

# THE INFLUENCE OF COMPATIBILISER ON THE PROPERTIES OF POLYMER COMPOSITES

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## THE INFLUENCE OF COMPATIBILISER ON THE PROPERTIES OF POLYMER COMPOSITES

**ABSTRACT.** Thermoplastic polymers are materials of the future, with special properties, depending on the type of elastomer, the degree of reinforcement, the type of reinforcement material, the functionalization of the reinforcing material, the type of functionalization agent, the elastomer-compatibiliser-reinforcing agent ratio, etc. Polycarbonate (PC) and polyamide (PA) are two elastomers with high hardness, immiscible due to differences in polarity, processing temperature, and solubility. These factors lead to a poor dispersion of PC in the PA matrix and vice versa. Mechanical and physical properties of these polymer blends come not only from the combination of polymeric compounds, but also from the developed morphological forms (interface). Therefore, an additive is required to act as a compatibiliser able to effectively reduce elastomer viscosity. In order to observe the influence of the selected compatibiliser on the properties of polymer composites, the latter were characterized physico-mechanically and morphologically. Thus, compatibilisers chosen for this study were polycaprolactone and polyalkyloxazoline. These compatibilisers, with specific surface and free energy, intervene in polymer-polymer interactions, increasing compatibility, forming polymer-compatibiliser-polymer bonds. Considering these properties formulations of polymer compounds were established (P1-P13) based on polyamide/compatibiliser/polycarbonate/fibreglass. Tested polymer composites contain different percentages of polyamide and polycarbonate (90, 70, 50, 30, 10), compatibiliser (caprolactone and oxazoline) 3-7%, and 10-30% fibreglass.

**KEY WORDS:** composites, polymers, polyamide, polycarbonate, compatibilisers

## INFLUENȚA AGENTULUI DE COMPATIBILIZARE ASUPRA CARACTERISTICILOR COMPOZITELOR POLIMERICE

**REZUMAT.** Materialele polimerice termoplastice sunt materiale de viitor, având proprietăți speciale, în funcție de tipul de elastomeri, gradul de armare, tipul de material de armare, funcționalizarea materialului de armare, tipul de agent de funcționalizare, raportul elastomer-agent de compatibilizare-agent de armare etc. Policarbonatul (PC) și poliāmida (PA) sunt doi elastomeri cu duritate mare, nemiscibili datorită diferențelor de polaritate, temperatură de prelucrare și solubilitate. Acești factori conduc la o slabă dispersie a PC în matricea de PA și invers. Proprietățile mecanice și fizice ale acestor amestecuri polimerice nu provin doar de la combinația de compuși polimerici, ci și de la formele morfologice dezvoltate (interfață). Prin urmare, este necesar un aditiv care să acționeze ca un compatibilizator capabil să reducă în mod eficient viscozitatea elastomerilor. În vederea observării influenței compatibilizatorului ales asupra proprietăților compozitelor polimerice, acestea au fost caracterizate din punct de vedere fizico-mecanic și morfologic. Astfel, compatibilizatorii aleși pentru acest studiu au fost policaprolactona și polialchiloxazolina. Acești compatibilizatori, cu suprafață specifică și energie liberă, intervin în interacțiunile polimer-polimer, măriind gradul de compatibilizare, realizând legături de tipul polimer-compatibilizator-polimer. Având în vedere aceste proprietăți, s-au stabilit recepturi de compozituri polimerice (P1-P13) pe bază de poliāmida/compatibilizator/policarbonat/fibră de sticlă. Compozitele polimerice testate conțin procente diferite de poliāmida și policarbonat (90, 70, 50, 30, 10), compatibilizator (caprolactonă și oxazolină) 3-7% și fibră de sticlă 10-30%.

