



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

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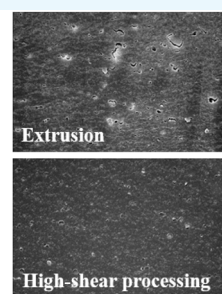
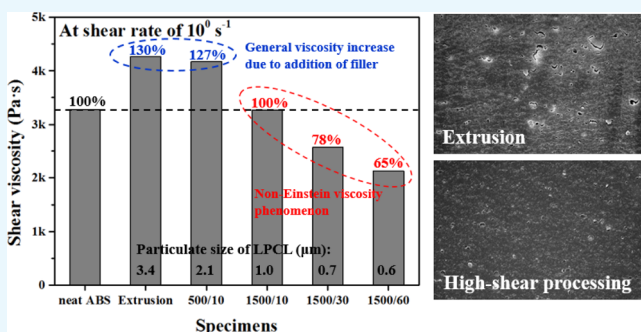
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Supporting Information

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 $210\text{ }^{\circ}\text{C}$. 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 (T_g , $83.7\text{ }^{\circ}\text{C}$) of the LPCL/ABS composite specimens, for example, giving a 21.8% decrement compared to that ($107\text{ }^{\circ}\text{C}$) 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.^{8–10}

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

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and increasing the viscosity of the polymer melt. A simple model suggested by Einstein to describe the increased viscosity (η) is as follows

$$\eta = \eta_0[1 + 2.5\varphi] \quad (1)$$

where η_0 is the viscosity of the dispersion medium and φ is the volume fraction of the dispersed particle.^{11,12} However, it has recently been reported that the assembly of filler particles dispersed in the polymer matrix can lower the melt viscosity, which contradicts the expression derived from Einstein. Specifically, the decrease of composite viscosity occurs when the mean interparticle half-distance (h) is smaller than the radius of gyration (R_g) and the molecular weight of the polymer is larger than the entanglement molecular weight^{13,14}

$$h/R_g = [\varphi_m/\varphi]^{1/3} - 1 \quad (2)$$

where φ_m is the maximum random packing volume fraction (~ 0.638 for monodispersed spherical particles) and φ is the volume fraction of nanoparticles. This decrease in the melt viscosity of the polymer–filler composite can be explained by dilution of the entanglement density of the polymer chains, increase in the free volume induced around the filler molecules, and decomposition of the polymer.¹⁵ However, it should be noted that until now, only well-dispersed spherical nanoparticles have caused viscosity reduction,¹⁶ that is, the viscosity reduction of composites to which nonspherical particles are applied must be accompanied by more innovative process conditions. The recently developed high-shear extruder used in this study can induce improved dispersibility of the composite and decrease of the aggregation size through applied shear stress.¹⁷ This can be expected to reduce the viscosity of the composite by reducing the chain entanglement of the polymer used as a matrix material and increasing the free volume induced around the well-dispersed filler. In general, the viscosity reduction of composites is considered to be very important because it leads to improved processability and productivity in composite manufacturing industries.¹⁸

Acrylonitrile–butadiene–styrene (ABS) is an engineering thermoplastic resin that is generally known for its excellent mechanical performance, chemical resistance, fine surface appearance, and easy processing characteristics.¹⁹ ABS, which is a terpolymer made up of acrylonitrile, butadiene, and styrene, is a long chain of polybutadiene crossed with shorter chains of poly(styrene-*co*-acrylonitrile). ABS is widely used for tough products, such as structural components in automotive and consumer products, pipes, and housing of electronic and electrical devices because its property–price profile is intermediate between inexpensive thermoplastic and high-performance engineering plastics.²⁰ However, one critical drawback of ABS is its poor UV resistance, which is caused by the butadiene component. When ABS is used in outdoor applications, the C=C bonds in butadiene easily undergo chemical aging under the condition of UV radiation and oxygen.²¹ To overcome this disadvantage, poly(acrylonitrile–styrene–acrylic) resin (in which butadiene has been replaced with acrylic to have no double bond in the main chain) may be used as an alternative, but UV stabilizers are generally added to the ABS resin.²² Especially, lignin can be used as an excellent UV stabilizer because it is known as a natural broad-spectrum UV blocker because of the presence of phenolics, ketones, and other chromophores.^{4,7}

In the current research, we synthesized the lignin–polycaprolactone (LPCL) particulate via ROP of caprolactone with lignin. The eco-friendly ABS composite containing the LPCL particulate as a biomass-based UV stabilizer was fabricated through a twin-screw extruder and high-shear extruder. The high-shear processing equipment was used to control the particulate size and improve the dispersibility of the lignin-based polymer in the ABS matrix. We optically investigated the dispersity of the LPCL particulate in the ABS matrix and thoroughly analyzed the thermal and rheological properties of the fabricated eco-friendly composites.

EXPERIMENTAL METHODS

Materials. ABS (HI121H) was purchased from LG. Chem. Co. Ltd., Korea. It was of general-purpose injection molding grade with a melt flow index of 23 g/10 min at 220 °C/10 kg load, as per ASTM D1238. Soft kraft lignin (the content of lignin and ash was about 97.1 and 1.6 wt %) was supplied by the Domtar Corporation (North Carolina, U.S.A.). According to the manufacturer, it was brown fine powder (elemental composition (wt % dry basis): carbon = 62.8, hydrogen = 5.0, oxygen = 28.1, sulfur = 3.6) with a bulk density of 348 kg/m³, number-average molecular weight (M_n) of 913 g/mol, weight-average molecular weight (M_w) of 1323 g/mol, and polydispersity of 1.45. ϵ -Caprolactone (CL), dibutyltin dilaurate (DBTDL), acetic acid, and tetrahydrofuran (THF) were obtained from Sigma-Aldrich. Two thermal antioxidants, SONGNOX 1010 (phenolic-based, Songwon) and SONGNOX 1680 (phosphite-based, Songwon) were used for composite preparation. All reagents were used without further purification.

