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Tensile characteristics for a class of polymeric blends (PP + PA6)

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Abstract. This paper presents the influence of component concentration of a class of polymeric blends with different concentration of PP and PA6 and a constant concentration of additives (CaCO₃, LDPE and an adhesive) Young's modulus does not have a clear tendency of depending on PA6 concentration and testing speeds, but performs in a band between 1500...1900 MPa, except for the value for PA6 at the lowest testing speed ($v=10$ mm/min), that is 1454.8 MPa. Under large testing speeds, there were cracks or voids towards the loading direction, forming large parallel 'empty channels'. Investigations are done on possible causes of these longitudinal voids in order to clear if they occur during molding or/and during testing and to eliminate them. Except for values at low testing speed, the average values for tensile stress at break perform in a band of less than 8 MPa. The elongation at break is less than 10% for all materials, except for PA6 at the lowest testing speed, when the highest value for this characteristic was obtained. The lowest values were obtained for material with 20% PA6. For blends with 60% and 80% PA6, the difference between values, at the same testing speed, is the smallest. Energy at break has a slightly increase with the concentration of PA6. From the mechanical point of view, among the formulated blends, material D (with 80% PA6) is the most promising as has the highest stress and energy at break (11.43 J at $v=10$ mm/min and 8.7 J at $v=1000$ mm/min), but values are still less than those for PA6.

1. About polymeric blends

Polymers have complex mechanical behavior and their blends could exhibit even more unexpected properties. This is the reason of testing and comparing data and having analyses that help engineers to avoid failure and to select the appropriate material for a particular application.

Some relevant works [1-5] underlined the close relationship between morphology of polymeric blend and its properties. Polymer blends could tailor the mechanical and thermal properties of polymeric materials, because the resulting mixtures keep some advantages of expensive polymers and shadow the non-desired features of low-cost one [6, 7].

Immiscible polymers blends exhibit sea-island morphologies with large droplet sizes and a lack of adhesion between components, as a result of the high interfacial tension between the two immiscible phases. Thus, these blends generally exhibit poor mechanical properties, since mechanical performance is a function of blend morphology and interfacial interactions. To overcome these issues, several



compatibilization strategies that include adding block copolymers, compatibilizing agents and nanoparticles have been developed in the last few decades [8].

Polypropylene (PP) and polyamide (PA6) are polymers still in the focus of research due to their properties. This introduction presents several studies that underline the interest in the blend containing one or both of these polymers. Polyamide/polypropylene (PA/PP) blends or composites are interesting because both components are relatively cheap (in 2018, PP was 1.50...3 \$/kg and PA6 was 1...5 \$/kg), with advantageous properties, and are processable by melt blending. The compatibilisation of binary polymer compounds may be made by adding graft copolymer, segments of which have physical or chemical affinity with two immiscible homopolymers.

The way to improve interface interaction of immiscible polymer blend is adding lowmolecular weight compatibilizers with “soft” nature, unfortunately with negative effects on the final mechanical strength. Shi [9] proposed an interfacial interlocking design strategy for immiscible polypropylene (PP)/polyamide (PA) blend.

Ruehle et al. [10] provided data on the physicochemical properties of a promising biorenewable blend system which exhibits the novel feature of thermodynamic miscibility Biorenewable polyamide-11 (PA11) is blended with partially biorenewable polyamide-6,10 (PA610) to produce thermoplastics of different carbon content. The two polyamides are fully miscible in the melt; the blends exhibit crystallization induced phase separation. Mechanical properties of the blends show intermediate values compared to the homopolymers; significant improvements in the properties of PA11 with the incorporation of 25wt% PA610 are pointed out.

Important dilatation is produced by plastic deformation under tension of neat PP and PP/PA6/POE blends, for which the POE to PA6 concentration ratio equals 1/2. The detailed mechanisms of this volume change are investigated by Bai [11]. At low alloy content, dilatation results from decohesion of PA6 particles from PP matrix. As the amount of PA6 and POE increases, voids are nucleated preferentially in the thicker POE interphase making a shell around the PA6 particles, and secondarily in isolated POE particles.

Recycled polyamide 6 (PA6) from post-industrial waste fibers (PIW) and carpet waste (PCW) indicate the presence of polypropylene (PP) in PCW. X-ray fluorescence and X-ray diffraction show that inorganic contaminants of PCW and PIW are calcium carbonate (CaCO_3) and titanium dioxide (TiO_2), respectively. Due to higher inorganic filler content, PCW exhibits higher melt viscosity and higher storage modulus than that of PIW. PIW has 20% higher tensile strength than that of PCW [12].

