Macromol. Symp. **2003**, *202*, 245—254

Surface Treated Cellulose Fibres in Flame Retarded PP Composites

*P. Anna, E. Zimonyi, A. Márton, A. Szép, Sz. Matkó, S. Keszei, Gy. Bertalan, Gy. Marosi**

Department of Organic Chemical Technology, Budapest University of Technology and Economics H-1111 Műegyetem rkp. 3, Budapest, Hungary
Email: gmarosi@mail.bme.hu

Summary: Polypropylene-based composites were prepared containing non-treated and various treated cotton fibre and wood flakes. A correlation was observed among the fibre treatment and compounding parameters, mechanical and discoloration properties. The structural changes in fibres were demonstrated by Raman spectroscopic and DSC measurements. The possibility for forming cellulose fibre containing flame retardant composites was also investigated. The efficiency of various treatments on compounding, discoloration and mechanical properties enhance in the following order: no treatment < non ionic surfactant < reactive silicone segment containing non ionic surfactant < special silylation treatment. The best results obtained with the special silylation treatment were explained with the more organophilic character and by the thermal stability of the treated fibres. Cellulose fibre as a polyol-charring component and ammonium-polyphosphate together constitute a high performance intumescent flame retardant system in the PP matrix.

Keywords: cellulose fibres; DSC; fire retardant; polypropylene composites; Raman spectroscopy; surface modification; wood flakes

Introduction

In modern polymer composite technology there is a great demand for environment friendly materials completely adapted to the environment, i.e. they should be biodegradable and should originate from renewable resources. One possible approach is the embedding of natural reinforcing fibres, e.g. flax, ramie, hemp, etc. into biopolymeric matrices made of derivatives from cellulose, starch, lactic acid, etc. New fibre reinforced materials called biocomposites have been created and are still being developed with the unique benefit, of the total biodegradable character.[1,2] The bio-fibres, however, do not possess the necessary thermal and mechanical properties desirable for the compounding of engineering plastics. On the other hand, best engineering plastics are obtained from synthetic polymers, but they are not biodegradable. The composites of natural fibres and non-biodegradable synthetic polymers may offer a new class of materials but are not completely biodegradable.

DOI: 10.1002/masy.200351221

Government regulations and growing environmental awareness throughout the world have triggered a paradigm shift towards designing materials compatible with the environment[3] such as the combination of natural fibres and non-biodegradable synthetic polymers. Advantages of bio-fibres over traditional reinforcing materials such as glass fibre, talc and mica are their low cost, low density, high toughness, acceptable specific strength.[4,5] The main drawback of these reinforcing materials is their hydrophilic nature, which lowers their compatibility with hydrophobic polymer matrices. The other disadvantage is the relatively low processing temperatures necessary to avoid fibre degradation and/or volatile emission that can deteriorate composite properties. Several approaches are described in the literature aiming at the improvement of the interfacial adhesion between organic fillers and polymer matrix, such as addition of maleic anhydride polymers as compatibiliser[6] or by combined application of maleic anhydride containing compatibiliser and treatment of the cellulose based filler with a silane coupling agent.[7,8] These methods improve the compatibility of cellulose fibres, but do not enhance the thermal stability of the fibres. The thermal stability of cellulose based fibres could be improved by a special silylation method,[9] which also resulted in enhanced mechanical properties of the polymer composites. Both effects were explained by structural changes in the amorphous phase of the cellulose fibres. It seems to be a promising way to use this special silylated cellulose fibre as reinforcing additive.

In the present work polypropylene composites were prepared using non-ionic surfactant, reactive silicone containing surfactant, a special silylated cotton fibre and wood flake. Interrelations among fiber treatment, compounding efficiency, mechanical and discoloration properties were demonstrated. Structural changes in fibres were demonstrated with Raman spectroscopic and DSC measurements. The possibility of preparing cellulose fibre containing composite was also investigated.

