

Mechanical properties of organosolv-lignin-filled thermoplastics

Joachim Rösch* and Rolf Mülhaupt

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Summary

Organosolv lignin was used as organic filler for polypropylene (PP) and poly(ethene-co-vinylacetate) (EVA) containing 13wt-% vinylacetate. As a function of the lignin content, which was varied between 0 and 30wt-%, mechanical properties such as Young's modulus, yield stress, fracture stress, and elongation at break of the thermoplastic lignin-based compounds were measured. Both lignin-filled thermoplastics exhibit pronounced matrix reinforcement with increasing lignin content. Due to better interfacial adhesion between lignin and EVA, 30wt-% lignin addition to EVA doubles Young's modulus without sacrificing high elongation at break.

Introduction

Wood contains about 25wt-% of lignin which together with cellulose forms the structural component of trees and various plants. In paper production lignin is separated from cellulose fibers. Today this lignin by-product is used almost exclusively as fuel to generate energy. Due to environmental concerns related to conventional chemical pulp production, organosolv pulping has received serious attention within the last decade. In contrast to kraft and sulfite pulping, organosolv processes afford lignin which is essentially free of sulfur and chlorine. Moreover, organosolv lignin properties are different from those of conventional lignin. For example, organosolv lignin is soluble in aqueous alkine solutions and certain organic solvents(1-4). Therefore, organosolv lignin represents an attractive class of raw materials derived from renewable resources. Instead of incineration, other applications of organosolv lignins are being explored. One approach to utilize organosolv lignin is to form chemical lignin derivatives by converting phenol, olefin or hydroxy moieties into other functional groups. Examples are hydroxypropyl lignins (5) or lignin-based epoxy resins (6). Yet another viable approach is to apply organosolv lignin or its derivatives as structural components of various thermosetting and thermoplastic polymers. For example, lignin was incorporated

*Corresponding author

successfully together with carbon black filler in rubber master batches (7) and as reactive filler in epoxy resins (8). Here we report melt compounding of lignin with polypropylene and poly(ethene-co-vinylacetate).

Experimental

Polypropylene (HostalenTM PPN 1060, $M_n=63000\text{g/mol}$, $M_w=182700\text{g/mol}$, $\text{MFI}(230/2.16)=2\text{dg/min}$, $T_m=165^\circ\text{C}$) was supplied by Hoechst AG. Poly(ethene-co-vinylacetate) containing 13wt-% vinylacetate with $\text{MFI}(150/5)=5\text{dg/min}$ was obtained from BASF AG. Organosolv lignin obtained by supercritical methanol extraction in the Organocell proprietary process was supplied by Organocell Co, Munich. Melt compounding was performed in a Haake Rheomix 90, equipped with a 60ml blender and twin screws, at 190°C in the case of polypropylene or at 130°C in the case of poly(ethene-co-vinylacetate) respectively. In a typical run, the preheated blender was charged with 40g of the lignin/polymer mixture containing 0.2g stabilizer (80wt-% IrganoxTM 1010 and 20wt-% IrgafosTM 168, both obtained from Ciba-Geigy AG). After blending for the duration of 4min at the temperatures indicated above, the resulting compounds were quenched between water-cooled metal plates. Then sheets of 1.5mm thickness were prepared by compression-molding samples, which were annealed for 10min at 190°C or 150°C respectively, followed by quenching as described above. For tensile testing dumbbell-shaped bars were cut and machined following standard procedures according to DIN53455. Young's modulus, yield stress, fracture stress, and elongation at break were determined at 10mm/min crosshead speed and 23°C using an Instron 4202.

Results and Discussion

Organosolv lignin, obtained by methanol extraction in the Organocell process, was melt compounded with polypropylene at 190°C and with poly(ethene-co-vinyl-acetate) containing 13wt-% vinylacetate at 150°C . Higher processing temperatures are not feasible because lignin starts to decompose when heated for prolonged periods of time above 150°C . The mechanical properties of the two classes of lignin-based compounds are listed in Table 1 as a function of the lignin content which varied between 0 and 30wt-%.