**CUVINTE CHEIE:** compozite, polimeri, poliāmida, policarbonat, compatibilizatori

## L'INFLUENCE DE L'AGENT COMPATIBILISANT SUR LES CARACTÉRISTIQUES DES COMPOSITES POLYMÉRIQUES

**RÉSUMÉ.** Les polymères thermoplastiques sont des matériaux d'avenir, ayant des propriétés particulières, en fonction du type d'élastomère, du degré de renforcement, du type de matériau de renforcement, de la fonctionnalisation du matériau de renforcement, du type d'agent de fonctionnalisation, du rapport de l'agent compatibilisant-élastomère-agent de renforcement, etc. Le polycarbonate (PC) et la polyamide (PA) sont deux élastomères avec une dureté élevée, immiscibles à raison de différences dans la polarité, la température de traitement et la solubilité. Ces facteurs conduisent à une faible dispersion de PC dans la matrice de PA et vice versa. Les propriétés physiques et mécaniques de ces mélanges de polymères ne proviennent pas seulement de la combinaison des composés polymères, mais aussi des formes morphologiques développées (interface). Par conséquent, un additif est nécessaire pour agir comme un agent compatibilisant qui peut réduire effectivement la viscosité des élastomères. Afin d'observer l'influence de l'agent compatibilisant choisi sur les propriétés des composites polymère, ceux-ci ont été caractérisés du point de vue physico-mécanique et morphologique. Ainsi, les agents compatibilisants choisis pour cette étude ont été la polycaprolactone et la polyalkyloxazoline. Ceux-ci, avec leur surface spécifique et leur énergie libre, interviennent dans les interactions polymère-polymère, ce qui augmente la compatibilité, en formant des liens de type polymère-compatibilisant-polymère. Compte tenu de ces propriétés on a établi des formulations de composés polymères (P1-P13) à base de polyamide/compatibilisant/polycarbonate/fibre de verre. Les composites polymères testés contiennent différents pourcentages de polyamide et de polycarbonate (90, 70, 50, 30, 10), de l'agent compatibilisant (caprolactone et oxazoline) 3-7% et 10-30% fibre de verre.

**MOTS CLÉS :** composites, polymères, polyamide, polycarbonate, agents compatibilisants

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## INTRODUCTION

A wide variety of new multicomponent polymeric materials have been developed in the last two decades. In the field of polymeric materials, leading companies have oriented towards the development of modified polymer structure with superior physical and mechanical properties compared to those of the base constituents taken individually, which offer superior versatility.

Thermoplastic polymeric composites are novelty materials, with special properties, depending on the type of elastomer, degree of reinforcement, the type of reinforcement material, the functionalization of the reinforcing material, the type of functionalization agent, the elastomer-compatibiliser-reinforcing agent ratio etc. These properties offer high use value in fields which require materials with advanced characteristics: dimensional stability, resistance to UV radiation, solvents, aggressive chemical agents [1-7], impact resistance, and possibility of use in a wide range of temperatures etc. Properties result from a set of summed specific characteristics of individual materials, which arise from physical, mechanical and chemical interactions that occur during manufacturing processes that result in a polymer nanostructure.

Grafted copolymers are currently widely used with the role of compatibility agents in blends with other plastic materials and are generally obtained by grafting free radicals in the melt onto the polymer chains. Most commonly used monomers are maleic anhydride, glycidyl methacrylate and acrylic and vinyl monomers containing reactive functionalized groups.

Based on the above, compatibiliser choice for mixed PA/PC requires special attention. Mechanical and physical properties of these polymer blends arise not only from the combination of polymeric compounds, but also from developed morphological forms (interface).

In this paper polyamide (PA) was used as dispersion phase, due to its processing property at high temperatures (200-230°C), which confers thermal resistance to the composite, and polycarbonate (PC), a polymer with wide

industrial application [8, 9] due to its high impact resistance, was used as the dispersed phase. Compatibiliser (polycaprolactone or polyalkyloxazoline) with specific surface and free energy is involved in polymer-polymer interactions, enhancing compatibility degree [10] and creating polymer-compatibiliser-polymer bonds. The interface can also serve as a nucleation center, as a preferential adsorption place and as a space for chemical reactions. The use of such composite systems is required by features such as heat resistance, mechanical strength, resistance to aggressive agents, low weight, processability, etc.

By establishing optimal types and amounts of polycarbonate, polyamide, compatibiliser (polycaprolactone or polyalkyloxazoline), and optimum processing technological parameters, high performance properties can be achieved, such as: impact and thermal resistance.

The formulations were designed to have predetermined physical (hardness, thermal stability, impact resistance), chemical (vapor, aggressive chemical agents resistance), technological (processing by injection/extrusion, at controlled temperature and pressure, recyclable, optimized processing time, etc.), and fireproof properties.

