

**NEW POLYMERIC COMPOUNDS WITH HIGH TEMPERATURE AND
IMPACT RESISTANCE**

MIHAI GEORGESCU, LAUREN IA ALEXANDRESCU, MARIA DANIELA STELESCU,
MARIA SÓNMEZ, MIHAELA (VÍLSAN) NI UIC , DANA GUR U

*INC DTP - Division Leather and Footwear Research Institute (ICPI), 93 Ion Minulescu,
sector 3, Bucharest, mihai.georgescu@icpi.ro, mihai.georgesku@yahoo.com*

This paper focuses on development and characterization of new impact and flame resistant advanced materials based on polyamide / compatibilizer / polycarbonate / glass fibers (GF) functionalized with organo silane. Polyamides (PA) are highly crystalline hard materials, that have high impact resistance, burn slowly or are self-extinguishing. Polycarbonates (PC) are thermoplastic polymers intended for oil and high temperatures resistant materials. To increase impact resistance, polymeric compounds were reinforced with short functionalized glass fibers. The thermoplastic polymeric materials are visionary and materials for the future, with special properties, depending on the type of elastomers, the type of reinforcement material, the ratio of reinforcement, the functionalization of the reinforcing material, the type of functionalization agent, the ratio of elastomer-compatibilizing agent-reinforcing agent, etc. Thus by determining the optimum types and ratios of polycarbonate, polyamide, compatibilizer, functionalized glass fibers and optimal processing conditions and parameters, special properties can be achieved: flame retardant and especially self-extinguishing properties, physical-mechanical, chemical and technological properties, superior to the current standards in the field. Due to their characteristics the new materials can be employed in development of finished goods for the automotive and electrical insulation industry, which must meet European legislation (directives) into force.

Keywords: hybrid composites, impact resistance, thermal resistance

INTRODUCTION

Manufacturers requested performant materials for processing and use, which determined development of new polymer structures, with reinforcing agents, having optimized properties compared to traditional materials used in this domain. Automotive and electrical insulation industries are interested in easy to process new polymeric materials, characterized by resistance to shock, high temperature, and direct flame or even self-extinguishing properties. The existence of new reinforcing agents such as glass fiber (Loewenstein, 1993), simple or functionalized, compounded with polymeric materials leads to new composites that provide expected qualitative performance and to greening their processing technology.

The thermoplastic polymers are innovative future materials, with special properties, depending on the type of elastomer, the type and degree of reinforcement material, the functionalization of the reinforcing material, the type of functionalization agent, the elastomer-compatibilizing-reinforcing agent ratio etc. These properties offer high use value in fields which require materials with performance characteristics: dimensional stability, resistance to UV radiation, solvents, aggressive chemical agents, waterproof, electric resistance (Pokharkar and Sivaram, 1995; Park *et al.*, 2002; Liu *et al.*, 2000; Jones and Ballone, 2010; Liaw and Chang, 1997; Kricheldorf and Luebbbers, 1990). In addition to the above, another important property is thermal resistance at a wide range of temperatures, and impact resistance. Properties are the result of a complex of original characteristics which arise from physical, mechanical and chemical interactions that occur during manufacturing processes that result in a polymer nanostructure.

New Polymeric Compounds with High Temperature and Impact Resistance

In this paper polyamide (PA) was selected as the continuous phase, due to the fact that it can be processed at high temperatures (200-230°C), giving the finished product thermal resistance properties. Polycarbonate (PC), disperse phase, polymer with wide industrial applications (Sweileh *et al.*, 2010; Lee *et al.*, 2002), was also selected due to its high impact resistance.

By establishing optimal types and amounts of polycarbonate, polyamide, compatibilizer (ε-caprolactam), functionalized glass fiber and optimum processing technological parameters, high performance properties can be achieved, such as: impact, thermal resistance and especially self-extinguishing properties.

MATERIALS AND METHODS

Materials

In order to achieve the thermal resistance hybrid composites, the following materials were used: (1) Polyamide - standard PA for injection - Sebamid 6 s3c (Basplast), (2) Polycarbonate - CALIBRE™ polycarbonate resin, density 1.2g/cm³ (Trinseo Gmb), (3) simple Glass Fiber - BMC3 4.5 mm, (4) Organosilane - 3-Aminopropyltrimethoxysilane, Mw-179.29 g/mol, bp:91-92°C (lit) (Sigma-Aldrich Chemistry, USA).

