Rheology of Composites with Nature Vegetal Origin Fibers

J. Bobek, M. Seidl, P. Lenfeld, L. Běhálek, A. Ausperger

Abstract—Conventional materials like glass, wood or metals replacement with polymer materials is still continuing. More simple thus cheaper production is the main reason. However due to high energy and petrochemical prices are polymer prices increasing too. That´s why various kinds of fillers are used to make polymers cheaper. Of course target is to maintain or improve properties of these compounds. In this paper are solved rheology issues of polymers compounded with vegetal origin fibers.

Keywords—Vegetal, fibers, polymer, rheology

I. INTRODUCTION

RHEOLOGY properties change by various fillers addition is the one of important problem during polymer filling with goal to make final compound cheaper. Often is necessary to make compromise between maintained or improved properties comparing with basic material and increased difficulty of processing. Of course is necessary to consider whole economics of polymers and fillers compounding because compounding is added step comparing to conventional polymer processing. Mainly filler price and price of compounding are decisive. Next to economic issue is necessary to take into consideration the higher viscosity of filled polymers which is leading to higher pressures in injection molds for example. This effect is limiting parts design which are not possible to design with too fine structure details because these are not possible to fill during injection molding with high viscosity polymer melt. Is obvious that problems associated with polymer and filler compounding is worth to accept in case of significant price reduction caused by addition of very cheap filler or significant

J. Bobek is with the Technical university of Liberec, Faculty of mechanical engineering, Plastic molding department, Liberec, 461 17, Czech republic (phone: +420485353164; fax: +420485353676; e-mail: jiri.bobek@tul.cz).

M. Seidl is with the Technical university of Liberec, Faculty of mechanical engineering, Plastic molding department, Liberec, 461 17, Czech republic (phone: +420485353333; fax: +420485353676; e-mail: martin.seidl1@tul.cz).

P. Lenfeld is with the Technical university of Liberec, Faculty of mechanical engineering, Plastic molding department, Liberec, 461 17, Czech republic (phone: +420485353350; fax: +420485353676; e-mail: petr.lenfeld@tul.cz).

L. Běhálek is with the Technical university of Liberec, Faculty of mechanical engineering, Plastic molding department, Liberec, 461 17, Czech republic (phone: +420485353331; fax: +420485353676; e-mail: lubos.behalek@tul.cz).

A. Ausperger is with the Technical university of Liberec, Faculty of mechanical engineering, Plastic molding department, Liberec, 461 17, Czech republic (phone: +420485353332; fax: +420485353676; e-mail: ales.ausperger@tul.cz).

properties improvement or acceptable compromise of both. In this paper will be this problem evaluated with respect to rheology properties. Description of the material under stress is possible to call rheology. The rheology will be discussed from various points of view namely steady shear viscous properties, fiber type, size, size distribution and polymer matrix type.

II. EFFECT OF FILLER TYPE

The filled systems containing like glass fibers, mica, aramid fibers, cellulose fibers of glass beads exhibit low shear Newtonian viscosities and a decreasing viscosity function at higher shear stress [1]. Filled system containing fillers like calcium carbonate, carbon black exhibit unbounded viscosity buildup at low shear rates. The extent of the steady shear viscosity increase is the lowest for three dimensional spherical fillers such a glass beads, higher for two dimensional fibrous fillers such cellulose or glass fibers.

III. EFFECT OF FILLER SIZE

Yield stress is a manifestation of strong particle to particle interaction and has direct relation to the particle size. The existence of yield stress in the steady shear viscosity curve for filled polymer systems containing small size fillers has been noted also by other research works [2], [3], [4], [5], [6], [7]. Filled systems with the decreasing particle size (for example carbon black or calcium carbonate) the entire steady shear viscosity curve is pushed to a significantly higher level [8,9]. For filled systems with larger particles (for example cellulose fibers or glass fibers) the response to deformation is determined by hydrodynamic interaction and not by particle to particle interaction. These non-interacting particle systems would not show the yield stress.

