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# The Influence of Recycling on the Properties of Wood Fibre – Plastic Composites

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Abstract: The manufacture of composites offers the greatest flexibility to convert and utilize waste plastics, paper and wood into high-value products. This paper reports on two studies regarding the recycling of these materials. In one study, recycling was simulated by regrinding and injection-moulding composites of polypropylene (PP), polyethylene (PE) and old newsprint (ONP) eight times. The results indicated that reprocessing had only minor deleterious effect on the mechanical properties (tensile and flexural). The viscosity of neat PP decreased with repeated recycling indicating some thermo-oxidative degradation. The overall rheological character of PP composites did not change much. PE composites, on the other hand, showed increasing melt flow with reprocessing. The second study examined the effects of various coupling agents on the properties of multicomponent PP composites. Maleated polypropylene (MAPP) was the most effective coupling agent.

## INTRODUCTION

Public interest in recycling has risen dramatically in recent years. Concerns over availability of landfill sites, dwindling non-renewable resources and mismanagement of renewable forest resources has resulted in widespread criticism of industry and government. Plastics have been frequently made a focal point in waste management concerns, yet they are only about 7 wt.-% of municipal solid waste (MSW). By far the largest components of MSW are paper and cardboard (36 wt.-%), followed by yard waste (20 wt.-%) and metals (10 wt.-%). In MSW, the plastic stream consists of approximately 75 wt.-% polyethylene (PE), 12 wt.-% poly(ethylene terephthalate) (PET) and 13 wt.-% other plastic types. Since waste plastics and paper make a significant component of the waste stream, the manufacture of composites consisting of lignocellulosic fibres and thermoplastic matrix polymers offers a unique opportunity to recycle these materials into industrially useful products (Refs.1-5).
The decomposition temperature of cellulose (about 220 °C) places an upper limit on the processing temperature of wood – plastic composites. Fortunately, PP- and PE-based cellulosic composites may be processed below this limit. A significant advantage of wood – plastic composites is that they can be melt-processed (Refs.2-6). One of the most effective melt-blending technologies are the high-intensity thermokinetic mixers. Turbine mixers effectively disperse wood fibres in molten plastic in a relatively short time. The resulting compounds may then be processed by conventional plastics technology such as injection moulding, extrusion and calendering. Melt-blending of hydrophobic polymers (e.g., PP and PE) with hydrophilic wood fibres is significantly aided by the addition of appropriate coupling agents (e.g., maleated PP and PE). This paper reports the results of two experimental studies on recycling of thermoplastic polymers into wood fibre – plastic composites.

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# EXPERIMENTAL

## Recyclability

The objective was to investigate the effects of repeated recycling on the properties of wood fibre – polyolefin composites. Himont Profax PP(6301) and DuPont S Clair HDPE (290 9) polymers were used as matrices. Hammer-milled old newspaper (ONP) fibres were used as filler. The study involved the use of the following processing aids: maleated polypropylene (MAPP-Epolene E-43) and 3 wt.-% of maleated polyethylene (MAPE-C-18) were added to each composite formulation. In addition, 0.2 wt.-% of an antioxidant (Irganox 1010) was added to some composite formulations. The following composite formulations were prepared:

| | | |
|---|---|---|
| 100 % polymer (control) | referred to as | 100-PP (or PE) |
| 100 % polymer with antioxidant | | 100-PP (or PE) -AO |
| 85 % polymer – 15 % fibre | | 85-PP (or PE) |
| 70 % polymer – 30 % fibre | | 70-PP (or PE) |
| 70 % polymer with antioxidant | | 70-PP (or PE) - AO |
| 55 % polymer – 45 % fibre | | 55-PP (or PE) |

In the compounding step, the fibres (plus wetting agent) were allowed to disperse in a high shear K-mixer (Werner and Pfleiderer Gelimat G-1) for 15 s after which the resin and additives were added. The settings for the K-mixer were as follows:

| | |
|---|---|
| Low temperature | 180 °C for PP (185 °C for PE) |
| High temperature | 185 °C for PP (190 °C for PE) |
| rpm | 3300 for PP (2820 for PE) |
| Tip speed | 22.8 m/s for PP (19.5 m/s for PE) |

Following thermokinetic mixing, the compounds were separated, allowed to cool and then granulated in a Brabender granulator (model S-10-0). The granulated material was then injection-moulded into ASTM test specimens using an Engel ES-80 injection-moulding machine. The settings for the machine were as follows:

| | | | |
|---|---|---|---|
| Nozzle | 60 % | Injection time | 15.0 s |
| Zone 2 | 205 °C | Cooling time | 20.0 s |
| Zone 2 | 205 °C | Mould open time | 2.0 s |
| Zone 3 | 205 °C | Ejector time | 2.0 s |

The samples were tested in accordance with ASTM standard (D 638M-89, D 790-86, and D 1238-89) for tensile, flexural and melt index properties. Recyclability was simulated by reprocessing and testing the materials up to eight times.