Experimental

Materials: Tipplen H535, polypropylene homo-polymer (TVK, Hungary), MFI 4 g/10 min (230°C, 2.16 kg). Wood flake: 1.2 mm chips of pinewood. Fibre: natural cotton fibre of 30 mm. A special silylated product of natural cellulosic fibre was prepared with 20% tetraetoxy silane TES in presence of catalytic amount of dibutyl tin dilaurate (DBTDL) by heating them to 140°C and keeping at constant temperature until ethanol development was observed. The excess of TES was removed by distillation. ESTOL 1474 (Unichema International): glycerol-monostearate (GMS), a non-ionic surfactant, white powder, melting temperature 60°C. Silicone containing reactive surfactant (SRS): a glycerol mono oleate-triethoxy silane, an experimental product, prepared from 1 mol tetra ethoxy silane and 1 mol glycerol mono oleate in presence of DBTDL by heating at 120°C until development of ethanol was observed, molecular mass was 1498 g/mol, as determined by the method of boiling point elevation. Tetra ethoxy silane (TES) (Wacker, Germany). EXOLIT 422 (HOECHST, Germany), ammonium-polyphosphate (APP), white powder, average degree of polymerisation 700, acidity of suspension (1 % in water) pH 5.5.

Sample preparation: Compounding was performed in the mixing chamber 350 of a Brabender Plasti-Corder PL2000 (Brabender, Germany) at a rotor speed of 50 rpm, at 200°C, with 10 min homogenisation time. Fibres added a rate of 30 wt% were previously homogenised physically with surface treating additives, (2 % of the fibre weight), then were fed into the PP melt. Sheets (100×100×3 mm) were formed using a laboratory compression moulding equipment.

Measurements: Tensile strength, and elongation at break were measured on a Textenser instrument (Textile Research Institute, Hungary), at an elongation rate of 10 mm/min.

Micro-Raman measurements were performed by a Labram Raman Microscope system (Jobin Yvon Horiba, France), excitation at 632,81 nm by HeNe laser. Thermo gravimetric measurements (TG) were performed using Setaram Labsys equipment (Setaram, France), with 10 mg test material, at heating rate of 7,5°C/min, in air atmosphere. Colour measurements with MOMCOLOR-100 device (MOM, Hungary) by using white reference, for colour characterisation the ΔL^* value, the lightness-difference between the sample and the reference was used according the CIE recommendation.[10] The flammability was characterised by LOI and UL 94 tests.

Results and Discussion

Effect of Surface Treatment on Compounding

The influence of various surface treatments on cellulose fibre manifested in the compounding, surface discoloration and mechanical properties of PP compounds. The extent of the effect was characterised by measuring the torque during the compounding, the colour of surface, the tensile strength and elongation at break of the plates prepared from the compounds. The influence of surface treatment on the processing characteristics of the wood flake containing composite is demonstrated in Figure 1. The homogenisation of the non-modified wood flake (NoM-W) containing PP composite requires a high torque (nearly 40 Nm) and a long mixing time, above 7 min. Addition of a non-ionic surfactant (NIS-W) reduces the torque maximum considerably (below 30 Nm), but the required homogenisation time could not be reduced. The homogenisation takes place in a multi-step process. The mixing torque as a measure of the power consumed during the compounding is related to the melt viscosity of the mixed system. The application of silicone containing reactive surfactant (SRS-W) results in a much more intense change on the torque curve. The maximum value reduces below 20 Nm, the homogenisation requires more than 7 min. The most intensive effect on the compounding characteristics can be observed in the preparation of the composite containing the special silylated wood flakes (Sil-W). In contrast to the former composites, the torque begins to increase immediately after feeding the wood flakes. The maximum of the torque reaches only 17 Nm, and the homogenisation is completed after 3 min. That means, the most favourable effect with respect to compounding can be achieved by the special Sil treatment.