Yousfi [13] reported that for talc filled PP systems, the incorporation of both natural and synthetic talc improves their thermal stability. For talc-filled PP systems, the addition of synthetic talc slightly improves the elastic modulus, but induced an improvement in thermal stability of polypropylene matrix, the mechanical and thermal-related properties being positively affected by this surface treatment. If the highest mechanical reinforcement is obtained in the presence of natural talc, the best ductility is reached in the presence of synthetic talc. For PA6/talc systems, the mechanical properties varied depending on the surface free energy of talc. The strongest improvement in strength properties was for synthetic talc-filled PA6 nanocomposites. Its highly polar character and its ability to create strong acid–base interactions with the functional groups of polyamide 6 are the main reasons to explain the strong interfacial interactions generated between the synthetic talc and the polar matrix.

Wang et al. [14] studied the morphology of polypropylene (PP)/polyamide 66 (PA66) blend, with organoclay and maleic anhydride grafted polypropylene (MAPP). Without MAPP, a transition from typical sea-island morphology to coarse co-continuous morphology is observed when organoclay add relative to PA66 phase reaches 10 wt%. With 10 wt% of organoclay, the coarse co-continuous morphology is transformed to fine fibrillar and then to rod-like morphology with increasing MAPP contents. For PP/PA66 blend mixed at an asymmetric composition (70/30w/w), coarse co-continuous morphology can be formed by intermediate feeding PP into premelted PA66/10 wt% organoclay compound, instead of typical sea-island morphology for the case without organoclay. With organoclay content of 10 wt%, the coarse co-continuous morphology can be transformed to fine fibrillar and then to fine rod-like morphology by adding increasing amounts of MAPP.

Palacios et al. [15] investigated silica nanoparticles (NS) and polypropylene grafted with maleic anhydride (PPgMA) to stabilize morphology and improve properties of an immiscible PP/Nylon 6 blends. Blends of 80% PP and 20% PA6 with a fixed amount of PPgMA and different NS content were prepared by melt mixing. Two PPgMA compatibilizing agents with different grafting level and two modified NS, one hydrophilic and other hydrophobic, were employed. Despite the PA6 drop reduced size, the blends exhibited unsatisfactory mechanical performance. In the end, a PP/PA6 blend stabilized with 1.6% hydrophobic NS and compatibilized with high grafting level PPgMA exhibited a fine-tuned morphology with enhanced ductility and barrier properties. NS nanoparticles act as outstanding stabilizers but do not promote interfacial adhesion between the phases.

The nanocomposites PA/PP/PP-g-MA (polypropylene grafted with maleic anhydride)/graphene oxide were characterized by Alexandrescu et al. [16]. The blends with initial proportion PA6/PP of 270/30 were produced by injection, for bearing seals, contact plates and components for railways, with shock resistance higher than 5-8 kJ/m², wear resistance, resistance to temperatures of -40...240°C, with environmental temperatures from -40 to 60°C, in rain, snow or sunshine. The value of tensile strength of nanocomposites increases compared to the value of polyamide and PA/PP-g-MA/PP blend. Graphene oxide concentrations higher than 1% lead to decrease the shock resistance (Izod method). Percentages in the range 0.1-1% lead to maximum values of physical mechanical parameters.

Properties of PA + PP blends have also been reported by [17-19].

Immiscible blends of 80 wt% polypropylene (PP) with 20 wt% polyamide (PA) or polycarbonate (PC) were prepared by melt mixing with or without the addition of 5% nanosilica. The nanosilica produced a strong reduction of the disperse phase droplet size, because of its preferential placement at the interface. PP developed spherulites, whose growth was unaffected by blending, while its overall isothermal crystallization kinetics was strongly influenced by nucleation effects caused by blending. Addition of nanosilica resulted in an enhancement of the strain at break of PP+PC blends whereas it was observed to weaken PP+PA blends [20].

The morphology of immiscible 80/20 polypropylene/polyamide 6 blends that contain different types of nanosilica and a compatibilizer agent was correlated with their linear and non-linear rheological behavior. Polypropylene grafted with maleic anhydride (PPgMA) was used as compatibilizer agent. Two types of modified silica nanoparticles were added in blends, one hydrophilic (NSE) and the other hydrophobic (NSH). The size of PA droplets was reduced 12 times when the compatibilizer agent was added; and 25 times when hydrophobic nanosilica (NSH) was additionally included in the formulation [21].

2. Materials

All samples were prepared by melt extrusion in molding machine at ICEFS Savinesti Romania. Details of the molding technology is presented in another work [6], [7]. The component concentration of tested materials are given in Table 1.

