Polymer sand composites based on the mixed and heavily contaminated thermoplastic waste

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Abstract. This paper represents production and characterization of highly filled polymer composites based on recycled plastics and sand as a filler. Composites produced on the bases of polyolefin (polyethylene PE and linear low-density polyethylene LLDPE) and polyester (PET) were compared. Different modification techniques, including filler surface treatment, compatibilizer introduction and polymer blend formation were used. Influence of the composition on the composite mechanical properties was evaluated. Newly developed composite based on PET – polycarbonate (PC) blend demonstrates improved mechanical properties and higher thermal stability compared to polyolefin based composites.

1. Introduction
One of the most adverse result of human activities is formation waste plastic. More than 400 different kinds of industrial and domestic plastic wastes are known and many of those are identified as mixed plastic waste, which is not recycling friendly [1]. Recycling of mixed plastic waste is very important topic with great environmental and industrial influence. Today recycling options for mixed plastic are incineration, landfilling and mechanical recycling from which mechanical recycling is sustainable and can be economically profitable. A challenge for recycling technology is highly contaminated and mixed plastic waste. Finding recycling option for this type of waste is dramatically important task.

The main part of the heavily contaminated waste consists of such as polymers: polyolefins (PE&PP), polyesters (PET&PET-G), chlorinated polymers, like polyvinylchloride (PVC), and styrenics (PS, ABS). Mixed polyolefin waste can be used for formation of composites, including polymer-wood and highly filled composites. For mixed and highly contaminated polyesters recycling options include chemical depolymerization and advanced sorting technics. Development of simple mechanical process for such type of raw material is seen to have great industrial importance. Highly filled polymer composites based on mixed waste plastics and sand called as “polymer sand composites” normally have low mechanical and thermal properties, which significantly limits their application [2-3]. The aim of current study is to develop highly filled composites based on polymer binder in combination with different modification techniques.
2. Experimental
This study deals with highly filled polymer composites based on mixed mixed polymer waste.
Following types of raw materials were used: polyethylene “Polimir” ™ PE-15803-020 (MFI=2-3),
linear low density polyethylene “ExxonMobil ™ LLDPE LL4004EL, industrial grade recycled PE
waste based on stretch film (R-LLDPE) (LLDPE modified with tactile additive) (MFI=3-4), virgin
PET type 8200 (IV=0,8), industrial grade recycled PET (R-PET) (IV=0,7), extrusion grade PET
glycol, PET-G, Skygreen S2008, polycarbonate TRIREX 3020U (PC), maleic anhydride grafted
polyethylene copolymer (PEgMA), which was synthesized in the laboratory, functional silan
Dynasylan® AMEO from “Evonik” ™. As
filler, purified and dried sand was used after 75 mesh sieve
classification.

2.1. Material preparation and testing
Before composite preparation all polymers were grinded to powder with average particle size 200 –
300 micron to facilitate homogenous mixing with the filler. Polymer components were dried in hot air
oven at following conditions: PET – 8 hours at 150°C, PC and PET-G – 6 hours at 100°C, PE-g-MA –
2 hours at 60°C. Sand with a particle size from 0.2 mm to 1.2 mm was dried until constant weight
before use. Silane treatment of sand was carried out in drum mixer by 5% aqueous solution of silane
followed by drying in air oven. PE-g-MA copolymer was obtained by reactive extrusion in 22 mm
laboratory twin-screw extruder. Powdered PE was pre-mixed with 2.0 weight % of initiator – dicumyl
peroxide (DCP) in high speed mixer and 3.0% of maleic anhydride. The resulting ternary system was
subjected to extrusion at 130-160°C to obtain pellets. Then the pellets were dried under vacuum to
remove volatiles. Degree of grafting, measured by titration, was in range from 1.2 to 1.3%.