Method

In order to obtain the impact and heat resistant polymeric composites, the first task was to functionalize the glass fiber. The treatment has an important role on the final properties of the glass fibers and consequently on the final polymer composite that incorporates them. Thus, the treatment method of the glass fiber was designed as follows:

- In a plastic container (to avoid silanization directly on the walls of the glass container) are added weighed glass fibers;
- Ethyl alcohol is added so that they are fully immersed in alcohol;
- They are mechanically mixed for 3-4 hours;
- Add 3-aminopropyltrimethoxysilane (APTMS), functionalization agent - 5% wt, dropwise into the mixture of glass fibers and alcohol. When introducing organosilane, the glass fibers should be completely immersed in alcohol and mixing continuous to ensure homogeneity of the mixture; mixing continues for 3 hours to ensure the binding of functionalization agent to the glass fiber;
- Treated glass fibers are dried for 24 hours at 80°C.

The PA/PC polymeric composites, compatibilized with ε-caprolactam, and reinforced with organosilane treated glass fiber, were made using a Plasti-Corder Brabender mixer, type 350 E (Figure 1). Considering the optimal technological parameters, compounds were processed into finished products (plates) by molding method, using electrically heated press. After stabilization for 24 hours at room temperature, the plates were submitted to physical-mechanical characterizations.

The method for achieving multiphase polymer composites is as follow: PA / ε-caprolactam / PC / GF (simple or treated with APTMS) was added in the mixer, temperature was 200°C (zone 1) / 200°C (zone 2) / 200°C (zone 3). Set mixing speed at 100 rot/min to ensure plasticizing components and uniform dispersion of glass fibers. Simple or treated fiberglass was added to the mixture in minute 8 and 13 respectively,

continuing mixing to a maximum of 15 minutes. The total mixing time is 10-15 minutes / formulation.

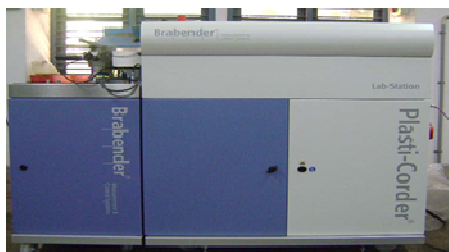


Figure 1. Plasti-Corder Brabender Mixer 350 E

The obtained polymer composite granules are added in the molds, to process them according to test specimens used for physical-mechanical characterization for finished products, using the electrically heated press, TP 600, by means of compression method, between its platters at temperature of 220°C and 300KN pressure for 2 minutes preheating, 2 minutes actual forming in the press and 10 minutes cooling.

Table 1. PA / -caprolactam / PC / GF polymeric composites

| Samples | UM | P1 | P2 | PG1 | PG2 | P3 | P4 | P5 | P6 | P7 | P8 |
|--|----|-----|-----|-----|-----|----|----|----|----|----|----|
| Polyamide | % | 100 | - | 90 | 50 | 70 | 70 | 70 | 70 | 70 | 70 |
| Polycarbonate | % | - | 100 | 10 | 50 | 30 | 30 | 30 | 30 | 30 | 30 |
| -caprolactam | % | - | - | - | - | - | 5 | - | - | 5 | 5 |
| Glass fiber (treated with APTMS) | % | - | - | - | - | - | - | - | 10 | - | 10 |
| Glass fiber (simple) | % | - | - | - | - | - | - | 10 | - | 10 | - |

RESULTS AND DISCUSSIONS

The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm⁻¹, using a 4200 FT-IR equipped with ATR crystal diamond and sapphire head. Samples analyzed are divided into four categories:

- Reference samples: PA, PC, and -caprolactam;
- Samples with different PA/PC ratio (90-50%) ,PG₁, PG₂,P₃;
- Samples with -caprolactam P₄;
- Samples with GF (simple or treated) P₅, P₆, P₇, P₈.