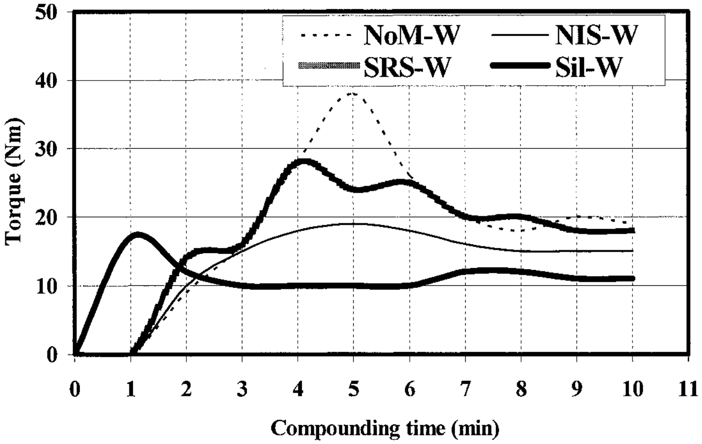

Fig. 1. Torques during the preparation of PP compounds containing various surface-treated wood flakes.

Figure 2 shows the torque values measured during the preparation of PP composites made with various treated cotton fibres..The observed tendencies are similar to those observed with wood flakes, but not so pronounced. Each modification reduces the torque maximum, and modifies the compounding time necessary for the homogenisation, similarly to the compounds discussed above,the differences are, however, not so pronounced. With respect to the homogenisation time the most favourable effect, similarly to the case of wood flakes, can be obtained by application of the special Sil treatment.

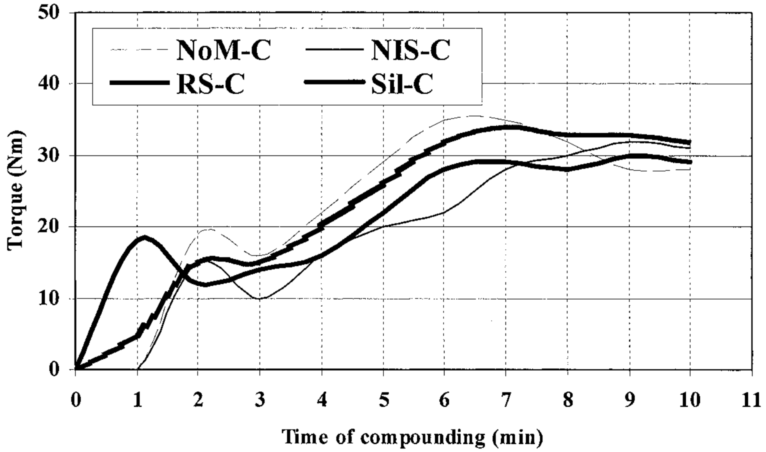

Fig. 2. Torque as function of compounding time of PP composites containing variously surface treated cotton fibres.

Considering the mixing curves discussed above one can conclude that the treatments, which render the surface of cellulose based fillers organophillic, promote the homogenisation during the compounding, making the surface more compatible with the matrix of the composite. The favourable effect is minimal for NIS and maximal for the special Sil treatment.

Effect of Surface Treatment on the Mechanical Properties

The beneficial effects of treatments are also reflected in other properties. Figure 3 shows the relative mechanical properties (related to the NoM-W sample) of the PP composites containing various modified wood flakes. NIS and the SRS treatments have a negligible, while the special Sil modification has a considerable effect on the mechanical properties. The relative strength of the Sil-W sample increased nearly by 100%, the elongation at break by more than 200%.

The effects of various treatments are similar in the case of cotton fibre reinforced PP composites, as demonstrated in Figure 4, only the improving effect on the characteristics has a reverse direction, i.e. the changes in the strength and elongation at break are reversed. This inverse improvement is most characteristic and most intense in the case of the special Sil treated sample, where the strength increases by 150%, and the elongation only by 50%, that is the improvement is higher for the strength. The improvement of the mechanical properties in both types of the fibre reinforced composites can be explained by the increased organophilic character of the fibre surfaces, which leads to an enhanced interaction between the originally hydrophilic fibre surface and the hydrophobic matrix. The higher increase of the strength of the special Sil treated cotton fibre reinforced composite, compared to the wood flake reinforcement, is in connection with the longer size of the cotton fibres. The longer fibre size, on the contrary, prevents the elongation, resulting in a lower elongation at break. The higher elongation at break of the wood flake-containing composite is due to the shorter fibre size of the wood flakes, which allows the orientation and movement of the matrix polymer chains during the tensile test.