The polymer-sand composite materials were obtained in two ways. By the first way, the polymer
powder and filler were mixed at room temperature and then, heated in muffle furnace at 250 - 270°C
for 10 - 15 minutes and mixed in the heated twin rotor mixer. In the second case - polymers were
melted in the single screw extruder and then fed in the twin blade mixer with hot sand by keeping the
mixing time mixing time from 3 to 10 minutes. After mixing soft polymer-sand composite (PSC) was
compression molded in hydraulic press.

Testing samples were mechanically milled or cut from bulk part produced by compression
molding. The density (ρ) was determined according to GOST 15139. Bending strength (σb) was
determined according to GOST 9550, while tensile elongation and strength were determined according
to GOST 11262. Heat deflection temperature (HDT) was determined according to GOST 15088
(comparable to ISO 306). Melt flow index of composite material was determined at weight of 21.6 kg.

3. Results and discussion
In the study properties of PSCs based on polyolefins and polyesters were compared. Initially, for
comparison basic composite samples were made by using neat polyolefin as binder. Basic properties
of PSCs based on polyolefin binder are listed in the Table 1.

With increase of filling degree from 50% to 80% decrease in tensile strength and increase in
compressive and bending strength is observed. From technological point of view R-LLDPE based
compositions have certain advantages because of higher flow and plasticity which results in easier
manufacturing. Advantage of R-LLDPE based compositions is also greater flexibility. In general
mechanical properties and HDT of polyolefin PSC are low which results in non-demanding
application of such material. Current industrial practice shows that it is possible to produce large,
heavy, parts thickness parts for non-demanding application like floor tiles, grooves and so.
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Table 1. Properties of polyolefin PSCs

| Polymer binder | Filling degree, mass % | Density (ρ), kg/m³ | Bending strength (σb), MPa | Tensile strength (σt), MPa | Tensile modulus, Eρ, MPa | MFI, g/10 min | HDT, °C |
|----------------|------------------------|--------------------|-----------------------------|---------------------------|--------------------------|--------------|--------|
| PE-158         | 50                     | 1650               | 21                          | 12.5                      | 16.1                     | 850          | 3.1    | 87    |
| PE-158         | 65                     | 1720               | 24                          | 8.4                       | 14.4                     | 900          | 1.6    | 92    |
| PE-158         | 80                     | 1950               | 30                          | 5.3                       | 12.2                     | 1300         | 1.2    | 97    |
| LLDPE          | 50                     | 1630               | 19                          | 14.2                      | 15.6                     | 790          | 2.8    | 87    |
| LLDPE          | 65                     | 1745               | 21                          | 9.5                       | 15.2                     | 900          | 1.9    | 91    |
| R- LLDPE       | 50                     | 1635               | 16                          | 15.4                      | 17.2                     | 550          | 4.3    | 75    |
| R- LLDPE       | 65                     | 1768               | 20                          | 11.3                      | 16.4                     | 750          | 3.1    | 84    |
| R- LLDPE       | 80                     | 1925               | 28                          | 7.6                       | 14.6                     | 1050         | 2.1    | 86    |

Usage of PET or PET-G as polymer matrices provides a possibility to produce composites with improved mechanical properties and higher temperature resistance. Manufacturing of polyester PSCs was carried out at relatively higher temperature (260 – 270°C) resulting in enhanced flow of the melted composition. Because of PET crystallization process, which occurs during cooling of the molded part such PSCs are much more rigid and heat stable. For amorphous PET-G based compositions heat stability is much lower that for PET based systems. Table 2 shows properties of PSCs based on thermoplastic polyesters. In comparison to polyolefin type PSC, polyester PSCs show advanced mechanical properties and thermal stability. HDT and mechanical strength of PET and R-PET based composites are more than two times higher than for polyolefin PSC. Possible explanation of behavior is better wetting of filler particles with PET melt and specific strength of polymer matrix. Amorphous PET-G composites demonstrate similar mechanical properties but much lower HTD. PET and R-PET composites, however, are more brittle than PET-G based systems PET-G.