## Recycling Multicomponent Mixtures

The objective was to investigate the properties of multicomponent composites containing recycled polymers and various coupling agents. Compression-molded sheets of polypropylene were granulated in a laboratory grinder and used as recycled PP. Wood fibre was old newsprint (ONP) which was obtained by repulping in a hydropulper and then milled to obtain an average fibre length of 5 mm and aspect ratio of about 120. Styrene – maleic anhydride copolymer (SMA) was obtained from a commercial source and contained about 4% of maleic anhydride. Four coupling agents used were titanates containing amine group as an additional functionality, maleated PP, amine-containing silane and a polyurethane prepolymer. Amine functionalities were selected to introduce acid-base interaction by modifying the surface of fibre. The mixing was carried out in a Brabender mixer with 40 wt-% ONP. The mixing temperature was kept as low as possible to avoid discoloration of fibre. Mixing was performed in two stages. In first stage, mixing temperature was 180 °C and mixing was carried out for about 3 min in order to melt-mix PP, SMA and ONP. The mixed composition was then granulated and again fed into the Brabender mixer where a higher temperature of 200 °C was used for further 3 min to obtain a homogeneous mixture. Proper venting arrangement was used to discharge volatiles. The molten composition was then cooled, granulated and stored for 24 h before compression-moulding into test specimens. The compression moulding temperature was 220 °C for 4 min.

In a related experiment, poly(ethylene terephthalate) (PET) was added to PP and themomechanical pulp (TMP) composites according to the formulation indicated in Table 1.

Table 1 Formulation of PP - PET - TMP composites (wt.-%)

| Composite | PP | PET | TMP | Coupling agent |
|---|---|---|---|---|
| 1 | 60 | 10 | 30 | none |
| 2 | 60 | 10 | 30 | 1.0 (maleated PP, MAPP) |
| 3 | 60 | 10 | 30 | 1.0 (bismaleimide, BMI) |
| 4 | 60 | 10 | 30 | 1.0 (oligoester with reactive terminal functionality, PES) |

PET from postconsumer soft drink bottles was ground into 40-mesh powder in a Willey mill and the powder was used for composite preparation. PET powder was oven-dried at 100 °C under vacuum for 24 h. TMP was also dried to a moisture content of less than 2 wt.-%. Composites were prepared in two stages: first PP, PET and TMP fibres were fed into a high-speed thermokinetic mixer and melt-mixed at 200 °C. The product was then granulated in a Brabender granulator and stored for injection moulding. Three different coupling agents were used to compatibilize these blends (as indicated above). Injection moulding of the composites was carried out at 220 °C and the moulded samples were tested for mechanical and creep properties.

## RESULTS AND DISCUSSION

### Recyclability

The results for the tensile and flexural properties and melt flow index (MF) of PP and PE composites in relation to repeated cycles of reprocessing are presented in Tables 2 to 5. The values in Table 2 indicate a slight decrease in tensile strength for PP composites. The decrease was more pronounced for composites containing higher percentage of fibres. This was probably due to the reduction in the fibre aspect ratio as a consequence of reprocessing cycles. The changes in the flexural strength (Table 3) and modulus (Table 4) of PP composites were minor in relation to repeated recycling. The melt flow of neat PP increased significantly with repeated reprocessing (Table 5). The addition of antioxidant prevented the increase in melt flow, thus likely preventing degradation of the polymer. The melt flow of PP composites showed little change with reprocessing.

Table 2 Effect of repeated recycling on the tensile strength (MPa) of PP and PE composites

| Formulation | Number of recycles | | | |
|---|---|---|---|---|
| | 0 | 3 | 6 | 8 |
| 100-PP | 30.7 | 28.3 | 29.0 | 28.0 |
| 100-PP-AO | 29.3 | 28.6 | 28.8 | 28.1 |
| 85-PP | 34.5 | 32.1 | 31.3 | 30.5 |
| 70-PP | 39.9 | 34.8 | 32.9 | 32.2 |
| 70-PP-AO | 39.8 | 35.3 | 32.2 | 31.4 |
| 55-PP | 38.7 | 31.4 | — | 33.0 |
| 100-PE | 20.9 | 21.3 | 21.4 | 21.2 |
| 100-PE-AO | 21.6 | 22.1 | 22.0 | 21.7 |
| 85-PE | 24.0 | 22.4 | 21.9 | 20.9 |
| 70-PE | 22.8 | 20.6 | 21.3 | 21.5 |
| 70-PE-AO | 22.8 | 21,0 | 21.9 | 20.9 |
| 55-PE | — | 20.1 | 19.9 | 19.5 |