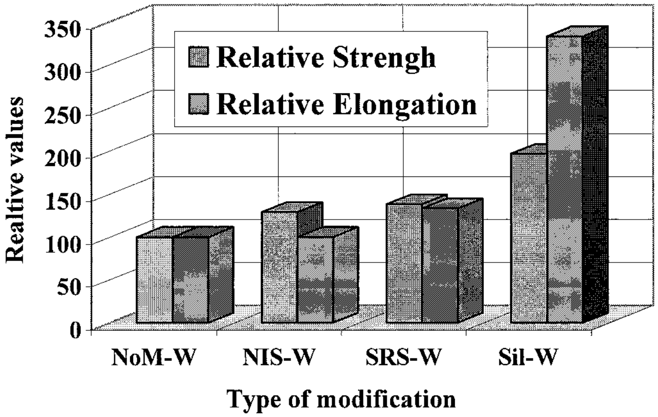

Fig. 3. Relative tensile strength and elongation at break of PP composites containing various treated wood flakes.

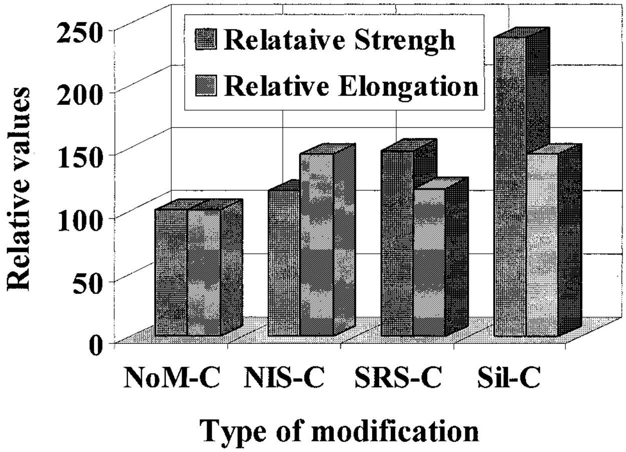

Fig. 4. Relative tensile strength and elongation at break of PP composites containing various treated cotton fibre.

Effects of Surface Treatment on the Discoloration of Composites

The various modifications manifest themselves also in the different discoloration of the PP composites, as demonstrated by Figure 5, where the lightness differences, ΔL*, as compared to the white reference, are presented for the compounds containing wood flakes and cotton fibre.

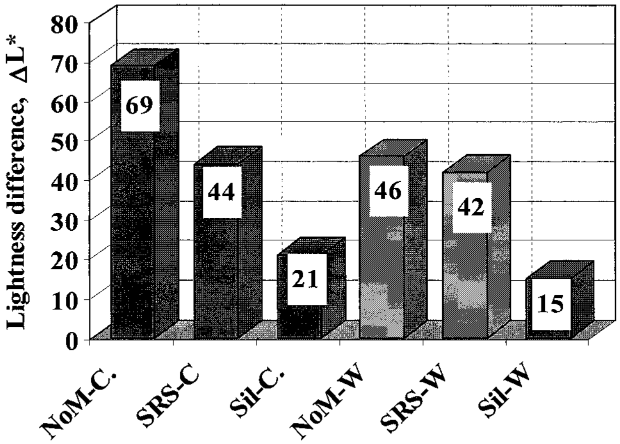

Fig. 5. Lightness differences of PP composites containing various treated cotton fibre and wood flakes.

