra Technology, U.K., (2002).
- [9]. Brydson, J.A. - *Plastics Materials*, 7th Edition, Butterworth-Heinemann, Oxford, (1999).
- [10]. Bula K., Jesionowski T., Krysztafkiewicz A., Janik J. - *The effect of filler surface modification and processing conditions on distribution behaviour of silica nanofillers in polyesters*, Colloid Polym Sci, 285, pp.1267-1273, (2007).
- [11]. Crowson R.J., Arridge R. G. C. - *The elastic properties in bulk and shear of a glass bead-reinforced epoxy resin composite*, Journal of Materials Science, 12, pp. 2154-2164, (1977).
- [12]. Dekkers M. E. J., Heikens D. - *Crazing and shear deformation in glass bead-filled glassy polymers*, Journal of Materials Science, 20, pp. 3873-3880, (1985).
- [13]. Dekkers M. E. J., Heikens D. - *Shear band formation in polycarbonate-glass bead composites*, Journal of Materials Science, 19, pp. 3271-3275, (1984).
- [14]. Deleanu L., Andrei G., Maftai L., Georgescu C., Cantaragiu A. - *Wear maps for a class of composites with polyamide matrix and micro glass spheres*, Journal of the Balkan Tribological Association, vol. 17, no 3, pp. 371-379, (2011).
- [15]. Deshmukh G.S., Peshwe D.R., Pathak S.U., Ekhe J.D. - *A study on effect of mineral additions on the mechanical, thermal, and structural properties of poly (butylene terephthalate) (PBT) composites*, J Polym Res, 18, pp. 1081-1090, (2011).
- [16]. Deshmukh G.S., Peshwe D.R., Pathak S.U., Ekhe J.D. - *Evaluation of mechanical and thermal properties of Poly (butylene terephthalate) (PBT) composites reinforced with wollastonite*, Transactions of The Indian Institute of Metals, vol. 64, issues 1 & 2, February-April, pp. 127-132, (2011).
- [17]. Kolesov Yu. I., Kudryavtsev M. Yu., Mikhailenko N. Yu. - *Science for Glass Production Types and Compositions of Glass for Production of Continuous Glass Fiber (Review)*, Glass and Ceramics, vol. 58, nos. 5-6, (2001).
- [18]. Lahiri J., Paul A. - *Effect of interface on the mechanical behaviour of glass bead-filled PVC*, Journal of Materials Science, 20, pp. 2253-2259, (1985).
- [19]. Le Blanc J. - *Filled Polymers. Science and Industrial Applications*, Taylor & Francis Group, (2010).
- [20]. Maftai L. - *Contribuții la studiul comportării tribologice a compozitelor cu poliamidă și microsferă de sticlă*, PhD, "Dunarea de Jos" University, Galati, (2010).
- [21]. Meddad A., Fisa B. - *Filler-matrix debonding in glass bead-filled polystyrene*, Journal of Materials Science, 32 pp. 1177-1185, (1997).



- [22]. Sánchez-Soto M., Gordillo A., Maspocho M. LL., Velasco J.I., Santana O.O., Martínez A.B. - *Glass bead filled polystyrene composites: morphology and fracture*, Polymer Bulletin, 47, 587-594, (2002).
- [23]. Tsui C.P., Chen D.Z., Tang C.Y., Uskokovic P.S., Fan J.P., Xie X.L. - *Prediction for debonding damage process and effective elastic properties of glass-bead-filled modified polyphenylene oxide*, Composites Science and Technology, 66, pp. 1521-1531, (2006).
- [24]. Vincent L., Connolly S. N., Dolan F., Willcocks P.H., Pendlebury R. - *Determination and Comparison of the Plane Stress Essential Work of Fracture of Three Polyesters PET, PPT and PBT*, Journal of Thermal Analysis and Calorimetry, Vol. 86, 1, pp. 147-154, (2006).
- [25]. Yang W., Liu Z.-Y., Shan G.-F., Li Z.-M., Xie B.-H., Yang M.-B. - *Study on the melt flow behavior of glass bead filled polypropylene*, Polymer Testing, 24, pp. 490-497, (2005).
- [26]. *** DuPont Engineering Polymers. *Blow Moulding of Technical Components*, Available from: http://www2.dupont.com/Plastics/en_US/assets/downloads/processing/BM_PM_e.pdf Accessed: 2012-01-12.
- [27]. *** DuPont. Crastin® PBT. thermoplastic polyester resin Crastin® 6130 NC010, Available from: <http://plastics.dupont.com/plastics/dsheets/crastin/CRASTIN6130NC010.pdf> Accessed: 2012-01-12.
- [28]. *** Polybutylene Terephthalate (PBT), on-line: <http://www.rtpcompany.com/info/guide/descriptions/1000.htm> Accessed: 2012-01-23.
- [29]. *** SR EN ISO 527-2:2000 Materiale plastice. Determinarea proprietăților de tracțiune. Partea 2: Condiții de încercare a materialelor plastice pentru injecție și extrudare.