Table 1. Symbols of formulated materials

	PA6	PP	LDPE	CaCO ₃	POLYBOND adhesive
Composition [wt%]					
PA6	100	-	-	-	-
A	20	65	5	7	3
B	40	45	5	7	3
C	60	25	5	7	3
D	80	5	5	7	3
PP	-	100	-	-	-

3. Tensile properties of the formulated blends

Bone samples made of neat polymers (PP and PA6) and blends with different concentrations of these polymers were tested in traction (see Figure 3 for samples tested at speed of 1000 mm/min). Figures 1 and 2 give the aspect of stress–strain curves for each tested polymeric material, for two different testing speeds.

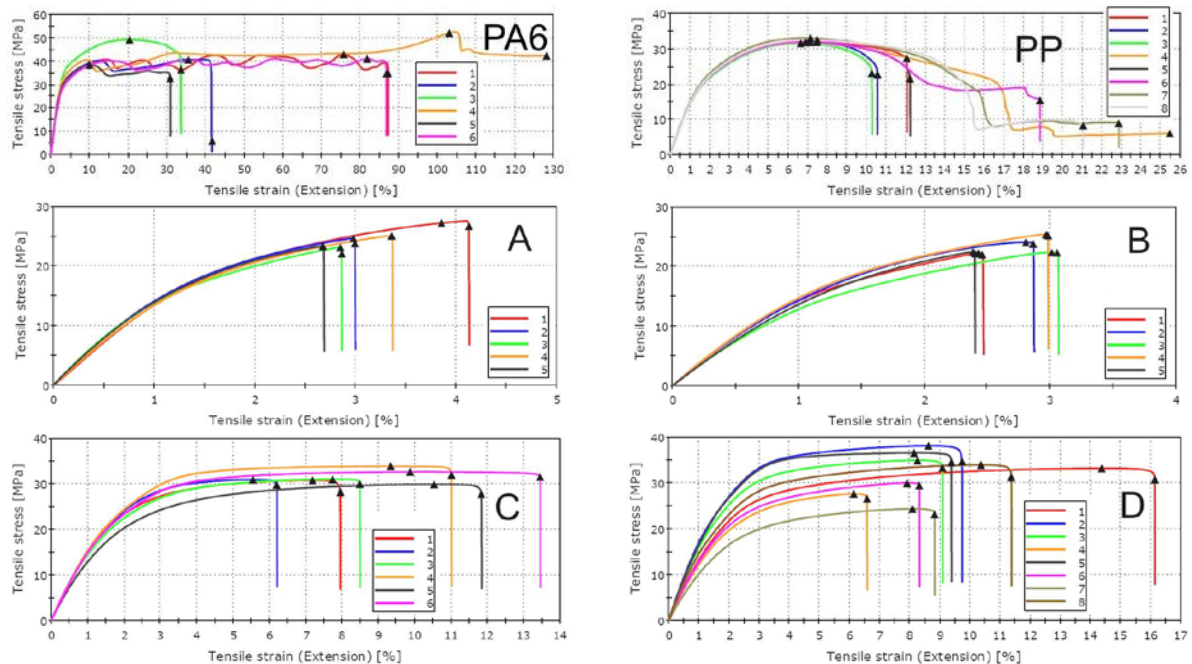


Figure 1. Strain - stress curves for all materials, tested at speed $v=10$ mm/min