The larger the lightness difference, the higher the discoloration of the sample. As it can be seen, the cotton fibre is more susceptible to discoloration. Each treatment reduces the lightness difference. The Sil treatment is most effective in preventing discoloration.

The mechanical properties, mainly the tensile strength and the discoloration measurements suggest, that the Sil treatments improve the thermal stability of cellulose fibres. This assumption was confirmed by thermo-gravimetric analysis. The DTG curves of the non-treated and Sil treated cotton fibres are illustrated in Figure 6. The DTG curve of non-treated (NoM-C) cotton fibre shows a starting degradation already above 180°C, while the degradation of the Sil treated fibre, Sil-C begins only above 200°C. The degradation of the non treated fibre is negligible with respect to weight loss, but considerable with respect to discoloration.

For the explanation of the improved thermal stability, Raman spectra, illustrated in Figure 7, of the non-treated and Sil treated cotton fibre samples were studied. Comparing the spectra of the non treated (NoM-C) and the Sil treated (Sil-C) fibres considerable differences can be observed is some region of the spectra:[11]

- in the range of 1000 cm^{-1} characteristic for the cyclic axial secondary alcoholic -OH-groups,
- around 1340 cm^{-1}, which band can be attributed to $-CH_2-$ deformational vibration and
- in the region 3200 to 3500 cm^{-1} characteristic for the stretching vibration of the -OH→O bond system.

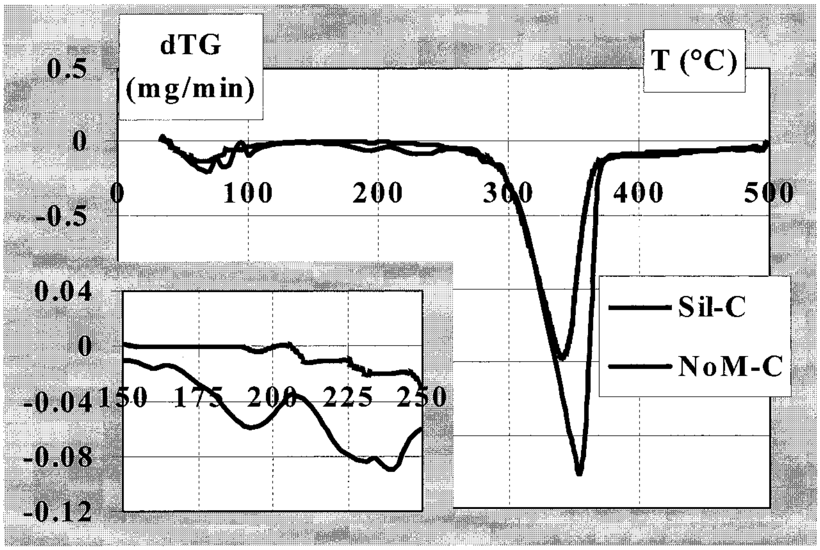

Fig. 6. DTG curves of natural and Sil treated cotton fiber.

Typically, the intensity of the peaks mentioned above increase after Sil treatment. The complex peak system in the 3200 to 3500 cm^{-1} region becomes not only more intense, but also narrower. These changes indicate an apparent increase in the concentration of the -OH groups in the ordered phase, an increase of crystallinity and a reduction of the amorphous phase. The reduction of -OH groups in the amorphous phase is an evident result of the Sil treatment, as the silylation reaction can not take place in the crystalline phase. The increase of the concentration of the -OH groups in the crystalline phase is a result of post-crystallization, which is the consequence of the easier segmental movement, which was facilitated by the reduction of secondary chemical bonds in the amorphous phase. These structural changes explain the reduced discoloration and the higher thermal stability of the Sil treated fibre containing PP composites. The -OH groups in the amorphous phase have higher susceptibility for easy thermal dehydration, as their concentration was reduced, the thermal stability of the system increased.

