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Using elongational flow to enhance the properties of polypropylene nanocomposites

Sundaresan Arunachalam, Markus Battisti, Leonhard Perko, Sebastian Stieger, and Walter Friesenbichler

Different nozzle geometries were investigated to find the optimum injection molding strategy for the production of polymer nanoclay composites.

Polymer nanoclay composites (PNCs) have received much attention in recent years because of their good material properties, e.g., their strength, stiffness, and barrier properties. PNCs are commonly produced by solution mixing and in situ polymerization, but the most interesting method of production for industrial applications is melt blending (because of its simplicity and applicability to large amounts of material). In this process, the PNC is produced directly in the polymer melt.[1–5] To produce PNCs in this way, the nanoclay particles need to be dispersed within the polymer matrix. Although such nanoclay dispersion is commonly achieved through shear deformation, it is thought that elongational deformation can also be used to significantly increase the effectiveness of the compounding process.[6–8]

Several elongational-flow mixing devices have therefore recently been developed.[9–12] As part of these efforts, a basic study of the effect of converging nozzle geometries on the homogeneity of polymer compounds has previously been conducted.[11] The results indicated that the best mixing efficiency was achieved when a conically shaped nozzle (with a half-angle of 60°), or a hyperbolically shaped nozzle, was used. The hyperbolically shaped nozzles were especially suitable for mixing polymers that had only slight differences in viscosity, whereas the conically shaped nozzles gave rise to sharper peaks in the elongation rate and were therefore more suitable for the mixing of polymer blends with higher viscosities. The elongation rate as a function of nozzle length (for different nozzle geometries) was also investigated as part of this study.[11] Although some mixing devices that are based on elongation flow are now commercially available,[13,14] these have not yet been applied broadly in industrial situations.

In this work,[9] we have focused on achieving improved material properties for PNCs by optimizing the injection molding process. To do this, we employed two different processing strategies. In the first strategy—a two-step process known as a masterbatch (MB) process—we first compounded the compatibilizer (polypropylene-grafted maleic anhydride) and the organoclay (organically treated montmorillonite, which here serves as the nanoclay) in a 50/50 (weight/weight) ratio to form the MB. In the second step, we mixed the MB with polypropylene (PP) to obtain the final PNCs. In contrast, in our second strategy, we added

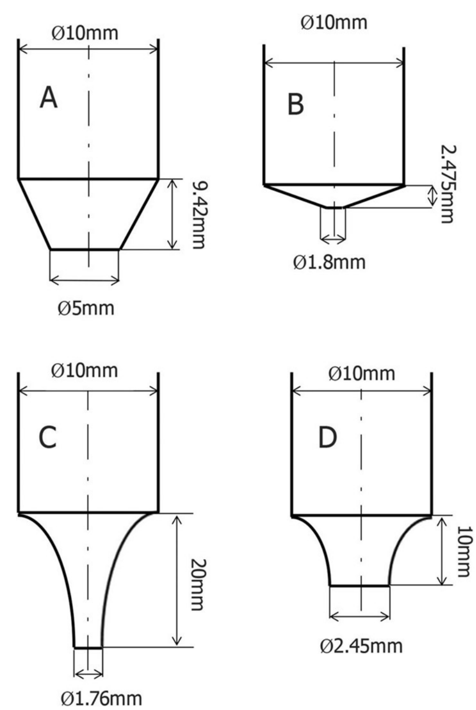

Figure 1. *Diagrams of the flow channel within the different nozzle geometries used in the elongational deformation experiments. The geometry of the (A) standard injection nozzle, (B) short, conically shaped nozzle, (C) long, hyperbolically shaped nozzle, and (D) short, hyperbolically shaped nozzle are shown.[9] ϕ: Diameter.*

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Table 1. Process parameters for the injection molding process.[9]

Parameter	Value
Holding pressure	Tensile test specimens: 90MPa; plates: 60MPa
Holding pressure time	Tensile test specimens: 30s; plates: 12s
Inlet temperature of cooling water	45°C
Dosing speed*	$0.3ms^{-1}$
Back pressure*	5MPa
Barrel temperature$^{(Zone\ 1-6)}$* (°C)	$210^{(1)}$, $215^{(2)}$, $215^{(3)}$, $220^{(4-6)}$
Volumetric flow rate$^{(Zone\ 1-6)}$* (cm^3s^{-1})	$10^{(1)}$, $30^{(2)}$, $50^{(3)}$, $100^{(4)}$, $150^{(5)}$, $200^{(6)}$
Remaining cooling time after holding phase	35–40s
Shot volume*	$80cm^3$