## MATERIALS AND METHODS

Polycarbonate and polyamide are two very hard elastomers, immiscible due to polarity, processing temperature, and solubility differences. These factors lead to a poor dispersion of PC in the PA matrix and vice-versa. In this situation, an additive is required [11, 12], that can act as a compatibiliser, which can effectively reduce the elastomer's viscosity.

Multiphase polymeric composites need an adequate dispersion and compatibility method. Thus, the employed compatibiliser has to meet three essential requirements:

- To reduce interfacial tensions, thus achieving a fine dispersion;
- To stabilise the thermal and shearing effect morphology in the obtaining process;

- To make possible the adhesion between phases, in solid state.

In this regard, the role of the additives, such as compatibilisers, was investigated. The compatibilisers are necessary to adjust the mechanical properties or to promote miscibility in complex systems.

Thus, the compatibiliser (polycaprolactone or polyalkyloxazoline) with specific surface and free energy is involved in polymer-polymer interactions, enhancing compatibility degree, creating polymer-compatibiliser-polymer bonds. The interface can also serve as a nucleation center, as a preferential adsorption place and as a space for chemical reactions. The use of such composite systems is required by features such as heat resistance, mechanical strength, resistance to aggressive agents, low weight, processability, etc.

**Materials**

In order to achieve hybrid composites with thermal resistance, the following materials were used:

- (1) Polyamide - standard PA for injection - Sebamid 6 s3c (Basplast),
- (2) Polycarbonate - CALIBRETM polycarbonate resin, density 1.2g/cm<sup>3</sup> (Trinseo Gmb),
- (3) Polycaprolactone, mp: 60°C(lit), density: 1.145 g/cm<sup>3</sup> (Sigma-Aldrich Chemistry, USA).
- (4) 2-ethyl-2-oxazoline – Mw-500.000, density: 1.14g/cm<sup>3</sup> (lit) (Sigma-Aldrich Chemistry, USA).
- (5) simple fibreglass - BMC3 4.5 mm,
- (6) (Organosilane-3-Aminopropyl) trimethoxysilane, Mw-179.29 g/mol, bp: 91-92°C (lit) (Sigma-Aldrich Chemistry, USA).

Tables 1 and 2 show the multiphase polymeric composite formulations, based on PA/PC, with two types of compatibiliser (polycaprolactone, polyalkyloxazoline) and reinforced with simple and treated fibreglass. In order to make the comparison between composites possible, the base simple polymers PA, and PC, were shown in the table. The ratio between the components of the polymeric composites is as follows: 90-70% PA, 10-30% PC, 3-7% compatibiliser and 10-30%

Table 1: Formulations of polymer composites based on PA/PC compatibilised with polycaprolactone

Sample	UM	PA	PC	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>	P <sub>7</sub>	P <sub>8</sub>
Polyamide	%	100	-	90	50	70	70	70	70	70	70
Polycarbonate	%	-	100	10	50	30	30	30	30	30	30
Polycaprolactone	%	-	-	-	-	-	3	3	5	5	7
Fibreglass (treated)	%	-	-	-	-	-	-	-	10	-	30
Fibreglass (simple)	%	-	-	-	-	-	-	10	-	30	-

Table 2: Formulations of polymer composites based on PA/PC compatibilised with polyalkyloxazoline

Sample	UM	P <sub>9</sub>	P <sub>10</sub>	P <sub>11</sub>	P <sub>12</sub>	P <sub>13</sub>
Polyamide	%	70	70	70	70	70
Polycarbonate	%	30	30	30	30	30
Polyalkyloxazoline	%	3	3	5	5	7
Fibreglass (treated)	%	-	-	10	-	30
Fibreglass (simple)	%	-	10	-	30	-