IV. EFFECT OF FILLER CONCENTRATION

With increasing concentration of the filler interparticle interactions increase weakly at the first and then strongly as the concentration becomes higher and higher. The concentration at which particle to particle interactions begin depends on the geometry and surface activity of the filler particles. For example high aspect ratio fillers would begin to interact at much lower concentrations while non-agglomerated large size spherical would not interact until about 20 w.t. % [10]. The higher surface roughness the greater the resistance to flow deformation and hence the viscosity of filled system would be higher.

V. Effect Of Filler Size Distribution

Higher packing densities can be achieved if the particle sizes are not uniform. This enables finer particles to fill the holes between the larger particles. The particle size range can be broadened in two ways. Mixture of two particle size can be blended for example coarse and fine particles or a continuous wide distribution of particle size can be selected. Increasing the number of particle sizes in the mixture can increase the packing density.

VI. Effect Of Filler Surface Treatment

An approach to improving filler and polymer compatibility is the use of surface modifiers on the filler through a pretreatment process. Surface treatment is meant to help the polymer wet the filler and disperse it. However the extent of wetting and degree of adhesion are different for each polymer, filler and surface modifier combination. Some modifier that will effectively coat the filler surface may not interact with the polymer whereas others that are compatible with the polymer may not adhere to the filler and hence will not effectively modify its surface

Surface modifiers are generally bifunctional molecules with one end capable of adhering to the filler and the other end compatible with the polymer and at times even capable of reacting with. Increased melt viscosity introduced by filler addition can be significantly reduced by the application of surface modifiers to the fillers [11], [12], [13], [14], [15], [16], [17], [18].

The normal expected behavior from the use of surface modifiers is one in which viscosity reduction occurs to a different extent depending on the type of surface modifier its amount and method of treatment. The maximum achievable reduction would most likely be very close to the flow behavior of the unfilled polymer at least at higher shear rates.

VII. Effect Of Polymer Matrix

The effect of polymer matrix on the steady shear viscosity of filled systems would depend on the chemical nature of the polymer as well as its unfilled viscous characteristics. The polymer itself could be Newtonian moderately shear thinning or predominantly shear thinning.

In the case of polymer like PET or PC the steady shear viscosity is near Newtonian up to even a shear rate of a little over $100 \ s^{-1}$. As an example of moderately shear thinning polymer PEI could be considered while for a predominantly shear thinning polymer PP is a reasonable example.

VIII. Effect Of Filler Nature

The fibrous fillers (cellulose, glass, aramid) tend to increase the normal stress difference value at a fixed shear stress. Particulate fillers (carbon black, calcium carbonate) tend to depress it while spherical fillers (glass beads) leave it nearly unchanged. The large increase in normal stresses in fiber filled polymer systems is probably due to a hydrodynamic particle effect associated with orientation in the direction of flow.

IX. Experimental Procedure

Based on facts mentioned in Chap. II. – Chap. VIII. was designed experimental work with target to find applicable polymer matrix – fiber combination which comply next requirements:

1) Keep melt flow index (viscosity) to the most possibly similar values as basic polymer matrix.
2) Final compound price will be the lowest possible.
3) Fiber type will be ecological based.

Due to requirement mentioned in point 3 was selection narrowed to natural nature fibers. As polymer matrix was chosen polypropylene with very low melting temperature – by manufacturer recommended 180 °C. Low melting temperature is necessary mainly due to temperature toughness to higher temperatures of the nature fibers. In point 2 is mentioned requirement to the lowest possible price. A lot of vegetal origin fibers are comply this requirement. Finally were chosen five types of vegetal origin fibers mainly according to three mentioned requirements. But also according to basic premises about right fiber surface which could not be too rough due to too high viscosity decrease and could not be to too smooth due to too high mechanical properties decrease. These five fiber types (kapok fibers, coconut fibers, hemp fibers, linen fibers, jute fibers) were compounded in two screw extrusion machine and granulated in next ratio: 80 w. t. % of PP with 20 w. t. % of each fiber type. Fraction of used fibers is 0,3 mm – 1,2 mm. In the first rough selection were also ramie fibers, soy fibers, tencel fibers and banana fibers. But due to their relatively high prices were eliminated from the selection according above mentioned three basic requirements for final compound. Schematically is the compounding process shown in the Fig. 1.
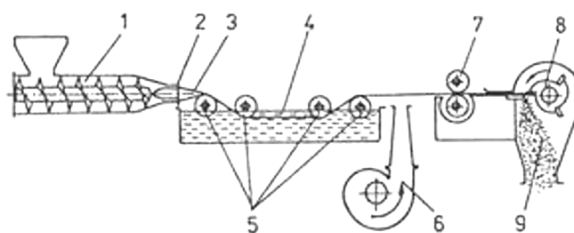