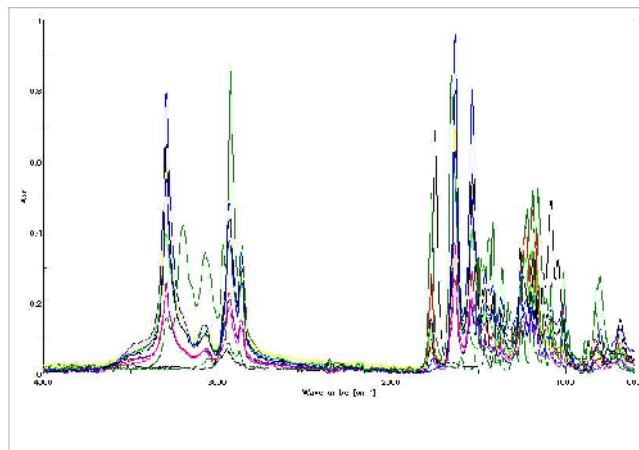


Figure 2. Overlapping IR spectra of PA / -caprolactam / PA/GF polymer architectures

From overlapping spectra is noted the presence of PA and PC in the polymeric composites. The presence of PA and PC in variable percentages, by the intensity of characteristic peaks, is observed. Note that the elastomer (PA and PC) is in excess of the other components, being the main ingredient. The compatibilizer, and GF cannot be distinguished very well in this image, due to the small amount (-caprolactam max.5% and GF 10% wt elastomer).

The results of the physical-mechanical properties of the samples obtained for the polymer composites based on PA and PC, compatibilized with -caprolactam and glass fiber reinforced, compared with the reference samples are shown in Figures 3, 4 and 5.

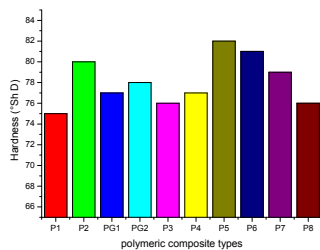


Figure 3. Variation of hardness for composites P1-P8

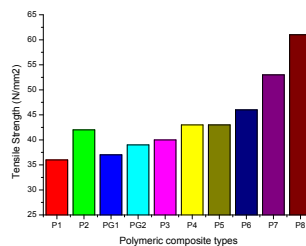


Figure 4. Variation of tensile strength for composites P1-P8

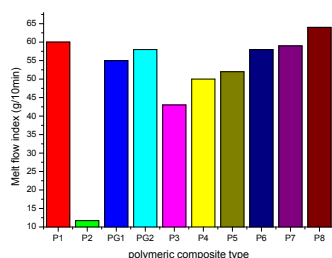


Figure 5. Variation of Melt Flow Index for composites P1-P8

Hardness decreases when adding the ϵ -caprolactam compatibilizer. When adding simple glass fibers, hardness increases but using the treated glass fibers instead, the hardness decreases by 1-2°Sh D. Thus, for the polymeric composites containing compatibilizer and treated fiberglass this property decreases by 2-3°Sh D.

Tensile strength decreases when mixing the plastomers, PA and PC, based on the ratio used between them. The addition of compatibilizer improves the tensile strength compared to composites P₃. Treated glass fiber without the compatibilizer decreases the tensile strength to the PG₂ (PA / PC 50/50%) level; while the use of compatibilizer between the two polymers (PA/ PC) increases the value of the tensile strength. In that sense P₈ composite presents values of 61 N/mm².

Elongation at break in composites PG₁-P₈, with added compatibilizer, simple or treated glass fibers could not be read due to the fact that they demonstrate increased stiffening.

Melt Flow Index - It is noted that there are considerable differences between the viscosities of the two base polymers (PA and PC) which affects the flow of material. Thus, there were obtained values for PA 60g / 10 min and 11.7g / 10 min PC. Melt flow Index ranges, for the obtained composite materials, varies widely between these two extremes, by the base polymer ratio, absence/presence of compatibilizer, absence/presence and the type of glass fiber. Thus, flow index of composites PG₁-P₃ decreases with increasing percentage of PC. The addition of the compatibilizing agent in a proportion of 5% increases the melt index value. Using 10% simple glass fiber in composite P₃ (70/30), without compatibilizing agent has no major effect. When using compatibilizer and treated glass fiber the melt flow index strongly increases. Thus, composites PA / compatibilizer / PC / with treated GF - P₈ present flow values of 64 g/10 min, at a temperature of 230°C.

