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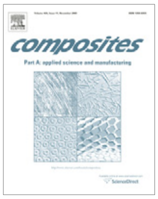

Rheological behavior of original and recycled cellulose–polyolefin composite materials

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ABSTRACT

The effects of shear rate, fiber content and type of matrix on the melt rheological behavior of cellulose–reinforced polyolefin composites before and after their mechanical recycling was investigated, due to their relevance for the suitable engineering design of their processing operations. Original composites of HDPE or PP with residual Kraft pulp fiber contents of 10, 25, 40 and 48 wt% were obtained in a thermokinetic mixer. Five-cycle reprocessed composites were produced by successive injection molding. Capillary rheometry enabled us to obtain rheological curves for all these composites, and developing a new statistically checked modified Ostwald-de-Waele model for predicting their rheological behavior in real situations. The rheological data collected, along with SEM and TGA analysis, mainly revealed a more pronounced degradation of cellulose fibers for the HDPE-matrix reprocessed composites, a greater pseudoplasticity loss upon recycling for the PP-matrix composites than for HDPE-matrix ones, and that fiber's dispersion was independent of matrices used.

1. Introduction

The use of cellulosic materials for reinforcing polyolefinic matrices (such as polyethylene and polypropylene) is of great interest due to the inherent advantages of cellulosic reinforcements. Among others, these are low density, low abrasion of processing equipment, reduced health hazard, relatively good specific mechanical properties, as well as sustainability advantages. These include the use of renewable natural resources and reduced energy consumption as a consequence of the relatively low processing temperatures of these composites. Due to such advantages cellulose-reinforced thermoplastic composite materials are an emerging research and development area and are the object of several emerging applications in fields such as the automobile, construction and aerospace industries.

The manufacture of end products using these thermoplastic composites requires their melting and flow through the existing plastic processing equipment (e.g., extruders and injection molding machines) and their tooling (e.g., extrusion dies and injection mold runners). However, in order to obtain end products with a good performance a suitable engineering design of the polymer processing unit operations involved is required as well as the choice of suitable processing parameters. For this purpose, knowledge about the melt flow behavior of these composites at shear rates encountered in the most relevant polymer processing operations is necessary.

On the other hand, as a general rule, the introduction of new polymeric materials in the market is nowadays subjected to fulfilling certain recyclability criteria. Recyclability of new polymeric materials is a main concern all over the world, due to the vast amount of waste polymeric materials generated by industrialized societies and the associated environmental impact. Mechanical recycling of polymeric materials allows for the integration of their wastes into their production cycle, thus providing new raw material and extending their life cycle. Therefore, it is considered a very interesting recycling way from both economical and environmental points of view. As is well known, one of the main disadvantages of cellulosic reinforcements is their poor thermal stability, which explains the severe degradation that may occur during the processing of their corresponding composites by extrusion and injection [1]. One of the results of the degradation during such operations may be the change in the rheological behavior of the composites, which may limit their recycling and the manufacture of new end products using recycled composites.

Several works have been devoted to the study of the rheological properties of composites with matrices such as LDPE, PP, HDPE or SBR reinforced with several kinds of cellulosic fibers (pineapple, sisal, glass, sisal–glass mixtures, jute, maple wood, pine wood), among others [2–9]. Thus, it has been shown that they exhibit a pseudoplastic behavior as well as a decrease in their melt viscosity

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with increasing temperature, as a consequence of the increase in the free volume and the weakening of the intermolecular or fiber–matrix interactions when temperature increases [2–5,9]. The chemical treatment of fibers and composites with different chemicals (e.g., acetic acid, benzoyl chloride) and several kinds of coupling agents (e.g., isocyanates, silanes, graft copolymers of maleic anhydride) has shown a general increase in the shear viscosity of these composites as a consequence of the strong interaction induced at the fiber–matrix interface, which increases friction between the polymer and fiber, and results in increased resistance to shearing [2,4–6,8–10]. However, some lubrication effects of the coupling agents, which reduce the shear viscosity of composites, were also observed in some cases [8,10]. The effects of particle size on shear and extensional viscosities of composites were also studied, showing that the changes with wood filler particle size were much less significant than those with filler content and only a weak tendency to increase of the shear viscosity with decreasing particle size was perceived [8]. For maple wood flour-filled composites, at a 30 wt% filler loading, the smaller particles provide the higher apparent shear viscosity, but for higher loadings the effect of particle size becomes negligible [11]. On the other hand, the study of the effects of different molecular weights and molecular weight distributions (MWD) of HDPE matrices on the rheology of maple wood flour/HDPE composites revealed that low molecular weight and narrow MWD polyethylenes provide the greater resistance to shearing (i.e., higher relative viscosities) [10].