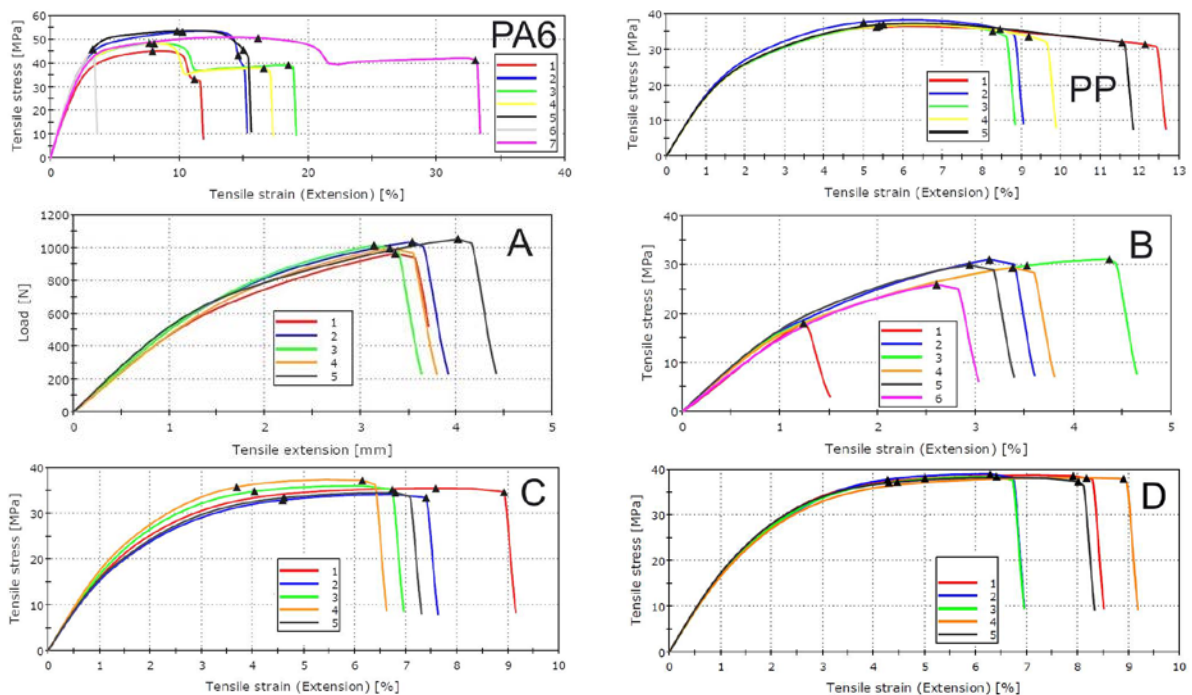


Figure 2. Strain - stress curves for all materials, tested at speed $v=500$ mm/min

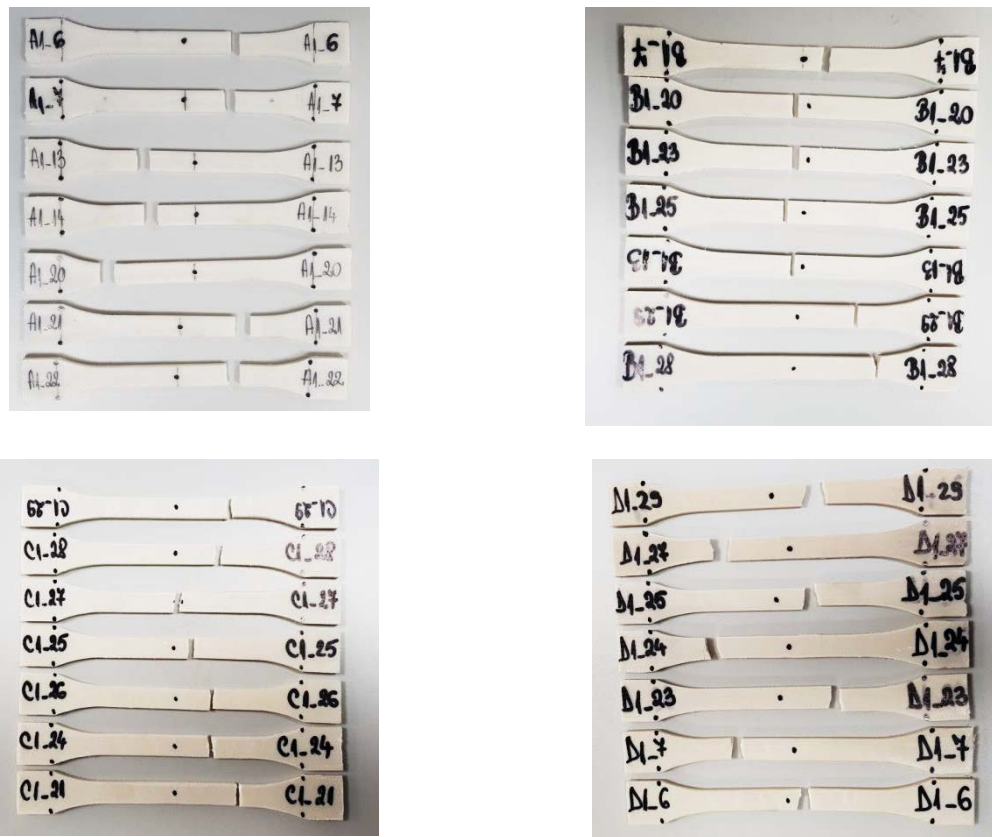


Figure 3. Samples broken in tensile tests, at testing speed of 1000 mm/min (The capital letter designates the material as in Table 1.)