Table 3 Effect of repeated recycling on the flexural strength (MPa) of PP and PE composites

| Formulation | Number of recycles | | | |
|---|---|---|---|---|
| | 0 | 3 | 6 | 8 |
| 100-PP | 45.4 | 39.6 | 45.8 | 43.2 |
| 100-PP-AO | 39.1 | 39.2 | 44.4 | 42.4 |
| 85-PP | 55.6 | 51.3 | 53.9 | 52.0 |
| 70-PP | 60.8 | 59.0 | 60.0 | 56.8 |
| 70-PP-AO | 61.0 | 62.4 | 57.6 | 55.6 |
| 55-PP | 69.3 | 64.1 | 58.3 | — |
| 100-PE | 27.3 | 29.6 | 26.7 | 25.9 |
| 100-PE-AO | 28.4 | 31.7 | 27.8 | 27.5 |
| 85-PE | 36.3 | 37.3 | 34.8 | 33.3 |
| 70-PE | 40.5 | 41.3 | 39.2 | 37.7 |
| 70-PE-AO | 42.3 | 42.2 | 39.7 | 37.1 |
| 55-PE | — | 43.5 | 41.2 | 37.4 |

The tensile and flexural properties of PE composites showed only a slight decrease with reprocessing. Different patterns in melt flow between PP and PE likely indicate different modes of thermal oxidative changes. Oxidation initiates a degradation mechanism by which free radicals are formed in the polymer chains. Due to the differing structures of polypropylene and polyethylene, different degradations are characteristic of each. In polyethylene, crosslinking is the primary degradation. In polypropylene, the primary mechanism is chain scission (breaking up of the polymer chain into smaller units) (Ref. 7). This explains why the opposite effects were observed in melt flow for PP and PE. If polyethylene is crosslinking, it is forming larger polymer molecules, which would have a higher viscosity. Polypropylene, on the other hand, is being broken up into smaller chains and will have a lower viscosity.

Table 4 Effect of repeated recycling on the flexural modulus (GPa) of PP and PE composites

| Formulation | Number of recycles | | | |
|---|---|---|---|---|
| | 0 | 3 | 6 | 8 |
| 100-PP | 3.70 | 3.07 | 3.80 | 3.41 |
| 100-PP-AO | 3.00 | 2.93 | 3.62 | 3.19 |
| 85-PP | 5.00 | 4.72 | 5.02 | 4.59 |
| 70-PP | 6.32 | 7.02 | 7.08 | 6.00 |
| 70-PP-AO | 6.15 | 8.17 | 6.94 | 5.92 |
| 55-PP | 9.86 | 13.30 | 7.97 | — |
| 100-PE | 0.82 | 1.03 | 0.89 | 0.89 |
| 100-PE-AO | 0.89 | 1.12 | 0.89 | 0.91 |
| 85-PE | 1.48 | 1.54 | 1.38 | 1.32 |
| 70-PE | 2.36 | 2.19 | 2.01 | 1.97 |
| 70-PE-AO | 2.42 | 2.24 | 2.14 | 1.91 |
| 55-PE | — | 3.49 | 3.00 | 2.45 |

Table 5 Effect of repeated recycling on the melt flow index (g/10min) of PP and PE composites

| Formulation | Number of recycles | | | |
|---|---|---|---|---|
| | 0 | 3 | 6 | 8 |
| 100-PP | 11.3 | 17.0 | 25.2 | — |
| 100-PP-AO | 11.0 | 10.4 | 11.9 | — |
| 85-PP | 6.4 | 7.5 | 9.5 | — |
| 70-PP | 1.4 | 2.1 | 4.2 | — |
| 70-PP-AO | 0.8 | 1.3 | 3.1 | — |
| 55-PP | 0.1 | 1.1 | 1.3 | — |
| 100-PE | 20.0 | 20.0 | 17.0 | 14.8 |
| 100-PE-AO | 17.0 | 18.8 | 16.8 | 17.0 |
| 85-PE | 4.1 | 10.5 | 10.4 | 12.2 |
| 70-PE | 0.6 | 4.5 | 6.0 | 8.5 |
| 70-PE-AO | 0.3 | 4.3 | 6.0 | 8.5 |
| 55-PE | — | 1.3 | 4.3 | 6.9 |