Table 2. Properties of polyester PSCs

| Polymer binder | Filling degree, mass % | Density (ρ), kg/m³ | Bending strength (σb), MPa | Tensile strength (σt), MPa | Tensile modulus, Eρ, MPa | MFI, g/10 min | HDT, °C |
|----------------|------------------------|--------------------|-----------------------------|---------------------------|--------------------------|--------------|--------|
| PET            | 50                     | 1840               | 74.2                        | 4.4                       | 31.3                     | 1858         | 12.6   | 210   |
| PET            | 65                     | 2150               | 85.4                        | 3.5                       | 30.5                     | 2250         | 8.3    | 215   |
| PET            | 80                     | 2350               | 105.2                       | 2.1                       | 24.6                     | 2500         | 6.4    | 225   |
| R-PET          | 50                     | 1920               | 72.5                        | 3.3                       | 26.4                     | 1950         | 14.5   | 216   |
| R-PET          | 65                     | 2205               | 86.4                        | 2.2                       | 24.3                     | 2300         | 12.1   | 225   |
| R-PET          | 80                     | 2390               | 92.6                        | 2.6                       | 28.2                     | 2650         | 13.0   | 220   |
| PET-G          | 50                     | 1730               | 76.4                        | 8.3                       | 31.5                     | 1650         | 9.2    | 95    |
| PET-G          | 65                     | 1950               | 77.3                        | 6.5                       | 36.3                     | 1800         | 6.3    | 98    |
| PET-G          | 80                     | 2150               | 87.4                        | 5.7                       | 34.7                     | 1950         | 4.5    | 102   |

Further study was focused on investigation of influence of filler surface modification on PSC properties. Initially silane coupling agent was dispersed in water (5 mass% aqueous dispersion) and stored for 1 hour to promote hydrolysis. Then sand was treated with silane-water suspension (3 mass % from the sand content) and mixed for 30 min. in a tumble mixer. Finally silane treated sand was dried in an oven at 80°C. Properties of silane treated sand modified PSCs are shown in the table 3.
Table 3. Properties of surface treated PSC

| Binder polymer | Filling degree, mass % | Density (ρ), kg/m³ | Bending strength (σb), MPa | Tensile elongation, % | Tensile strength, (σt), MPa | Tensile modulus, (E_p), MPa | MFI, g/10 min | HDT, °C |
|----------------|------------------------|-------------------|---------------------------|----------------------|---------------------------|---------------------------|--------------|--------|
| R-PET          | 65                     | 2160              | 89                        | 5.4                  | 26.5                      | 2400                      | 14.6         | 221    |
| R-PET          | 80                     | 2380              | 98                        | 3.7                  | 32.3                      | 25000                     | 16.5         | 220    |
| PETG           | 65                     | 1970              | 68                        | 8.2                  | 36.5                      | 1700                      | 7.8          | 97     |
| PETG           | 80                     | 2145              | 76                        | 6.4                  | 36.5                      | 1890                      | 7.5          | 100    |

Silane treated PSC show enhanced mechanical properties, which can be due to interfacial adhesion between filler and polymer matrix.

Another way of modification of PSCs is by enhancing polymer matrix adhesion to filler by using of compatibilizing agent. Graft copolymers of PE with maleic anhydride are common adhesion promoters between filler and polymer matrix.Compatibilizer was premixed with polymer matrix by using single screw extruder, then granulated and used for composite forming. Table 4 shows properties of polyester and polyolefin PSCs modified by graft copolymer. Modification lead to some properties enhancement like tensile strength and most, especially, elongation that increased simultaneously with compatibilizer loading level. The most visible property enhancement occurs in the case of polyolefin-based system, which can be associated with good interaction of PE158 with polyethylene backbone of the compatibilizer. Introduction of PEGMA also lead to reduction of melt viscosity and improvement of surface finish of the test specimens.