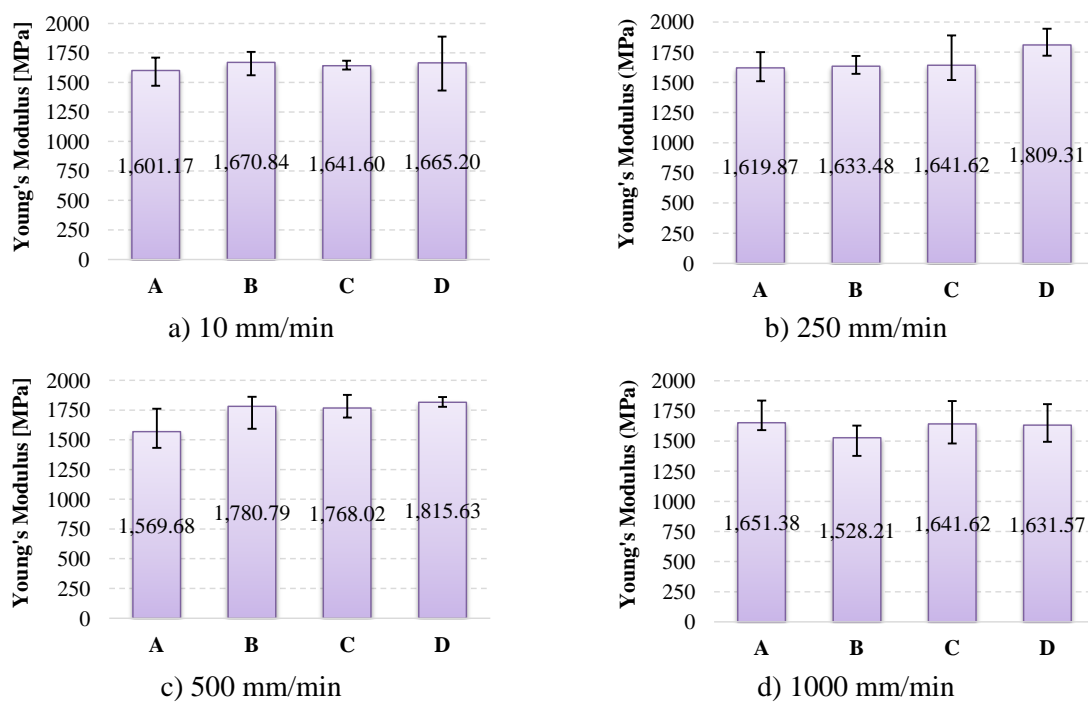


Figure 4. Young modulus for all formulated blends at different testing speeds

Taking into account the stress–strain curves, both neat polymers have exhibit a dual behavior at the lowest testing speed ($v=10$ mm/min). For PA6, some samples were broken at 30...40% strain but others were broken after 87...130%. PP has several samples broken at 10...15%, others at higher values (till 17...25%) with an intermediate plateau of stress between 10...20 MPa. At low concentration of PA6 (20...40% wt, materials A and B), the curves are very close and the strain at break has values in a narrow range (1.5% for 20% PA6 and less than 1% for 40% PA6). For higher contents of PA6 (materials C and D), the curves are similar, but spread on a larger space. At the testing speed of $v=500$ mm/min (Figure 2), PP have the curves almost overlapping and PA6 exhibit a distribution more distinct for each sample, with plateaux of stress at approximately 40 MPa.

The tensile properties of polymeric blends, obtained from averaging at least 5 valid tests, are summarized in Figures 4 to 7.

Young's modulus does not spectacularly depends on blend concentration in PP and PA6, but, unexpectedly, this characteristic is less sensitive for $v=10$ mm/min and $v=1000$ mm/min. For the intermediate test speeds ($v=250$ mm/min and $v=500$ mm/min) there is a slight tendency of increasing it with the PA6 content. Thus, the concentration of components has no evident influence on this mechanical characteristic. For the same testing speed, the greatest difference in this parameter was obtained when comparing material A to material D at $v=500$ mm/min (15.67%).