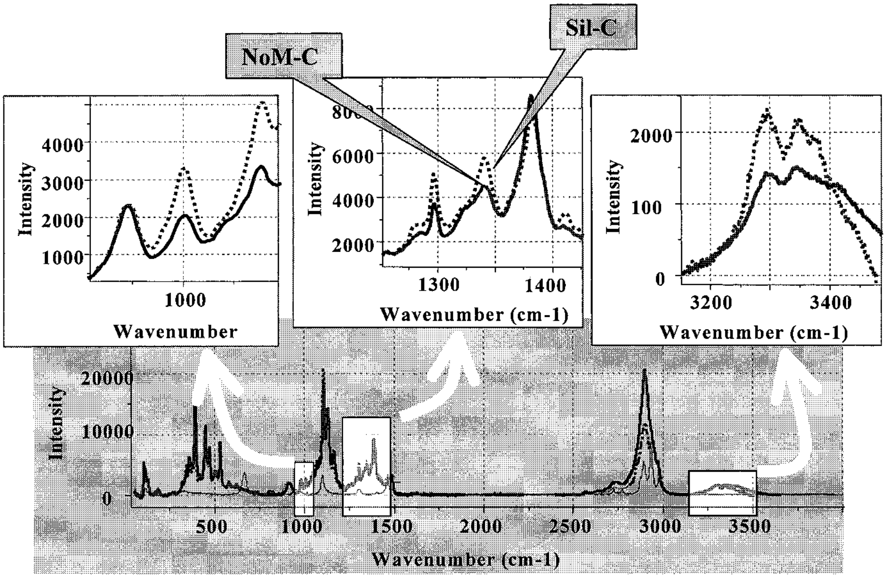

Fig. 7. Overview Raman spectra of non-treated and Sil treated cellulose and TES, and magnified spectra sections of non-treated and Sil treated cellulose.

Flame Retarding of Cellulose Fiber Containing PP Composite

The cellulose fiber containing composites contain a large amount of -OH groups. The polyols are effective char forming components in intumescent flame retardant polyolefin compounds.[12,13,14] It is an obvious suggestion to combine the -OH groups of cellulose-PP composite as char former with an acid source (APP) to form natural fiber reinforced composite in flame retarded form. The Figure 8 shows the LOI values of the SRS modified wood flake containing PP composites prepared with 10% APP. As it can be seen, LOI hardly changes between 10 and 40% wood flake content. Increasing the fiber content to 50% the flammability strongly changes and reaches 30%. With 50% wood flake content the composite achieves the V0 flammability grade in the UL 94 test. The combination of cellulose fiber reinforced PP composite with APP acid source results in flame-retardant compound.

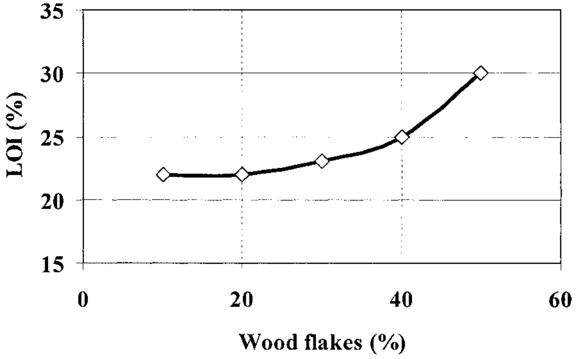

Fig. 8. LOI values of PP composites containing various amounts of SRS treated wood flakes and 10% ammonium polyphosphate.

Conclusion

The pre-treatment of cellulose fibres with non-ionic, ionic, reactive non ionic surfactants and by silylation, improves the compounding, thermal stability, mechanical properties and reduces the discoloration when used in PP compounds. Silylation has the most favourable effect, owing to the organophilisation and modification of crystalline structure, that is to the reduction of –OH groups in the amorphous phase. The addition of ammonium polyphosphate to the cellulose fibre containing composite results in flame retardant compound.

Acknowledgement

This work has been financially supported by the Hungarian Research Fund through projects OTKA T32941, NKFP 00169/2001 and NKFP 3A/0036/2002.

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