Fig. 1 Compounding process principle

1, Two screw extruder; 2, Granulating head; 3, Plastic wire; 4, Cooling water; 5, Guiding cylinders; 6, Blower; 7, Feeding cylinders; 8, Knives; 9, Granules

Each produced series was remitted to melt flow index measurement according ISO 1133 with temperature 180 °C and 2,16 kg load on melt flow tester CEAST. Measured values were compared with melt flow index of basic polymer matrix (PP). For polymer matrix was chosen basic polypropylene without talc from SABIC used for common internal non-sight automotive parts. In Fig. 2 – Fig. 6 is possible to see SEM pictures of each type of fiber before compounding.
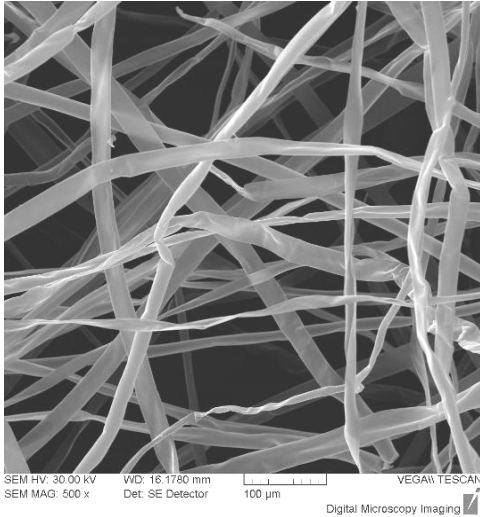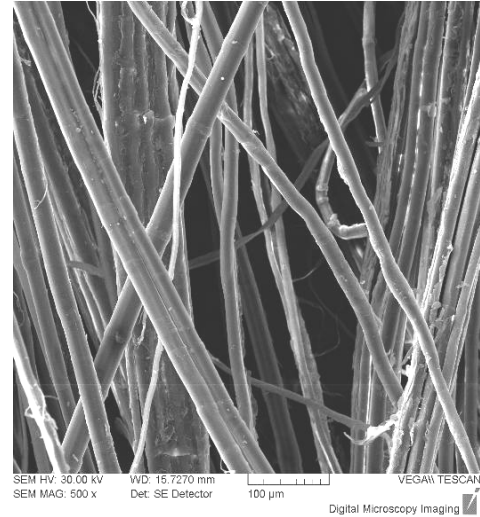
Fig. 2 Kapok fibers

Fig. 5 Linen fibers
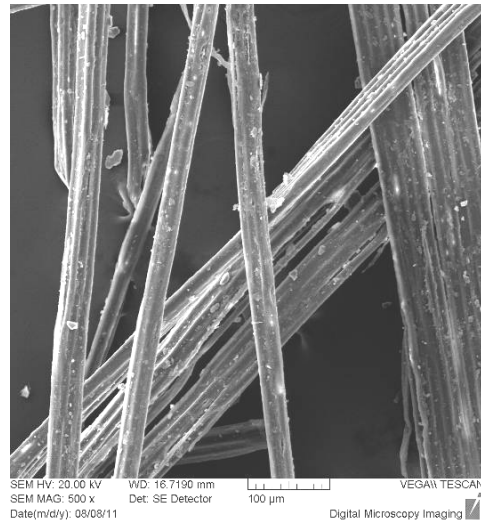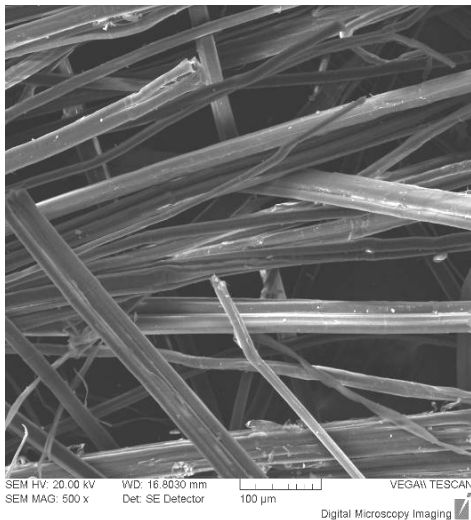