*Process parameters for the pressure and temperature measurements in pilot tests.

all the components to the polymer during compounding to produce the final PNCs in one step. We subsequently conducted injection molding (see Table 1) of the two sets of compounds, and thus obtained tensile test specimens and rectangular plates. To apply the elongational deformation to the melts, we modified the injection unit by using injection nozzles with different geometries that we designed based on the previous work of Meller and coworkers[11] (see Figure 1). In particular, we designed the geometry of the hyperbolically shaped nozzles—Figure 1(C) and (D)—so that we could achieve a steady elongation rate along the entire nozzle length.[9]

Through our set of experiments (see Table 2), we tested the influence of the compounding process (i.e., MB or one-step process), the volumetric flow rate, and the nozzle geometry on the mechanical properties of the samples. Our tensile test results (see Figure 2) indicate that the Young's modulus has a slight dependence on the MB material at different volumetric flow rates, when different nozzles were used. There is also evidence that the Young's modulus of the PNC samples was improved by 45% compared with pure PP (for experiments using the standard nozzle at $100cm^3s^{-1}$ and 1585±21MPa). Among the nozzles we investigated, we find that the short, hyperbolically shaped nozzle and the conically shaped nozzles performed best. For the MB process, however, we did not observe any significant improvement to the material properties by using the conically or hyperbolically shaped nozzles. Furthermore, the PNCs we produced with the conical and short, hyperbolically shaped nozzles in the one-step process generally have lower Young's modulus values than the equivalent samples produced via the MB process (see Figure 2). The use of the standard nozzle in the MB process gave rise to the best tensile properties we observe, followed by the long, hyperbolically shaped nozzle. This is because the additional energy input in these nozzles causes a pressure decrease, which in turn influences the material properties. Overall, we find that the MB process produces PNCs with better tensile properties, but it is possible to achieve similar performance levels with the conical or short, hyperbolically shaped nozzles in the one-step process.

We also made rheological measurements of our PNC samples and found that there was no degradation of the polymer from more intense

Table 2. Experimental plan for the compounding and injection molding experiments.[9]

Parameter	Variation
Compounding steps	One-step process
	Two-step/masterbatch process (MB)
Nozzle design* (see Figure 1)	(A) Standard injection nozzle
	(B) Short, conically shaped nozzle
	(C) Long, hyperbolically shaped nozzle
	(D) Short, hyperbolically shaped nozzle
Volumetric flow rate (cm^3s^{-1})	10, 30, 50, 100, 150, 200

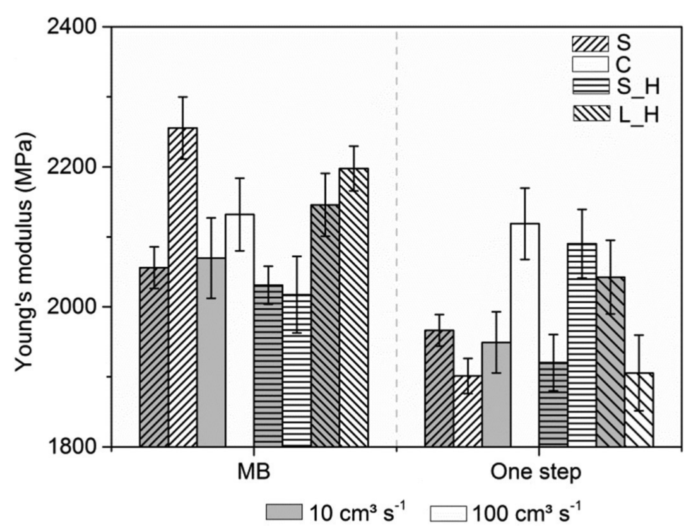

Figure 2. Young's modulus of the polymer nanoclay composites (PNCs) produced with the use of the standard (S), conical (C), short, hyperbolically shaped (S_H), and long, hyperbolically shaped (L_H) nozzles at volumetric flow rates of 10 or $100cm^3s^{-1}$ in the (left) MB and (right) one-step injection molding processes.[9]