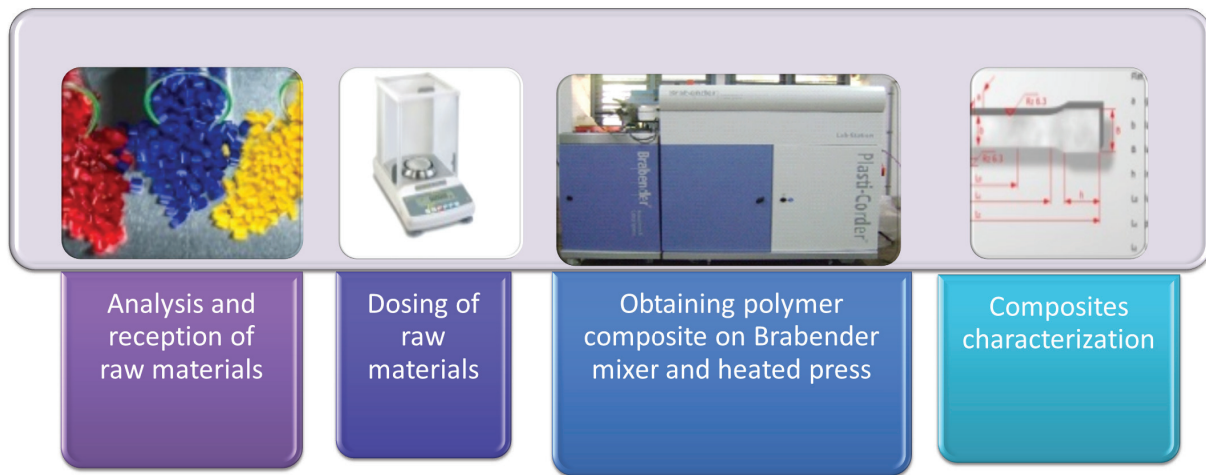


Figure 1. Stages for processing and characterization of the polymeric composites

fibreglass. In order to select the optimal variants, these new materials were characterized according to the rubber and plastic specific standards.

### Method

Regarding obtaining polymeric composites with resistance to high temperature, flame, and impact, a processing technology and formulations for these materials were designed. Thus, the laboratory-scale technological process for polymeric composites based on polyamide and polycarbonate compatibilised with polycaprolactone or polyalkyloxazoline (3-7%) and reinforced with fibreglass, is detailed in Figure 1.

The formulations in Tables 1 and 2 were processed in a Brabender mixer, shown in Figure 2. The method for achieving multiphase polymer composites is as follows:

- Weighing the raw materials, according to the formulations;
- Base components, PA and PC, along with the compatibiliser (polycaprolactone or polyalkyloxazoline) are mixed together;
- Setting up the processing parameters through the dedicated software. Temperature was 200°C (zone 1) / 200°C (zone 2) / 200°C (zone 3);
- The previous obtained mix is introduced in the mixing chamber, and depending on the formulation, the fibreglass is added.

Depending on the formulation, the simple or treated fibreglass was added to the mixture in minute 8 and 13, respectively, continuing the mixing in the Brabender chamber. The total mixing time is 15 minutes/formulation.

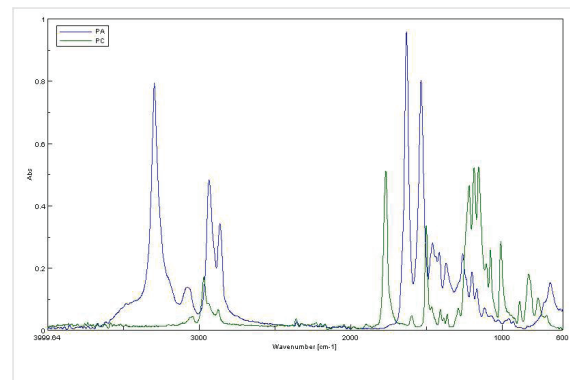


Figure 2. Overlapping IR spectra of PA and PC

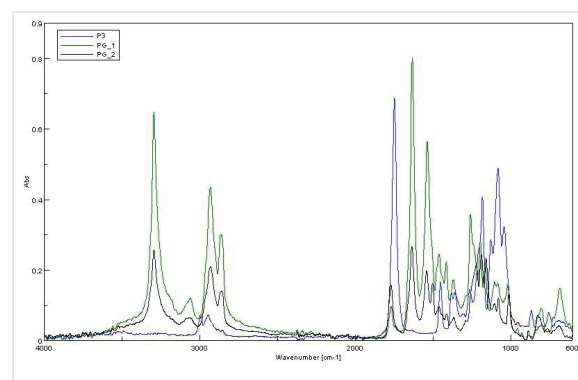


Figure 3. Overlapping IR spectra of PA and PC with various ratios (P1, P2, P3)