Fig. 3 Coconut fibers

Fig. 6 Jute fibers

X. RESULTS AND DISCUSSIONS

Melt flow index results are tabulated in Table 1.

TABLE I
MELT FLOW INDEX RESULTS

	Melt flow index [cm^3·10min^{-1}] ISO1133-180°C/2,16kg
PP matrix	14.7
PP + 20 w.t.% KAPOK fibers	5.2
PP + 20 w.t.% COCONUT fibers	8.3
PP + 20 w.t.% HEMP fibers	1.3
PP + 20 w.t.% LINEN fibers	2.0
PP + 20 w.t.% JUTE fibers	3.1

Fig. 4 Hemp fibers

From the melt flow index measurement results mentioned in Table 1 is possible to deduce connection between surface type and final melt flow index of compounded pure PP with each fiber type. Is possible to say that smoother surface of fibers is generating compound with higher values of melt flow index thus lower viscosity. Example of this is compound PP + 20 w.t. % kapok fibers. In. Fig. 2 is possible to see that kapok fibers are very smooth comparing to other mentioned. Only compound PP + 20 w.t. % coconut fibers has higher melt flow index thus lower viscosity. This is probably caused by coconut fiber size. With comparing Fig. 3 and Fig. 2 is possible to find out that coconut fiber has around 15 times higher diameter thus contact area between polymer matrix and fiber is lower in case of coconut fiber. Due this fact the compound with coconut fibers has lower resistance during the melt flow. Mentioned knowledge is also possible to use in case of the other fibers type. Jute fibers, linen fibers and hemp fibers have smaller diameter comparing to coconut fibers too. But in contrast with kapok fibers have much more rough surface with a lot of overhangs which are causing resistance during melt flow and thus they are increasing the viscosity. Melt flow index is than lower.

XI. CONCLUSION

Nature fiber using as filler in polymer matrix mainly could bring price reduction of final compound due to part substitution of relatively expensive basic polymer. But is necessary to know what this filler addition causes with respect to rheology properties of final compound because rheology properties are strongly connected with process ability for example during injection molding. In this paper was determined that from five used fiber types are coconut fibers the most suitable for possible material replacement in combination with used polymer matrix PP. Reasons are two: Melt flow index is relatively acceptable to avoid the problems with melt flow for example during injection molding. And price of coconut fibers is very low. In case of 20 w.t. % using in compound is price reduction about 22 %. In the case of large production volumes it could be interesting saving and it could be interesting using of material which is practically the waste.