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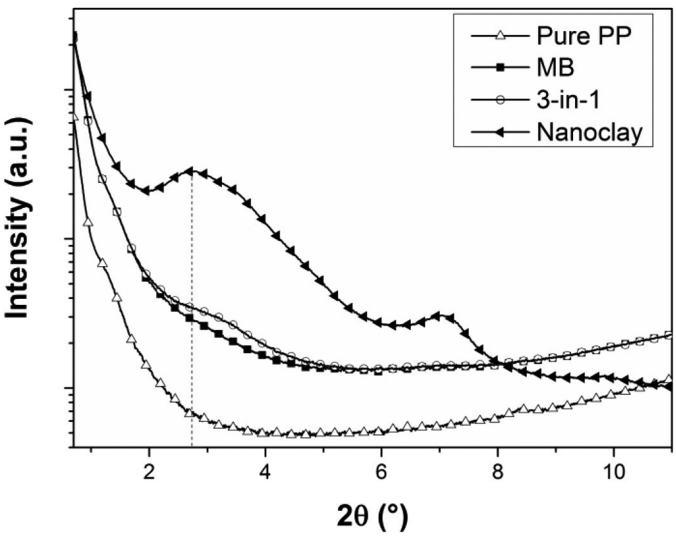

Figure 3. *Small-angle x-ray scattering measurements of pure polypropylene (PP), nanoclay, and PNCs produced via the MB process and the one-step process (3-in-1). These results were obtained with the use of the short, hyperbolically shaped nozzle, and a volumetric flow rate of* $100cm^3s^{-1}$.[9] *a.u.: Arbitrary units.* θ*: Scattering angle.*

levels of mixing in the converging nozzles. In addition, we observed an increase in the viscosity of the samples with more intense levels of shear and elongational deformation. This indicates the enhanced exfoliation of the nanoclay particles within the PNCs. These results also suggest an increase in the zero-shear viscosity with an increased rate of intercalation and exfoliation. The tensile properties of the samples are thus directly related to the intercalation/exfoliation level in the nanoclay disperson. Our small angle x-ray scattering results (see Figure 3) show that the use of the MB process produces a better interaction between the PP and nanoclay than the one-step process, as predicted from the tensile test results (i.e., where higher modulus and strength were obtained from the MB process than the one-step process).

In our study we also performed pressure and temperature measurements to characterize the pressure drop, and the temperature rise, generated in the different nozzles. Our results show that the short, hyperbolically shaped nozzle performed best—exhibiting only a moderate pressure loss (up to 60MPa) and strong mechanical properties—in the one-step process. We also used these experiments to test a calculation method (to predict the pressure and temperature changes). Although our predictions for the pressure decrease with the standard and conical nozzles matched the experimental results well, we obtained larger errors for the hyperbolically shaped nozzles (because elongational flow was neglected in the calculations).

In summary, we have conducted a series of injection molding experiments on polymer nanoclay composites to investigate ways to improve their material properties. We studied how different compounding processes, nozzle geometries, and flow rates affect the mechanical and rheological properties of the samples. Overall, we find that the MB process generally produces enhanced properties compared with samples produced via the one-step process. In our future research we will conduct follow-up work to investigate the material properties of PNCs with different compositions. We will also optimize the injection molding nozzles by systematically varying their geometry, and we will perform a detailed study into the rheological and structural behavior of PNCs.

Author Information

Sundaresan Arunachalam, Markus Battisti, Leonhard Perko, Sebastian Stieger, and Walter Friesenbichler
Institute of Injection Molding of Polymers
Montanuniversität Leoben
Leoben, Austria

Sundaresan Arunachalam is a master's student and a member of the Association of Leoben Plastics Engineers (Verband Leobener Kunststofftechniker). His research interests are focused on polymer injection molding, nanocomposites, rheology of polymers, and injection molding simulations.

Markus Battisti obtained his PhD in 2015 from Montanuniversität Leoben. His doctoral thesis focused on elongational-flow-generating nozzles for the production of property-enhanced polypropylene nanocomposites. He is now the leader of the Engineering Technology Plastics group at Hirschmann Automotive, Austria.

Walter Friesenbichler is a professor, and has conducted research and taught at Montanuniversität Leoben since he graduated in 1984. His research is centered around three areas: applied rheology (including pressure dependence of viscosity and extensional rheology), injection molding, and polymer nanocomposites.

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