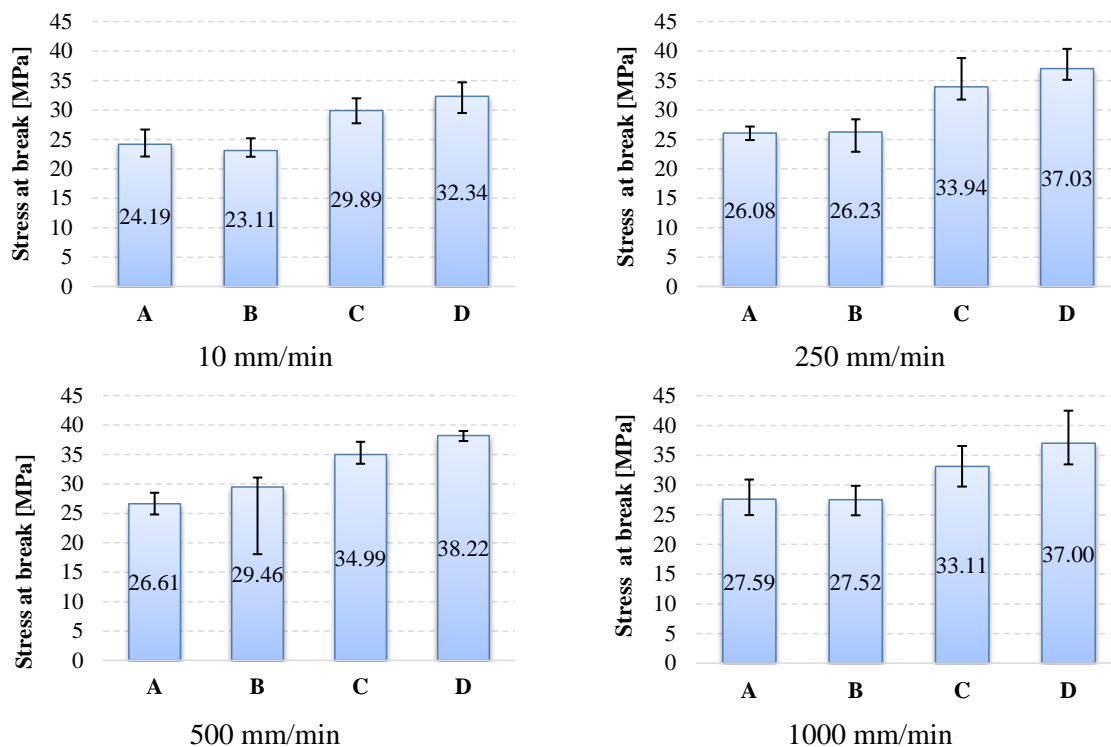


Figure 5. Stress at break for all formulated blends at different testing speed

Stress at break (Figure 5) grouped the results. Blends A and B (with low PP content) have lower values and blends with high content of PA6 (C and D) are higher. Comparing A to D, this characteristic is higher for the latest with 26% at $v=10$ mm/min, 41.9% at $v=250$ mm/min and $v=500$ mm/min, 34.1% for the highest testing speed ($v=1000$ mm/min). But the differences between C and D for this characteristic are smaller. D has the same value (37...38 MPa) for all testing speeds, except for the smallest one.

Bai et al [11] explained the behavior of their blends of PP/PA6/POE by: the increasing contribution of PA6 that intrinsically deforms with less cavitation than PP, the post-cavitation rubber-like stretching of POE particles and the early formation of a percolating network of shear bands from the diffuse array

of voids formed after the yield point. These mechanisms explained the gradual increase of the resistance to impact of the PP/PA6/POE as their alloying content is increased.

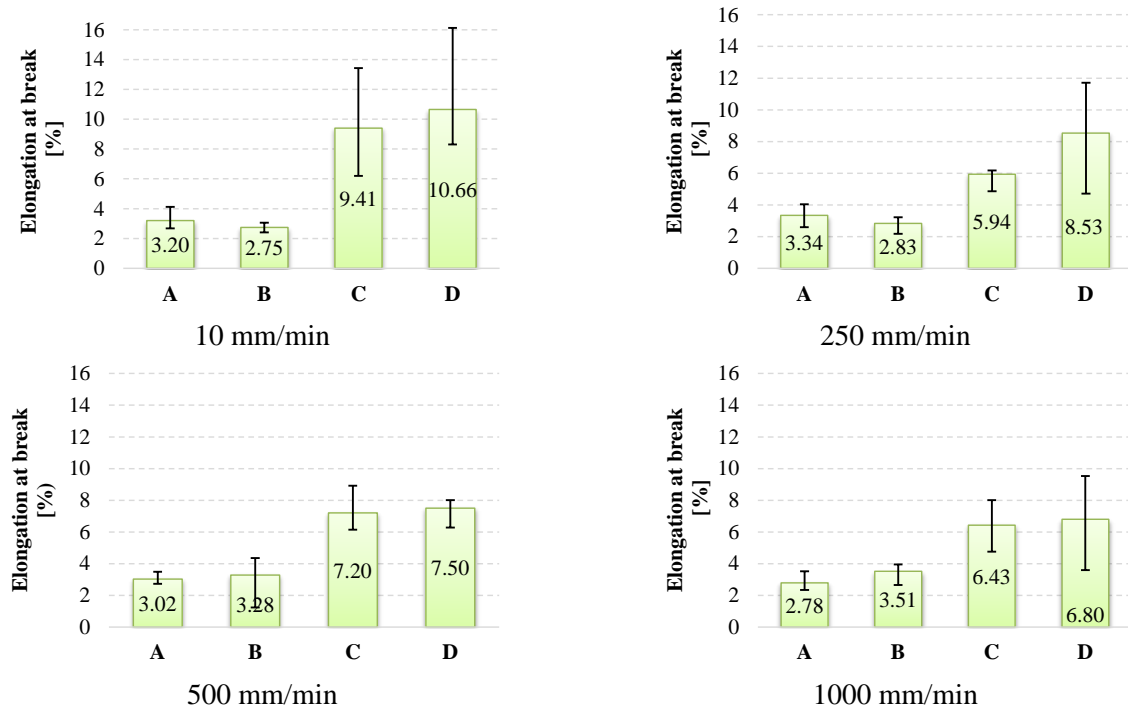


Figure 6. Elongation at break for all formulated blends at different deformation rate