## Recycling Multicomponent Mixtures

The results for selected mechanical properties of PP-SMA-ONP composites are given in Table 6. It is evident that the inclusion of SMA had a detrimental effect on mechanical properties. This is not unexpected since there is a significant difference in the surface energy of PP and SMA, which makes this mix more complex. The interfacial compatibility of PP and SMA with lignocellulosic fibres decreases substantially, which is evident from low breaking elongation. In order to improve the compatibility problem, four different coupling agents were tested. Best results were achieved with maleated PP. Maleated PP reduced the interfacial energy between the two polymers as well between the individual polymer and ONP. Hence, all three different interfaces became more compatible, which results in improved mechanical strength. On the other hand, aminosilanes and polyurethanes, which increase the acid-base interaction in a three-phase system, did not have any significant effect on mechanical strength.. Although functionalized titanates are very good adhesion promoters, particularly for inorganic-filled composites, practically no improvement was recorded when a titanate with amine functionality was used for lignocellulosic composites.

Table 6 Effect of styrene-maleic anhydride copolymer in recycled PP-ONP composites

| Component | Content (wt.-%) | | | | | |
|---|---|---|---|---|---|---|
| Recycled PP | 60 | 45 | 45 | 45 | - | - |
| SMA | - | 15 | 15 | 15 | - | - |
| ONP | 40 | 40 | 40 | 40 | - | - |
| MAPP | - | - | 3.0 | - | - | - |
| Aminosilane | - | - | - | 0.7 | - | - |
| Aminotitanate | - | - | - | - | 0.7 | - |
| Polyurethane prepolymer | - | - | - | - | - | 0.3 |
| | Properties | | | | | |
| Tensile modulus (GPa) | 1.2 | 1.4 | 1.23 | 1.31 | 1.28 | 1.27 |
| Tensile strength (MPa) | 26.6 | 24.3 | 38.4 | 30.5 | 28.3 | 26.5 |
| Elongation (%) | 2.4 | 1.8 | 2.5 | 2.1 | 1.7 | 1.5 |
| Break energy (kJ/m$^2$) | 1.21 | 0.98 | 1.87 | 1.62 | 1.15 | 1.05 |

The mechanical properties of PP-PET-TMP composites are given in Table 7. It is evident that the mechanical properties of composites containing PET are quite low. This is not surprising since PP and PET are dissimilar in nature; moreover, because of the very high melting temperature of PET, it remained ebbed in the PP matrix as a semirigid filler particle rather than as a plastic-ductile matrix component. Practically, no melt flow of PET has been achieved under the experimental condition at 220 °C. This lack of flow apparently influenced the mechanical properties. PET as a filler does not have any specific interaction with PP. In comparing the three coupling agents (e.g., MAPP, BMI and PES), only the functional oligoester (PES) provided improved tensile strength and ductibility to the PET-containing composites. The inclusion of PES in the composites also reduced creep deformation (which was the subject of a separate study). It is possible that PET acts as a less ductile filler compared to PP matrix, and PET is more thermally resistant than PP. These two factors could contribute to improved creep property, particularly at elevated temperature.

In an attempt to further improve the interface chemistry of these three-component blend systems we have synthesized several oligoesters with reactive functional groups which have better affinity toward PP and TMP. The mechanical properties in this case were somewhat better than with the unmodified composites but not good enough to compete with unmodified or modified recycled PP and TMP composites (without PET). Therefore, the problem of compatibilization will be the subject of future research.

Table 7 Mechanical properties of PP-PET-TMP composites

| Composite | Tensile modulus (GPa) | Tensile strength (MPa) | Elongation (%) | Break ($kJ/m^2$) |
|---|---|---|---|---|
| 1 | 2.5 | 25.9 | 1.42 | 0.88 |
| 2 | 2.5 | 21.1 | 1.14 | 0.57 |
| 3 | 2.2 | 20.4 | 1.51 | 0.77 |
| 4 | 2.7 | 28.3 | 1.49 | 1.02 |

## CONCLUSIONS

Composites based on consumer thermoplastics (PP, PE) and lignocellulosic fibres provide a unique opportunity of recycling these materials from waste streams to industrial products. Melt blending with appropriate coupling agents is an efficient processing technology for the manufacture of these composites, such as non-structural building components, furniture parts. Repeated recycling had only minor negative effects on the mechanical properties of PE and PP composites. Reprocessing without an antioxidant indicated some thermo-oxidative degradation in PP and crosslinking in PE polymers. Maleated PP performed best among several coupling agents investigated in this study of property enhancement of recycled PP-SMA-ONP composites. The inclusion of SMA improved the thermal stability of recycled PP-ONP composites.

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