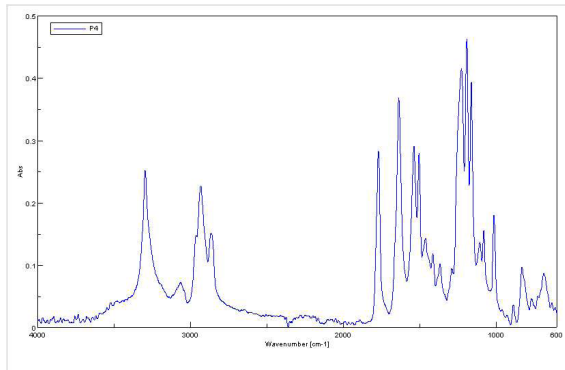


Figure 4. FT-IR spectra for PA/PC/polycaprolactone (P4)

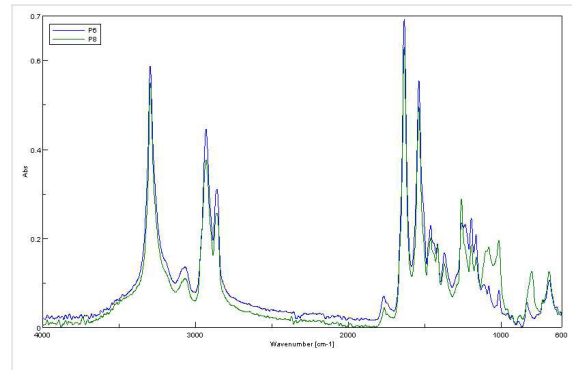


Figure 5. FT-IR spectra for PA/PC w/o compatibilizer (polyalkyloxazoline)

**Characterisation**

*FT-IR Spectrometry Characterisation*

IR spectrums represent the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 μm. IR domain for usual organic chemistry is between 2.5 and 25 μm.

The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm<sup>-1</sup>, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the pure elastomer spectrum, and with the spectra found in the literature or with the equipment’s spectra library.

Overlapping spectra show the presence of PA and PC in the polymeric composites in variable percentages, by the intensity of characteristic

peaks. The presence of polycaprolactone and polyalkyloxazoline compatibilisers in composites is outlined at 1040 cm<sup>-1</sup> and 801 cm<sup>-1</sup>, respectively, in IR spectra. Note that the plastomer (PA and PC) is in excess of the other components, being the main ingredient, thus the fibreglass cannot be distinguished very well in this image, due to its small amount (fibreglass 10%wt of plastomer).

*Physical-Mechanical Characterisation*

The results of the physical-mechanical properties of the samples obtained for the polymer composites based on PA, compatibiliser, PC, and reinforced with fibreglass, are shown in Table 3.

Physical-mechanical characterization was carried out according to standards in force. Following the basic composites characterisation, P3 variant was chosen (70% PA/30% PC) to obtain the composites with compatibiliser (3-7%), simple and treated fibreglass (10-30%).

*Hardness*

Hardness decreases when adding the polycaprolactone or polyalkyloxazoline compatibiliser. When adding simple fibreglass,

Table 3: Physical-mechanical characterisation of the polymeric composites

Characteristic / Sample	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13
Hardness °Sh D SR ISO 7619-1:2011	77	78	75	78	80	78	81	79	80	80	81	82	81
Tensile strength, N/mm <sup>2</sup> , (SR ISO 37:2012)	15	19	21	24	27	31	26	38	23.8	31.7	40	38.6	47

