

Water-Mediated Production of Thermoplastic Nanocomposites

J. Karger-Kocsis^{1,2} and Á. Kmetty²

¹Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Muegyetem rkp. 3., H-1111 Budapest, Hungary

²MTA–BME Research Group for Composite Science and Technology, Muegyetem rkp. 3., H-1111 Budapest, Hungary

Abstract

Water-mediated, or more generally liquid-mediated, melt compounding of nanocomposites is basically a combination of solution-assisted and traditional melt mixing methods. It is an emerging technique to overcome several disadvantages of the above methods which are shown through selected examples in this paper. Water or liquids do not work merely as provisional carrier materials of suitable nanofillers. Though these liquids are evaporated during compounding, they markedly contribute to a better dispersion of the nanofillers whereby affecting the properties (actual melting, molecular weight, final morphology) of the matrix, as well. A brief survey is given below on the present praxis and possible future developments of liquid-assisted melt mixing techniques for the production of thermoplastic nanocomposites.

1. Introduction

Thermoplastic polymer nanocomposites have received considerable scientific and technological interest. This is reasoned by the fact that the properties of the corresponding polymer matrix can be prominently enhanced at relatively low amount of nanofiller loading. The nanocomposites may show improved mechanical, barrier, flame retardant, electrical and magnetical behaviours. Recently, research interest turned to ensure the matrices with functional (conductivity, adaptive or stimulus-responsive features) rather with structural (i.e. mechanical) ones.

Thermoplastic nanocomposites are prepared by in situ polymerization, solvent-assisted techniques and melt mixing routes. Each of them has its advantage and disadvantage. As mentioned above the water- (or more generally liquid-) mediated technique represents a combination of solution-assisted (yielding mostly the best dispersion) and traditional melt mixing (yielding usually the poorest dispersion) methods. Basic benefits of the liquid-assisted technique are as follow:

- no need for surface modification of the nanofiller. This is especially important for such fillers which should be rendered organophilic in order to achieve their acceptable dispersions. For anionic and cationic clays ion exchange with suitable bulky surfactants is practiced for this purpose.
- no decomposition/degradation of the surface modifier being absent. This is a key issue for ammonium (onium) intercalated (surface modified) clays whose thermal decomposition limits the processing temperature and thus the possible range of polymers (they can never be used in high temperature resistant thermoplastics).
- reduced health risk when added in aqueous slurry compared to the dosage in dry powder form. This is a clear advantage when preformed (available *ob ovo* in nanoscale) nanoparticles should be incorporated.
- improved nanofiller dispersion due to “blow-up” phenomena when the pressurized liquid evaporates from the melt. This was the basic idea of the early patent [1]. The

other fundamental effect, linked with matrix/water (liquid) interactions, has been clarified later. The related interactions include cryoscopy (i.e. depression of the melting point associated with decreased melt viscosity), plasticization. It has to be born in mind that some polymers are prone for hygrothermal decomposition, resulting in substantially lower molecular weight (MW) products that should be counterbalanced.

- there are further aspects worth of mentioning. Water in some cases is an indispensable plasticizer that should not be removed during compounding. This is the case for the production of thermoplastic starch (TPS) from natural starch. So, gelatinization and nanoreinforcement of starch can be performed simultaneously. In other cases, the liquid may work as reactive compound, for example for coupling molecular chains thereby enhancing the MW [2].
- polymer and rubber latices are aqueous dispersions, too. Like nanofiller dispersions these latices can also be directly incorporated alone or in combination with suitable nanofillers to produce impact-modified (toughened) and nanoreinforced thermoplastic composites. This concept has been patented, as well [3].

The nanofillers can be grouped upon their origin, appearance, composition and the like. With respect to water (liquid) melt compounding the possible classification may consider the swelling ability, dispersibility. There are also several options for the matrix categorization. In our brief summary the nanocomposites are grouped according to their matrices (commodity, engineering, advanced or high temperature resistant) and appearance of the nanofillers (quasi-spherical, disc-like or platy and needle-like or fibrous). Our intention next is to show some general trends using examples rather than to give detailed review.

2. Thermoplastic polymer matrix-based nanocomposites

2.1. Commodity resins

The related works focused on the incorporation of pristine montmorillonite (MMT), usually in its Na⁺-form, into polyethylene (PE) [4-5] and polypropylene (PP) [6-7]. In all reported works an additional coupling agent, namely maleic anhydride grafted version of the corresponding matrix (-g-MA) was used as compatibilizer. Shahabadi and Garmabi [4] prepared PE/MMT nanocomposites whereby studying whether injection of the water, or aqueous surfactant solution or clay slurry in the compression zone of the extruder gives the best results. Kato *et al* [6] were able to prepare exfoliated PP/MMT nanocomposites extruding PP, PP-g-MA and organophilic clay surfactant along with high-pressure pumping of water. Rousseaux *et al* [7] compared whether dosage of Na⁺-MMT or its surface modifier version can be better dispersed when high-pressure water injection is adapted. The best results were achieved when a masterbatch composed of PP, PP-g-MA and organoclay (=surface modified clay), was diluted with PP through this water-assisted melt compounding. Intercalation/exfoliation of the clay was supported by chemical reaction between the organoclay's surfactant and acid groups formed from the PP-g-MA. Other fluids, such as ethylene glycol, naphta, n-heptane, were also tried as swelling agents for organoclays when compounded with PP. The new aspect here was to introduce the corresponding clay slurry in a pressureless or low pressure section (feeding zone) of the extruder screw [8]. Attempt was made to convert microcellulose to nanocellulose using this high pressure water injection method, however, without success [9]. In batch operation also carbon nanofiber has been introduced from its aqueous dispersion in a thermoplastic elastomer [10].