Table 1 Mechanical properties of organosolv-lignin-based compounds

Matrix Type	Lignin Content (wt-%)	Young's Modulus (MPa)	Yield Stress (MPa)	Fracture Stress (MPa)	Elongation at Break (%)

PP	0	1150	32	30	700
"	10	1270	27	30	600
"	20	1390	27	15	150
"	30	1590	26	9	50

EVA	0	74	4.0	11	750
"	10	93	4.6	10	750
"	20	113	4.3	10	650
"	30	142	4.3	6	600

From Table 1 it is apparent that lignin addition affords matrix reinforcement as expressed by markedly increased Young's moduli. In the case of polypropylene, matrix reinforcement is accompanied by substantial losses of yield stress, fracture stress, and elongation at break. The mechanical properties reflect drastic matrix embrittlement even at 10wt-% lignin content. In fact, at 30wt-% lignin content, small fracture stress of 9MPa is sufficient to cause mechanical failure and reduction of the elongation at break from 700 to 50%. Shown in Figure 1 are yield stress and fracture stress which decrease simultaneously with increasing lignin content. Interestingly, with increasing lignin content, fracture stresses decrease much stronger than yield stresses. Test specimen do not fail at the point of highest stress but rather gradually, e.g., by rupture of individual fibrils that develop between adjacent poorly adhering lignin particles. Furthermore it should be noted that coarse, irregularly shaped lignin particles can cause stress concentrations which can initiate cracks upon exposure to small mechanical stresses. As soon as cracks are formed, they are likely to propagate immediately along the poorly adhering interfaces.

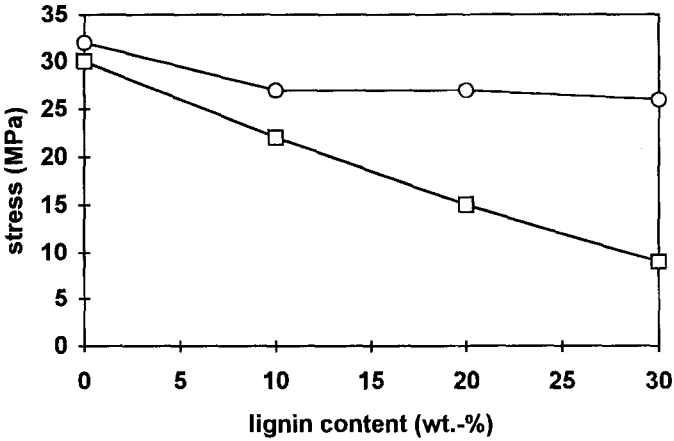


Figure 1 Yield stresses (O) and fracture stresses (□) of lignin-filled polypropylene as a function of lignin content

In contrast to lignin-filled polypropylene, lignin-filled poly(ethene-co-vinylacetate) exhibits much better retention of matrix toughness combined with matrix reinforcement as the lignin content increases. Depicted in Figure 2 is the influence of lignin on yield stress and fracture stress.

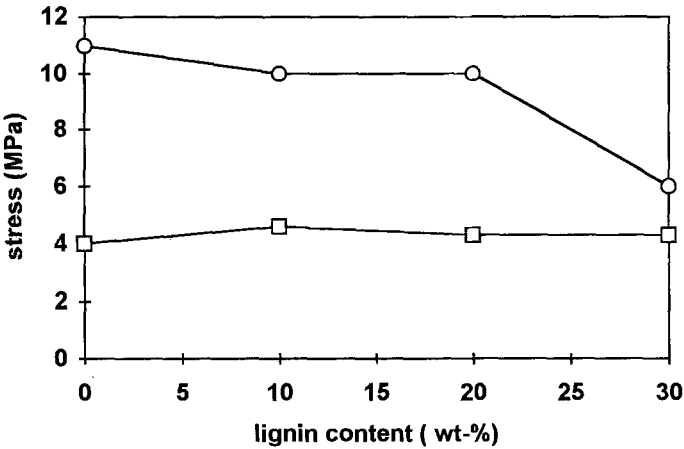


Figure 2 Fracture stresses (O) and yield stresses (□) of lignin-filled poly(ethene-co-vinylacetate) as a function of lignin content

Clearly, constant yield stress provides evidence that good interfacial adhesion is achieved. This is in accord with better compatibility of lignin and EVA, resulting from incorporation of polar vinylacetate units into the hydrocarbon backbone.

In the case of lignin-filled EVA, fracture stresses are much larger than yield stresses. Upon exposure to external mechanical stresses, the flexible EVA matrix undergoes large plastic deformation. Tightly adhering lignin particles account for EVA matrix reinforcement and prevent premature crack propagation by voiding at the interfaces. In conclusion, organosolv lignin is a suitable reinforcing organic filler for EVA and does not cause matrix embrittlement as observed in the case of polypropylene. Improved interfacial adhesion between lignin and the continuous polymer matrix is the key to property synergisms of matrix reinforcement combined with high toughness.

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