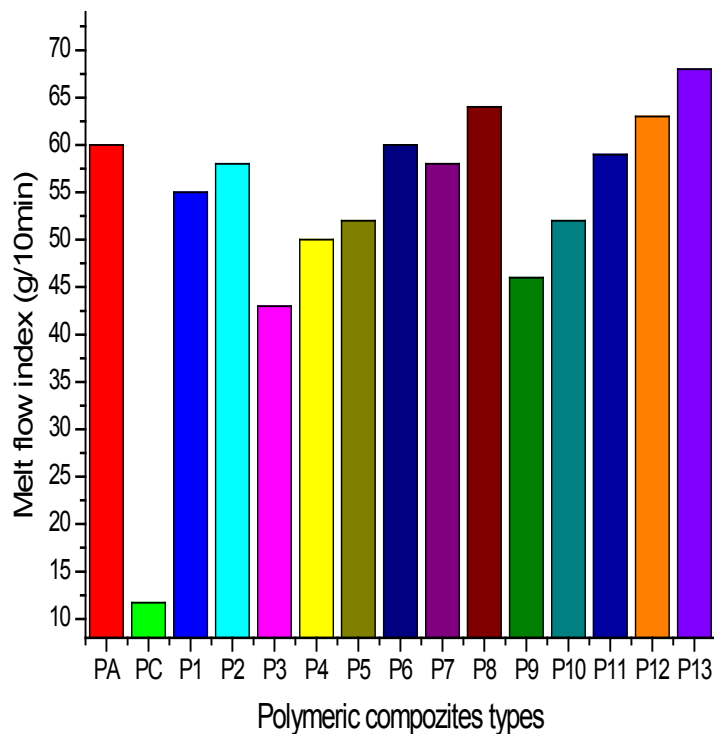


Figure 6. Melt flow index for polymeric composites

hardness increases but using the treated fibreglass instead, the hardness decreases by 1-2°Sh D. Thus, for the polymeric composites containing compatibiliser and treated fibreglass this property decreases by 2-3°Sh D.

#### Tensile Strength

Tensile strength decreases when mixing the elastomers, PA and PC, based on the ratio used between them. The addition of compatibiliser improves the tensile strength compared to P3 composites. With the addition of simple fibreglass tensile strength increases compared to P4 formulations. When using treated fibreglass with the compatibiliser, the value of tensile strength greatly improves. In that sense the composites P8 and P13 with 30% fibreglass show the best values of the tensile strength, of 38 N/mm<sup>2</sup> and 47 N/mm<sup>2</sup>, respectively.

#### Melt Flow Index

The materials used have different characteristics and properties, such as color, density, hardness, different processing temperature, etc. Thus, the melt flow index was determined at the same temperature, of 230°C,

and a pressure force of 5 Kg. The values of the melt flow index obtained for the polymeric composites processed in the Brabender mixer are shown in Figure 6.

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, the values obtained for PA were 60g/10 min and for PC, 11.7g/10 min. Melt flow index for the obtained composite materials varies widely between these two extremes, due to the base polymer ratio, absence/presence of compatibiliser, absence/presence and the type of fibreglass. Thus, the flow index of composites P1-P3 decreases with increasing percentage of PC. The addition of the polycaprolactone compatibilising agent in a proportion of 5% increases the melt index value from 43 to 50g/10min. While using the polyalkyloxazoline compatibiliser with the same amount of 5% increases the melt index value to 59g/10min.

This characteristic is important in establishing the processing parameters of the polymeric composites into finished products, on the industrial equipment.

## CONCLUSIONS

After testing the composite samples the following were found:

The compounds based on PA, PC thermoplastic polymers, compatibiliser and treated fibreglass have been selected because they will take advantage of the synergy of the two polymers such as chemical resistance, low water permeability, high temperature, flame, and impact resistance;

The composite sheets were obtained in an electrical heated press, by means of compression, between its plates, at a temperature of 220°C and at a pressure of 300 kN;

Developed formulations for polymer compounds (P1-P13) based on PA/compatibiliser/PC/fibreglass with different amounts of PA and PC (90, 70, 50, 30, 10), compatibiliser (polycaprolactone or polyalkyloxazoline) 5%, and fibreglass 10-30%.

Hardness decreases when adding the compatibiliser, and for the polymeric composites containing compatibiliser and treated fibreglass 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 compatibiliser improves the tensile strength compared to P3 composites. The composites P8 and P13 with 5% compatibilisers and 30% treated fibreglass show the best values of the tensile strength, of 38 N/mm<sup>2</sup> and 47 N/mm<sup>2</sup>, respectively.

Melt flow index ranges vary widely for the obtained polymeric composites. Thus, the flow index of composites P1-P3 decreases with increasing percentage of PC. The addition of the polycaprolactone compatibilising agent in a proportion of 5% increases the melt index value from 43 to 50g/10min. The usage of the polyalkyloxazoline compatibiliser with the same amount of 5%, increases the melt index value to 59g/10min.

The data presented show that the polyalkyloxazoline compatibilising agent favorably influences physical-mechanical and processing properties compared to polycaprolactone.

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