2.2. Engineering resins

Nanocomposites first produced by this water-assisted technique were polyamide (PA)-based ones [11-14]. Fedullo *et al* [14] quoted a dual role of water during this operation. Water is

completely miscible with PAs. This means a large cryoscopic effect that reduces the melting temperature of PA-6 at high pressure by about 60 °C. Surprisingly, water injection did not result in significant MW decrease. The other effect is already mentioned: water diffuses in to the intergallery space of MMT and hydrates the cations whereby causing it swelling. The latter yields an expansion of the intergallery distance. The sudden release of water in vapour form from the intergallery regions is termed “blow up” phenomenon by us. Note that the cryoscopic effect is the less, the higher that monomer length which belongs to one amide group in the corresponding PA [15-17]. Nonetheless, fully exfoliated morphology was found up to 10 wt.% pristine clay even for PA-11 [15], and at least such fine dispersion which is comparable with that received by organoclay for a PA-12-based thermoplastic rubber [16]. The water-assisted technique proved to be useful also for the production of PA-12/halloysite (HNT) nanocomposites [17]. HNT is a fibrous natural silicate. For the fine dispersion of HNT H-bonding between the PA chains and HNT surface through absorbed water was made responsible.

Even polyethylene terephthalate (PET)/clay nanocomposites were prepared by this technique though PET is far more prone for hygrothermal degradation than PA. It was reported that using centrifuged MMT slurry a better dispersion than with uncentrifuged one (containing large particle agglomerates) can be reached. Unexpectedly, the fine dispersion of clay causes lesser degradation of the PET than the coarser one. Dini *et al* [19] incorporated organoclay into PET by water-mediated method. The MW reduction, observed for PET, has been compensated by subsequent solid-phase polymerization which is widely followed to enhance the MW of PET.

Water-assisted melt compounding was adapted also to prepare polyoxymethylene (POM)-based nanocomposites [20-21]. In these works instead of MMT water dispersible synthetic boehmite alumina was added. This boehmite, available in different primary crystal sizes, can well be dispersed in water in nanoscale. Water was injected into the pressureless feeding zone of the compounding extruder. On the example of POM the toughening and toughening/reinforcing strategies using polyurethane (PU) latex and PU latex + boehmite nanoparticles were also checked [20]. Simultaneous incorporation of the PU toughener and boehmite nanofiller was not successful because the latter migrated into the PU particle phase. By contrast, prominent toughening was achieved by dosing the PU latex alone.

2.3. Advanced (high temperature-resistant) thermoplastic resins

Only very few works were published on this field. For example, Jana and Jain [22] dispersed fumed silica using low MW epoxy dispersant in polyethersulphone (PES). Nevertheless, great efforts will be dedicated to produce nanocomposites based on high temperature-resistant thermoplastics next. Needless to say that instead of water suitable fluids with high boiling point and low volatility will be selected. This may contain several steps of solvents/fluids' changes, as well. Moreover, untreated nanofillers will be replaced by properly treated ones.

2.4. Natural polymers

Water-assisted melt compounding seems to be the right way when water is an essential additive that remains in the final polymer, for example as plasticizer. This is the case with TPS. To boost the properties of TPS water-assisted melt compounding with layered and fibrous silicates (MMT and HNT, respectively), boehmites, and especially with micro- and nanofibrillated cellulose particles seems to be appealing. The feasibility of the last one has been recently shown by Hietala *et al* [23]. The latex route has not yet been explored for TPS though looks very promising.

3. Conclusion

Water-assisted melt compounding remains under spot of research interest further. In order to improve its efficiency different water soluble additives, promoting the dispersion and surface modification of the corresponding nanofillers (salts, surfactants, thickeners) will be used. Attention will be paid on optimizing the extruder parameters (screw configuration along with the pressure profile, temperatures, residence time...). It is still an open question whether introduction of water should occur in the feeding or in the compression zone of the extruder. Vivid research and development works are expected for the production of high temperature resistant thermoplastic nanocomposites. Here new concepts will be elaborated and their feasibility checked. Instead of water, however, other fluids of high boiling point, monomers and polymers, which may overtake further roles (e.g. chain coupling, reactive surface modification) will be preferentially tried.

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