Non-Einstein Viscosity Phenomenon of Acrylonitrile—Butadiene—Styrene Composites Containing Lignin—Polycaprolactone Particulates Highly Dispersed by High-Shear Stress

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Supporting Information

ABSTRACT: Lignin powder was modified via ring-opening polymerization of caprolactone to form a lignin—polycaprolactone (LPCL) particulate. The LPCL particulates were mixed with an acrylonitrile—butadiene—styrene (ABS) matrix at an extremely high rotational speed of up to 3000 rpm, which was achieved by a closed-loop screw mixer and in-line melt extruder. Using this high-shear extruding mixer, the LPCL particulate size was controlled in the range of 3395 nm (conventional twin-screw extrusion) down to 638 nm (high-shear mixer of 3000 rpm) by altering the mixing speed and time. The resulting LPCL/ABS composites clearly showed non-Einstein viscosity phenomena, exhibiting reduced viscosity (2130 Pa•s) compared to the general extruded composite one (4270 Pa•s) at 1 s⁻¹ and 210 °C. This is due to the conformational rearrangement and the increased free volume of ABS molecular chains in the vicinity of LPCL particulates. This was supported by the decreased glass transition temperature (Tg, 83.7 °C) of the LPCL/ABS composite specimens, for example, giving a 21.8% decrement compared to that (107 °C) of the neat ABS by the incorporation of 10 wt % LPCL particulates in ABS. The LPCL particulate morphology, damping characteristics, and light transmittance of the developed composites were thoroughly investigated at various levels of applied shear rates and mixing conditions. The non-Einstein rheological phenomena stemming from the incorporation of LPCL particulates suggest an interesting plasticization methodology: to improve the processability of high-loading filler/polymer composites and ultra-high molecular weight polymers that are difficult to process because of their high viscosity.

INTRODUCTION

As the severity of environmental pollution by petrochemical products increases, interest in novel materials derived from renewable resources as polymer (or polymer composite) materials is increasing.¹ Lignin, which is the second most abundant polymer after cellulose, possesses many attractive properties such as biodegradability, abundance, antioxidant property, and non-food-based feedstock, making it an ideal candidate for developing value-added products for various applications.²,³ In addition, it is known as a natural broad-spectrum UV blocker because of the presence of phenolics, ketones, and other chromophores.⁴ Lignin, which is mainly used as an additive or filler in the polymer composite, can be applied in various forms such as kraft lignin and lignosulfonate, or in combination with other materials including cellulose, inorganic substance, and so forth.⁵,⁶ However, there is a limit to the use of raw lignin as a polymeric material. Natural lignin tends to aggregate because of the π–π stacking of aromatic rings, van der Waals attraction of chains, and strong hydrogen bonding between lignin molecules and has a problem of poor compatibility with other polymers.⁷ The surface characteristics of lignin powder may be altered by adopting freely moving molecular chains that could change the rheological properties and compatibility with matrix polymers. In this sense, we have reported that the esterification of lignin via ring-opening polymerization (ROP) of ε-caprolactone (as a reactive solvent with biodegradability, low activation energy) not only lowers the agglomeration through hydroxyl substitution of lignin but also improves the processability and compatibility with other polymers.⁸,⁹

When fillers (or particles) are incorporated in a polymer melt (or liquid), they usually act as obstacles impeding the flow...