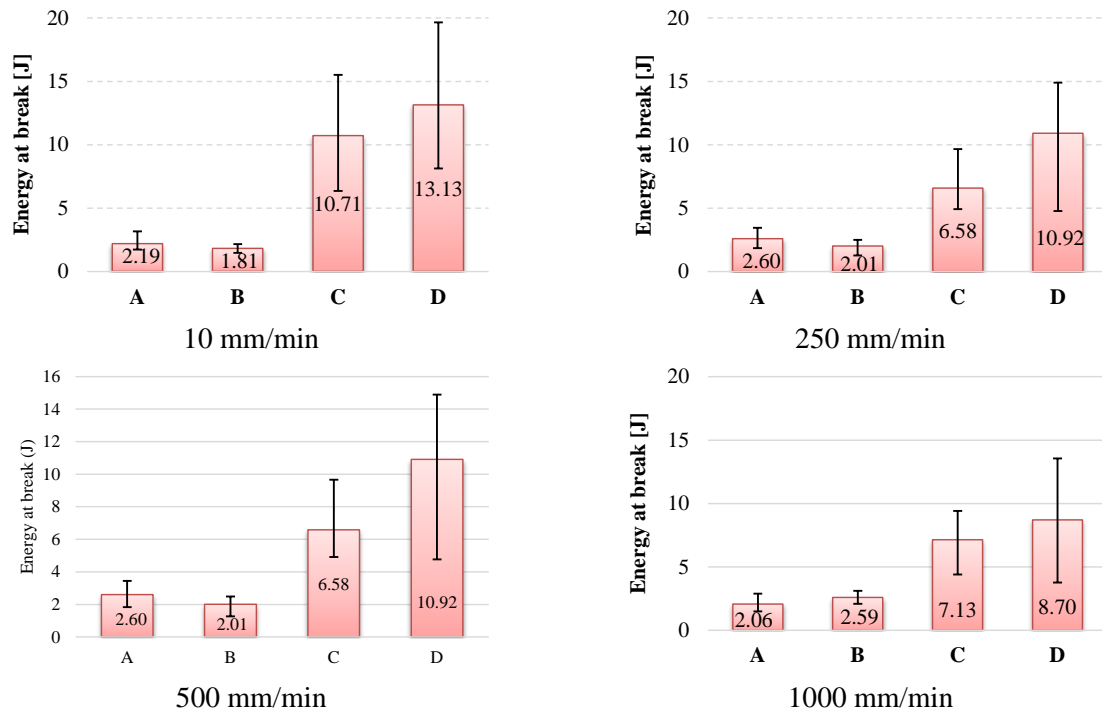


Figure 7. Energy at break for all formulated blends at different testing speeds

Elongation at break also grouped the blends in two classes (Figure 6):

- materials A and B have low values (2.75%...3.51%), slightly decreasing with the testing speeds,
- materials C and D with higher values.

Energy at break (Figure 7) also makes distinctive the same groups of materials: A and B with lower values (2.75 J... 3.51J) and the group of materials C and D with higher values and a more pronounced dependence on testing speed.

For PA6, at testing speeds of 250 mm/min to 1000 mm/min, the Young's modulus is insensitive to deformation rate (Figure 8). Young's modulus does not have a clear tendency of depending on PA6 concentration and testing speeds, but performs in a band between 1500...1900 MPa, except for the value obtained for PA6 at the lowest testing speed ($v=10$ mm/min), that is 1454.8 MPa. For PP and PA6 there were obtained the lowest values at testing speed $v=10$ mm/min. For the blends, the dependence of Young's modulus on the testing speed and PP/PA6 concentrations is weak.

Under large testing speeds, the cracks are turned towards the loading direction, forming large parallel 'empty channels'. Investigations are needed on possible causes of these longitudinal voids in order to clear if they occur during molding or/and during testing and to eliminate them.