REFERENCES

[1] White, J.L., Czarnecki, I. and Tanaka, H. (1980) Experimental studies of the influence of particle and fiber reinforcement on the rheological properties of polymer melts, *Rubber Chem. Tech.,* 53, 823-35.
[2] Chapman, P.M. and Lee, T.S. (1970) Effect of talc filler on the melt rheology of polypropylene, SPE /., 26, 37-40.
[3] Mills, NJ. (1971) The rheology of filled polymers, /. *Appl Polym. ScL,* 15, 2791-805.
[4] Minagawa, N. and White, J.L. (1976) The influence of titanium dioxide on the rheological extrusion properties of polymer melts, /. *Appl. Polym. Sd.,* 20, 501-23.
[5] Kataoka, T., Kitano, T., Sasahara, M. and Nishijima, K. (1978) Viscosity of particle filled polymer melts, *Rheol. Ada,* 17,149-55.
[6] Kataoka, T., Kitano, T. and Nishimura, T. (1978) Utility of parallel-plate plastometer for rheological study of filled polymer melts, *Rheol Ada,* 17, 626-31.
[7] Suetsugu, Y. and White, J.L. (1983) The influence of particle size and surface coating of calcium carbonate on the rheological properties of its suspension in molten polystyrene, /. *Appl. Polym. ScL,* 28,1481-501.
[8] Lobe, V.M. and White, J.L. (1979) An experimental study of the influence of carbon black on the rheological properties of a polystyrene melt, *Polym. Engg ScL,* 19, 617-24.
[9] Tanaka, H. and White, J.L. (1980) Experimental investigations of shear and elongational flow properties of polystyrene melts reinforced with calcium carbonate, titanium dioxide and carbon black, *Polym. Engg ScL,* 20, 949-56.
[10] Bell, J.P. (1969) Flow orientation of short fibre composites, /. *Comp. Mater.,* 3,244.
[11] Boira, M.S. and Chaffey, C.E. (1977) Effects of coupling agents on the mechanical and rheological properties of mica-reinforced polypropylene, *Polym. Engg ScL,* 17, 715-18
[12] Copeland, J.R. and Rush, O.W. (1978) Wollastonite: short fiber filler/reinforcement, *Plastic Compounding,* 1, 26-36 (Nov./Dec.).
[13] Han, C.D., Sandford, C. and Yoo, HJ. (1978) Effects of titanate coupling agents on the rheological and mechanical properties of filled polyolefins, *Polym. Engg ScL,* 18, 849-54
[14] Monte, SJ. and Sugerman, G. (1979) A new generation of age and waterresistant reinforced plastics, *Polym. Plastics Tech. Engg,* 12,115-35.
[15] Han, C.D., Sandford, C. and Yoo, HJ. (1978) Effects of titanate coupling agents on the rheological and mechanical properties of filled polyolefins, *Polym. Engg ScL,* 18, 849-54
[16] Han, C.D., Van der Weghe, T., Shete, P. and Haw, J.R. (1981) Effect of coupling agents on the rheological properties, processing and mechanical properties of filled polypropylene, *Polym. Engg ScL,* 21,196-204.
[17] Sharma, Y.N., Patel, R.D., Dhimmar, I.H. and Bhardwaj, LS. (1982) Studies of the effect of titanate coupling agent on the performance of polypropylenecalcium carbonate composite, /. *Appl. Polym. ScL, 27,* 97-104.
[18] Lee, W.M., Abe, D.A., Chipalkatti, M.H. and Liaw, T.F. (1982) Rheological properties of particulate-filled linear low density polyethylenes, *Proc. Ann. Conf. Reinf. Plast. Compos, lnst. Soc., Plast. lnd.,* 37(12D), 7.

J. Bobek received his MSc from Technical University of Liberec in 2007. Presently is pursuing his PhD in Technical university of Liberec, Department of plastics molding. He is working on new trends in injection molding technology development.

M. Seidl received his MSc from Technical University of Liberec in 2007. Presently is pursuing his PhD in Technical university of Liberec, Department of plastics molding. He is working on innovative ways for injection molds cooling development.

P. Lenfeld is the head of Department of plastics molding in Technical university of Liberec. He received his MSc from VSST Liberec in 1989, doc from Technical University of Liberec in 2001 and prof. in 2008 from Technical University of Liberec. He is working on injection molding process optimization, temperature and thermal research of injection molding and injection mold optimization.

L. Běhálek received his MSc in 2001 from Technical university of Liberec. He is working on polymer morphology research, injection mold temperature control systems development and injection molding process management.

A. Ausperger received his MSc in 1998 from Technical university of Liberec, PhD in 2005 from Technical university of Liberec. He is working on internal defects and stresses in injection molded parts research, plastics shearing research. He is also working on injection molding process and textile injection process prediction.