Summary of the research

For the better understanding of the results, the summary is divided into three subsections, depending on the matrix used for the preparation of nanocomposites via water-mediated melt compounding [1], namely: i) thermoplastic starch (renewable resource); ii) polypropylene and polyamide 6 (petroleum-based); iii) polytetrafluoro ethylene.

i) Thermoplastic starch based nanocomposites prepared via water-assisted route

This first part of the summary describes the results achieved on thermoplastic starch (TPS) based nanocomposites. In all these cases water served a dual role of being a plasticizer for starch when processing it to TPS, and a carrier for mineral and natural micro- and nanosized fillers. As mineral reinforcement we applied two types of clays: bentonite and montmorillonite. As natural reinforcement we used cellulose.

1) Thermoplastic starch/cellulose micro- and nanocomposites

Thermoplastic starch matrix based microfibrillated cellulose (MFC) reinforced composites were prepared first by using our batch-type mixer. Later, when necessary modifications were done on our co-rotating twin-screw extruder, we adapted the processing on that machine. Starch was simultaneously plasticized with distilled water and glycerol. Two different MFC types were incorporated into the TPS matrix. Mechanical, morphological and thermal tests were done. The mechanical properties of TPS were markedly enhanced by the introduction of cellulose. It has been shown that the mean length and diameter of MFCs, yielding similar aspect ratio values which were below the estimated critical aspect ratio, influenced the mechanical, thermal and thermo-mechanical properties marginally. There were two graduate diploma works (MSc) done about this research, and the related results were published in a paper [2].

2) Thermoplastic starch/natural rubber/cellulose composites

Throughout the researches described in 1) it became clear for us, how important is the moisture content of TPS based composites processed with our method. To get a comprehensive picture about matrix-water-reinforcement relations, we applied a broadband dielectric spectroscopic analysis. Thermoplastic starch (TPS) containing microfibrillated cellulose (MFC) and natural rubber (NR) modifiers was prepared in our co-rotating twin-screw extruder and the corresponding systems were characterized by broadband dielectric spectroscopy as a function of both temperature and frequency. It was shown that there are two relaxation processes attributed to matrix-water-reinforcement interfacial polarization and glass to rubber transition of the TPS, respectively. The evaporation of water significantly affected the first process and only slightly the second one. The matrix-water-reinforcement interfacial polarization relaxation process is assigned to the existence of water molecules between the polymer chains and constituents, decreasing their reinforcing effect. It was observed that evaporated water can be partially retrieved inside the composites, under proper environmental conditions, indicating that the effect of absorption/evaporation is reversible. Hence, TPS biocomposites modified with microfibrillated cellulose and latex microparticles could be considered as functional materials also exhibiting sensing capabilities. Throughout this step of our research we managed to build a successful relationship with a fellow Greek research group, which helped us with their expertise to get a deeper insight in the morphology. The related results were published in the journal Carbohydrate Polymers [3].

3) Thermoplastic starch/layered silicate nanocomposites

TPS/bentonite (BT) nanocomposites containing up to 7.5 (parts per hundred parts resin (phr) bentonite were produced. Maize starch was plasticized with glycerol and water, in presence or absence of BT, in our twin-screw extruder. Water had a double role in this case: plasticizer for starch and carrier for BT nanoparticles. Moreover, water was expected to widen the intergallery distance in BT and thus facilitating its intercalation by the TPS molecules. Mechanical, morphological and thermal properties of the TPS/BT nanocomposites were determined and discussed. Scanning electron microscopic (SEM) images revealed a good dispersion of the BT particles, however, with some remaining agglomerates in the range of 0.1 to 1.5 μm. According to the tensile test results the tensile strength and Young's modulus increased significantly with increasing BT content, however, at cost of the ductility. Thermogravimetric analysis (TGA) showed that the presence of bentonite exerted little to no effect on the thermal stability of TPS. The related results were summarized in a paper [4]. A follow-up study addressed the effect of BT on the residual properties of TPS as a function of aging (storage time up to four months). Retrogradation (a time dependent alteration of the crystalline structure of TPS) has been analyzed by carrying out wide angle X-ray investigations (WAXD) and performing mechanical and thermal tests. The presence of BT increased the rate of transformation from the initial A-type (starch) to V-type (thermoplastic starch) crystalline form. It was also found that BT particles hindered the recrystallization (retrogradation) of TPS. BT became intercalated in TPS, which was supported by the water used as additional plasticizer for the compounding of maize starch. According to gravimetric measurements, TPS samples lost part of their water content during retrogradation/aging. Both the incorporation of BT and the time of aging resulted in increased strength and stiffness, however at the cost of elongation at break. This was associated with enhanced strength and stiffness, which was ascribed to a change (from more to less hydrated) in the interphase. According to scanning electron and atomic force microscopy analysis, the reinforcing BT particles were homogenously dispersed on nano and micron scale within the TPS matrix. There was a graduate diploma work (MSc) done about this research, and a paper containing these results has been submitted [5].