Table 4. Properties of PEGMA modified PSC

| Polymer binder | Filling degree, mass % | Density (ρ), kg/m³ | Bending strength (σb), MPa | Tensile elongation, % | Tensile strength, (σt), MPa | Tensile modulus, (E_p), MPa | MFI, g/10 min | HDT, °C |
|----------------|------------------------|-------------------|---------------------------|----------------------|---------------------------|---------------------------|--------------|--------|
| PET-G + PEGMA-2% | 65                     | 1920              | 68.2                      | 11.5                 | 37.3                      | 1650                      | 8.4          | 101    |
| PET-G + PEGMA-2% | 80                     | 2095              | 79.4                      | 9.5                  | 35.4                      | 1900                      | 9.2          | 103    |
| PET-G + PEGMA-5% | 65                     | 1930              | 64.3                      | 14.4                 | 34.7                      | 1700                      | 9.2          | 101    |
| PET-G + PEGMA-5% | 80                     | 2080              | 80.5                      | 11.3                 | 34.3                      | 1950                      | 10.8         | 102    |
| PE158 + PEGMA-2% | 65                     | 1730              | 23.6                      | 18.5                 | 13.6                      | 800                       | 3.5          | 93     |
| PE158 + PEGMA-2% | 80                     | 1920              | 25.4                      | 7.6                  | 21.4                      | 1350                      | 2.3          | 98     |
| PE158 + PEGMA-5% | 65                     | 1705              | 23.3                      | 21.3                 | 14.5                      | 900                       | 4.8          | 93     |
| PE158 + PEGMA-5% | 80                     | 1960              | 24.5                      | 11.2                 | 15.6                      | 1300                      | 2.5          | 99     |

Another way of modification of PSCs is formation of matrix from polymer blends. For this purpose bisphenol polycarbonate (PC) was used, mainly, because of good technological compatibility with PET. In the chosen processing temperature range PC and PET have similar values of melt viscosities and both are readily available in post-consumer polymer waste stream. Properties of PSCs based on PC/PET blend are summarized in Table 5.

Introduction of PC into PET matrix leads to great mechanical property enhancement and allows stable production of composite with 90% filling level. For experimental reason recycled PC
derived from CD\DVD discs was also used for modification of PSCs. Obtained results shown similar modification efficiency as virgin PC.

Table 5. Properties of PSCs based on PC/PET blend

| Polymer binder | Filling degree, mass % | Density (ρ), kg/m³ | Bending strength (ob), MPa | Tensile elongation, % | Tensile strength, (ot), MPa | Tensile modulus, Eₚ, MPa | MFI, g/10 min | HDT, °C |
|----------------|------------------------|-------------------|---------------------------|----------------------|-----------------------------|-----------------------------|----------------|--------|
| PET +PC 5%     | 65                     | 2130              | 92.3                      | 4.3                  | 39.1                        | 2400                        | 9.2            | 211    |
| PET +PC 5%     | 80                     | 2450              | 118.6                     | 3.5                  | 31.3                        | 2700                        | 5.6            | 220    |
| PET +PC 5%     | 90                     | 2750              | 91.2                      | 1.2                  | 21.5                        | 3000                        | 3.2            | 225    |
| PET +PC 10%    | 65                     | 2170              | 105.5                     | 6.3                  | 46.5                        | 2500                        | 9.5            | 201    |
| PET +PC 10%    | 80                     | 2380              | 123.4                     | 4.7                  | 33.7                        | 2700                        | 6.2            | 212    |
| PET +R-PC 10%  | 80                     | 2420              | 118.4                     | 4.2                  | 30.2                        | 2750                        | 7.3            | 214    |

4. Conclusion

Introduction of PC or RPC into PSCs leads to the greatest property enhancement over other modification techniques and can be simply realized in existed production flow. Recycled PC is readily available and is inexpensive, if the waste stream is contaminated, like CD\DVD discs waste. This modification technology of PSCs has great economic perspectives and will be target for future study. In the case of polyolefin PSCs properties enhancement occur if graft copolymer is added but economical application is possible only with own copolymer production.

Polymer sand composites based on contaminated polyester waste have much higher properties in comparison to the systems based on polyolefines. Application of such composites allows to produces thinner and lighter parts with high rigidity and excellent thermal stability. They claim attention for further detailed scientific and industrial investigation and implementation.

5. References

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