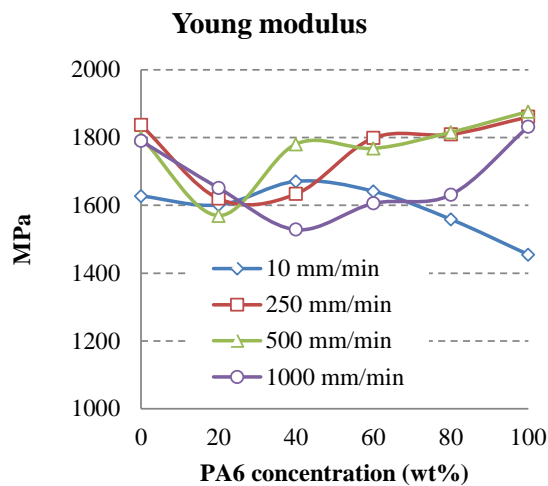


Figure 8. The Young's modulus as function of PA6 concentration and testing speed

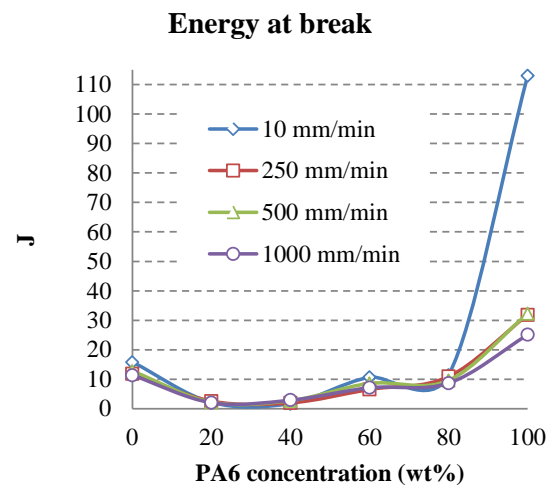


Figure 9. The energy at break as function of PA6 concentration and testing speed

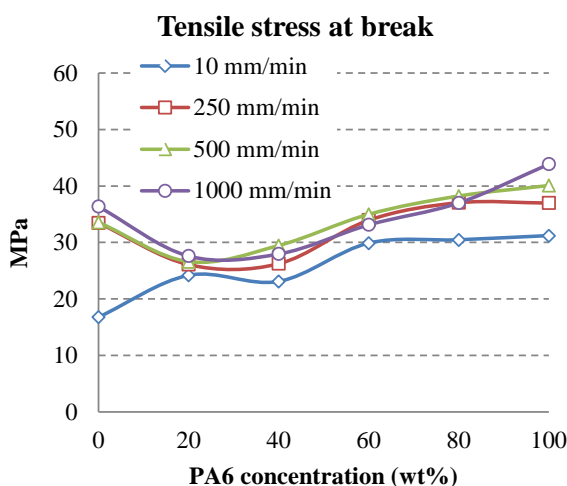


Figure 10. The tensile at break as function of PA6 concentration and testing speed

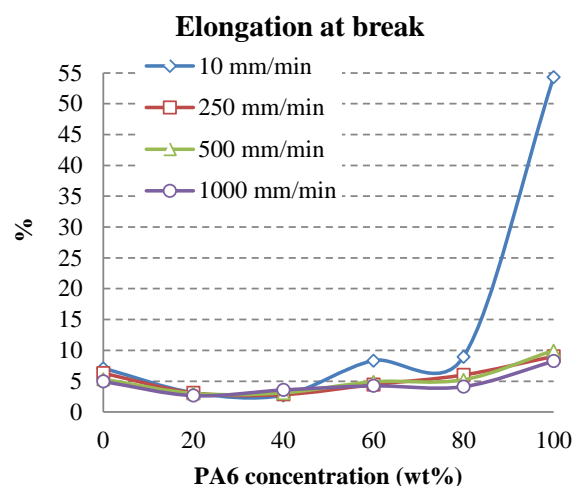


Figure 11. The elongation at break as function of PA6 concentration and testing speed

Energy at break is high only for PA6 at the lowest testing speed ($v=10$ mm/min). For PP, this characteristic has only a variation of 28.2% having as reference the value for $v=10$ mm/min. Each of designed materials has the values for the energy at break very concentrated, in spite of very different testing speeds. Analyzing Figure 9, one may notice a slightly increase of this characteristic with the concentration of PA6. The value of energy at break for material D (80% PA6), which has the highest values of this characteristic among the formulated blends, is three or four times smaller than those obtained for PA6.

Except for values at the lowest testing speed ($v=10$ mm/min), the average values for tensile stress at break perform in a band of less than 8 MPa, these being hard to be ranked based on testing speed (Figure 10).

The elongation at break is less than 4% for materials with 20% and 40% PA6, between 6 and 10% for the materials with 60% and 80% PA6. The lowest values were obtained for A (with 20% PA6). For C and D, the difference between values, at the same testing speed, is the smallest.

4. Conclusion

From the mechanical point of view, among the formulated blends, material D (with 80% PA6) is the most promising as has the highest stress and energy at break (11.43 J at $v=10$ mm/min and 8.7 J at $v=1000$ mm/min), but values are still less than PA6.

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