However, by the time of writing, the authors found no comparative rheological studies covering the typical range of fiber contents found in cellulose-reinforced thermoplastic composites addressing to their transformation into end products by injection molding (i.e., below 50 wt% of cellulose fibers) before and after their recycling. Also, from open literature review, it was observed that rheological studies on composites obtained by melt compounding and transformation methods closer to those used by the industry are rather scarce. All those studies are not only necessary for the choice of suitable processing parameters and the suitable engineering design of the extrusion and injection molding operations involved in the manufacture of end products using original composites, but also for those operations involved in the recycling and the manufacture of new end products using the recycled composites. Moreover, there is the need for rheological models that allow the prediction of the flow behavior of original and recycled cellulose-reinforced composites with different fiber contents at the shear rates range where the shear viscosity of polymer drops drastically (i.e., between 0 and 2000 s^{-1}), as consequence of their pseudoplastic behavior. The shear rates range up to 1000 s^{-1} can be encountered at the die in extrusion operations and also while filling a mold during injection molding. During the injection molding operations, the shear rates at the injection molding machine nozzle may reach up to 10,000 s^{-1}. However, the variations in the shear viscosity of polymers over 2000 s^{-1} are much lower than in the range between 0 and 2000 s^{-1}, and tend to approach asymptotically a finite constant level (second Newtonian range). The aforementioned models are also specifically needed for running extrusion and injection molding simulation packages as well as for plastic tooling design.

Therefore, this work aims at studying the rheological behavior of cellulose-reinforced composites before and after mechanical recycling by injection molding, at the shear rates range where the shear viscosity drops drastically (i.e., between 0 and 2000 s^{-1}), which is encountered in the most relevant polymer processing operations. On the other hand, this work was also devoted to finding reliable model equations to enable the prediction of their rheological behavior in real situations. For this purpose, capillary rheology was used for obtaining the rheological experimental data regarding the variation of shear viscosity with the fiber content of composites, before and after recycling. Experimental data obtained were finally fitted to a new modified Ostwald-de-Waele model. It was based on the Ostwald-de-Waele equation because this usually provides a well fitting of the polymers behavior up to shear rates around 2000 s^{-1}.

2. Experimental

2.1. Materials

Two commercially available polyolefins (high density polyethylene and polypropylene) were used as polymeric matrices. The high density polyethylene (HDPE) was Eraclene MQ-74 homopolymer (Polimeri Europa, Milan, Italy) with a density of 952 kg/m^3 (ASTM D1505) and a melt flow index of 11 g/10 min measured at 190 °C and 2.16 kg, according to ASTM D1238. The polypropylene was NOVOLEN 1100 N homopolymer (BASF, Barcelona, Spain) with a density of 908 kg/m^3 (ISO 1183) and a melt flow index of 31 g/10 min measured at 190 °C and 2.16 kg, according to ISO 1133 standard. Both polymeric matrices contained a 0.1 wt%, approx., of a general-purpose phenol–phosphite antioxidant package.

Cellulosic fibers used as a reinforcement in composites were supplied by ENCE-Navia, a Kraft pulp mill located in Navia, Asturias (Spain). These were a by-product obtained in the manufacture of Kraft cellulose pulp, mainly consisting of unbleached *Eucaliptus globulus* cellulose. The average diameter of the cellulose fibers was 16 μm, their average length was 752 μm and their average aspect ratio (L/D) was 47.

A commercially available maleic anhydride-modified polypropylene polymer (Epolene E-43) was used as a coupling agent for improving the interfacial adhesion between the non-polar polyolefins used as the matrix and the polar cellulosic fibers, obtaining composites with improved final properties. Epolene E-43 (Eastman Chemical Products, Kingsport, TN) has an acid number of 45, a weight-average molecular weight of 9100, and a number-average molecular weight of 3900.

2.2. Composites preparation and reprocessing

Two series of original composites were prepared by melt-blending of the raw materials (i.e., the polyolefin chosen as the polymeric matrix, cellulosic fibers and the coupling agent) in a 1-liter thermokinetic mixer (Gelimat GL II, DRAISWERKE Inc., Mahwah, NJ, USA). Rotation speed of the blades of the mixer was 5520 rpm when HDPE was used as the matrix and 4830 rpm when the matrix was PP. The dump temperature of the melt-blended composite was 200 °C when HDPE was used as the matrix and 210 °C when the matrix was PP. The main advantage of this mixer is its ability to obtain optimum dispersion of fibers in the polymeric matrix in a very short time (generally 60 to 120 s). Composites containing 10%, 25%, 40% and 48%, by weight, of the cellulosic fibers, and 1.5%, by weight, of the coupling agent were thus prepared.

Composites from the thermokinetic mixer were grinded to obtain pellets suitable for injection molding. For obtaining results of wide applicability to different real situations, the general molding principles set by the ISO 294-1 standard were followed. ISO 1-A composite multipurpose testing specimens, according to ISO 3167 standard, were made by injection molding in a computer-controlled 400 kN-injection molding machine provided with a 35 mm-diameter screw (SETTE 40, SANDRETTO, Collegno, Italy). Particular injection molding conditions for the composite materials studied in this research were set after a previous study, which allowed the determining of the range of conditions suitable for the injection molding of this kind of composites. At higher cylinder temperatures, or at longer cycle times, the excessive thermal