4) Thermoplastic starch/NR blends

To increase the toughness of TPS trials were made to modify it with natural rubber (NR), introduced in form of latex. Contrary to our expectations the mechanical properties of TPS decreased, mostly due to the different characteristic of components and the rather poor adhesion between them. The results were published in in the local journal “Polimerek” [6].

5) Thermoplastic starch/polylactic acid (PLA) blends

Works were addressed to the compatibilization of blends composed of polylactic acid (PLA) and TPS. Different types of coupling agents (maleic anhydride, polyisocyanate, epoxy functionalized chain extender) have been introduced to increase the adhesion between the components. Static and dynamic mechanical tests, thermal analysis were performed. The morphology was analyzed through various microscopic techniques. Since the results were less encouraging than expected, these works were not followed further. There was a graduate diploma work (BSc) done about this part of the research.

6) Thermoplastic starch/ poly(butylene adipate-co-terephthalate) blends with and without layered silicates (clay)

Because NR did not increase the ductility of TPS/BT and TPS/organophil-modified montmorillonite (oMMT) nanocomposites, the latter were blended poly(butylene-adipate-co-terephthalate) (PBAT). PBAT is a biodegradable polymer just like TPS, however of petrol-based origins with high ductility. Blending PBAT with TPS and TPS/layered silicate nanocomposites seemed to be a proper way to increase the toughness of the related systems. The blends were prepared via a two-step melt blending procedure including extrusion (where nanoparticles were introduced into TPS in a water-assisted way) and batch-type mixing (where TPS and its nancomposites were blended with PBAT). The water played a dual role also in this case: it was a plasticizer for starch and it was also a liquid media to facilitate the intercalation and disintegration of the clay particles. The blends of TPS and PBAT showed acceptable ductility, however at cost of strength and stiffness. By contrast to the oMMT, BT became intercalated and worked as nanoreinforcement in both TPS and TPS/PBAT blends. The related results were made public in a paper [7].

ii) *Petroleum-based polymer nanocomposites prepared via water-assisted route*

Synthetic boehmite alumina (BA) with the composition AlO(OH), being available by the firm of Sasol Germany, was one of the preferred water dispersible nanofillers. In order to have a clear overlook on what has been done in this field, we have prepared and exhaustive review on this topic [8]. In this overlook the matrices were grouped into thermoplastics, thermosets and rubbers. During presentation of the results special attention was paid on the water- and solvent-assisted preparation techniques. Based on this survey trials were made to produce toughened and nanoboehmite-reinforced thermoplastics, namely polypropylene (PP) and polyamide-6 (PA-6). As toughening agents rubber latices (natural rubber (NR) and carboxylated acrylonitrile butadiene rubber (XNBR) served in which the rubber particles are available in micron-submicron scale. With their use we tried to bypass agglomeration problems owing to compatibility issues and differences in the melt viscosities. Note that both of them are the controlling factors of the morphology development in polymer blends. The other aim of the common use of nanofillers and rubber was to compensate the toughness deterioration ceased by the nanoreinforcement. The additives (boehmite and rubber) were introduced in their dry form and through water-assisted melt compounding, separately and together, as well. The purpose of this comparison was to investigate the effects of the different preparation methods, whereby focusing on the quality of the dispersion of the toughener and that of the reinforcement.