CONCLUSIONS

Samples of PA / PC without compatibilizer are not homogeneous, which makes the dispersion of the matrix PC on PA matrix to be achieved at high speed, the mixture is rigid and becomes brittle after cooling.

Introducing compatibilizer (ϵ -caprolactam) significantly improves the mixture processing, dispersion of discontinuous phase - PC is uniform, the mixture is homogenous and non-brittle after cooling.

Increasing the percentage of compatibilizer does not visibly improve processability.

New Polymeric Compounds with High Temperature and Impact Resistance

Functionalization was carried out by immersing the glass fibers in a solution of ethanol and 3-aminopropyl trimethoxysilane (5%) was added dropwise. Then the fibers were dried at 80°C for 24 hours.

Treated glass fiber increases tensile strength and slightly decrease hardness, it disperses evenly, it is not necessary to increase the rate of mixing.

Hardness decreases when adding the ϵ -caprolactam compatibilizer. For the polymeric composites containing compatibilizer and treated fiberglass, this property decreases by 2-3°Sh D.

Tensile strength decreases when mixing the elastomers, PA and PC, based on the ratio used between them. Treated glass fiber with the compatibilizer between the two polymers (PA/ PC), greatly improve the tensile strength. In that sense P₈ composite presents values of 61 N/mm².

Melt Flow Index - It is noted that there are considerable differences between the viscosities of the two base polymers (PA and PC) which affects the flow of material. Using 10% treated glass fiber in composite P₃ (70/30), with compatibilizing agent, increases the melt flow. Composites PA / compatibilizer / PC / with treated GF - P₈ present flow values of 64 g/10 min, at a temperature of 230°C.

Acknowledgements

This research was financed through PN 16 34 01 09/2016 project: "New compound types based on polycarbonate / polyamide / fiberglass with impact resistance used in the automotive and electrical insulation industry" supported by Romanian Ministry of Education.

REFERENCES

- Jones, R.O. and Ballone, P.A. (2010), "Combined density functional and study of polycarbonate", *Molecules*, 15, 3680.
- Kricheldorf, H. and Luebbbers, D. (1990), "Polymers of carbonic acid. 3. Thermotropic polycarbonates derived from 4,4'-dihydroxybiphenyl and various diphenols", *Macromolecules*, 23, 2656-2662.
- Lee, J., Song, C., Kim, J.I. and Kim, J.H. (2002), "Preparation of aromatic polycarbonates nanoparticles using supercritical carbon dioxide." *Journal of Nanoparticle Research*, 4, 53-59.
- Liaw, D.J. and Chang, P. (1997), "Synthesis and characterization of aromatic and brominated aromatic polycarbonates by two-phase-transfer-catalyzed polycondensation of bisphenols with trichloromethyl chloroformate", *Journal of Applied Polymer Science*, 63, 195-204.
- Liu, Z., Cunha, A.M., Yi, X.S. and Bernardo, A.C. (2000), "Key properties to understand the performance of polycarbonate reprocessed by injection molding", *Journal of Applied Polymer Science*, 77, 1393-1400.
- Loewenstein, K.L. (1993), *The Manufacturing Technology of Continuous Glass Fibers*, 3rd revised ed., Elsevier.
- Park, J.H., Hyun, J.C., Kim, W.N., Kim, S.R. and Ryu, S.C. (2002), "Extensional and complex viscosities of linear and branched polycarbonates", *Macromolecular Research*, 10, 135-139.
- Pokharkar, V. and Sivaram, S. (1995), "Poly(alkylene carbonate)s by the carbonate interchange reaction of aliphatic diols with dimethyl carbonate: Synthesis and characterization", *Polymer*, 36, 4851-4854.
- Sweileh, B.A., Al-Hiari, Y.M., Kailani, M.H. and Mohammad, H.A. (2010), "Synthesis and Characterization of Polycarbonates by Melt Phase Interchange Reactions of Alkylene and Arylene Diacetates with Alkylene and Arylene Diphenyl Dicarbonates", *Molecules*, 15, 3661-3682.