1) Polypropylene based blends and nanocomposites

Morphological tests confirmed, that the water-mediated melt compounding resulted in a better dispersion of BA within the matrices. This was reflected by strongly enhanced Young's moduli of the nanocomposites compared to the dry compounded counterparts. BA particles did not affect significantly the impact strength, on the other hand, both types of rubbers worked as efficient tougheners for the PA-6. The addition of rubber in latex led to a better dispersion than in "dry" form. In case of PP NR rubber performed much better than XNBR that was attributed to better compatibility. The structure (rubber particles size)-property (mechanical properties incl. toughness) relationships in NR- and XNBR-toughened PPs were deduced and the related results published [9, 10]. As we were faced to difficulties during introduction of the aqueous dispersions of BA nanofillers in the PP melt in batchwise operations, the dispersion was "thickened" by carboxymethylcellulose (CMC). CMC thickener markedly facilitated the water-mediated "nanoreinforcing" route. The nanocomposites showed increased stiffness at rather constant strength, however with some toughness loss.

2) Polyamide 6 based blends and nanocomposites

In this research we prepared polyamide 6 (PA6) based, boehmite reinforced, rubber toughened nanocomposites. The nanocomposites were prepared via direct and water-mediated melt compounding, depending on the filler type. Throughout this work we mostly focused on the effects of the presence of aqueous media. Changes in the material properties were determined by performing tensile tests, Charpy impact tests, dynamic mechanical analyses, and differential scanning calorimetry. The morphology has been analyzed by SEM images taken from the fracture surfaces of the samples. In the early phase of this work we compared the samples prepared with dry boehmite particles, and when they were introduced as an aqueous slurry into the molten PA6. In both cases, boehmite aggregates were observed on the fracture surfaces. On the latter case, the Leidenfrost-effect could also be observed during the processing due to the relatively low boiling point of the water. To “thicken” the aqueous dispersion we used polyethylene-glycol (more suitable for PA6 than CMC) in this case. Morever, we tried to incorporate boehmite into the PA6 matrix simultaneously with NR and XNBR. Introducing PEG improved the quality of processing. To evaluate the effect of the presence of water we used NR and NBR in their dry and latex form also. Mechanical and thermal tests showed, that the presence of aqueous media resulted a better dispersion of the boehmite nanofillers, thus increased the Young’s modulus of PA-6 remarkably. Boehmite particles however had no significant effect on the impact strength. Both types of rubber had a toughening effect on the PA6, while the Young’s modulus decreased due to rubber content, as expected. The addition of rubber in latex form led to a better dispersion. The aqueous media played a key role in dispersing the rubber particles. There was a graduate diploma work (MSc) done about this research. Publication of these results are expected after further control measurements.

iii) Polytetrafluoro ethylene/graphene nanocomposites

The research work has been expanded for a further nanofiller, namely graphene (GR). GR was incorporated in polytetrafluoro ethylene (PTFE) via a solvent-assisted technique before sintering. This technique resulted in a far better dispersion of the GR nanoplatelets than conventional dry blending. In order to enhance the solvent dispersibility and compatibility of GR toward PTFE, GR was chemically modified via oxyfluorination (OFGR). The related PTFE/graphene nanocomposites, containing up to 7 vol% graphene derivatives were subjected to tribological and thermooxidative degradation tests, and the related results already published [11, 12]. The most important finding was that the coefficient of friction of PTFE (at about 0.3) was reduced by almost 30% already at 0.75 vol% graphene content and scattered in this range as a function of further graphene loading. The specific wear rate values dropped into the ultralow wear rate at about 1 to 2 vol% graphene content and above. This change was attributed to the formation of a robust transfer film on the metal ring countersurface according to SEM inspection.

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