Synthesis of LPCL Copolymer Particulate.⁸ The dried lignin powder (100 g) was mixed with ϵ -caprolactone (100 g). The mixture was stirred for 30 min at 1200 rpm, 90 °C by the twin-screw kneader under the nitrogen atmosphere. After increasing the temperature to 150 °C, DBTDL was added as a catalyst to the lignin and ϵ -caprolactone mixture. The LPCL copolymer was synthesized via ROP for 4 h and then cooled to room temperature (RT). LPCL was dried in a vacuum oven at RT overnight before use. More detailed information can be found in ref 8.

Fabrication of LPCL/ABS Composite. ABS, as a polymer matrix, was dried using a laboratory convection oven at 60 °C overnight before use, to remove the residual water. LPCL/ABS composites with 10 wt % LPCL contents were melt-compounded using a twin-screw extruder (L/D ratio of 40, BA-19, BauTech, Korea). The temperature of the barrel was set to 150–220 °C, and the screw speed was 200 rpm. The extruded pellets of the LPCL/ABS composite were dried in an oven at 60 °C overnight.

In another way, high-shear processing was performed using an NHSS2-28 high-shear extruder (Niigata Machine Techno Co., Ltd., Japan), which consists of a plasticization section and a high-shear section in a separate arrangement, as shown in Figure 1A. The plasticization section keeps the material in a plasticized state suitable for high-shear processing and injects constant amount into the high-shear part. In the high-shear section, the injected material is processed at a controlled rotation speed and time with an internal feedback type screw (Figure 1B).¹⁷ In order to observe the variation of the size and dispersion state of LPCL particulates (which are easily aggregated by strong hydrogen bonding) in the ABS matrix

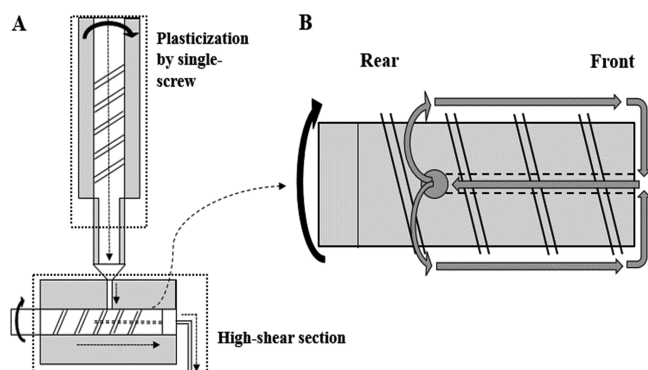


Figure 1. Schematics of (A) the internal structure for the high-shear processing machine and (B) the flow route of the injected material during mixing around the screw in the high-shear extruder.

through high-shear processing, various shear stress conditions were tested as follows. The rotation speed of the screw used in current research was set to be 500, 1500, and 3000 rpm, and the processing time was 10, 30, and 60 s. The temperature of the barrel in the plasticization section was set to 135–205 °C, while that of the high-shear section was 200–220 °C. The compounded samples were then extruded from a filament-die. For the property measurements, the processed samples were hot-pressed at 190 °C to a film with a thickness of 80 μm .

Characterization. The infrared spectra of lignin and LPCL were obtained using Fourier transform infrared (FT-IR) spectroscopy (IFS-66/S, Bruker, USA). Scanning electron microscopy (SEM, S-2400, Hitachi, Japan) was used to observe the morphology of the LPCL/ABS composites with an accelerating voltage of 18 kV. The samples were sputter-coated with gold using a sputter coater (E-1010, Hitachi,

Japan). Optical properties were measured using an ultraviolet–visible/near-infrared spectrometer (UV–VIS/NIR, Varian Cary 5000, Agilent, USA) and an optical microscope (Nikon Eclipse Ni-E). The agglomeration size of the composite was conducted by a Zetasizer (Nano ZS, Malvern Instruments Ltd., UK). The Z-average mean was calculated from DTS Nano version 7.12, supplied by the manufacturer (Malvern Instruments Ltd.). Thermogravimetric analysis (TGA, TG/DTA 7300, Seiko Inst., Japan) was conducted in a nitrogen atmosphere from ambient temperature to 600 °C at a heating rate of 10 °C/min. Gel permeation chromatography (GPC, Agilent 1100S, Agilent, USA) was used to measure the molecular weights of ABS before and after high-shear processing. The column set was calibrated using monodispersed poly(methyl methacrylate) (PMMA) standards in the THF solvent. The thermal transitions of the composites were analyzed using differential scanning calorimetry (DSC, DSC 7020, Seiko Inst., Japan) and a thermal mechanical analyzer (TMA, TMA6100, Seiko Inst., Japan). Dynamic mechanical analysis (DMA, DMA/SS6100, Seiko Inst., Japan) was carried out in the tension mode at a frequency of 1 Hz with a 5 μm amplitude under the heating rate of 3 °C/min up to 150 °C. The DMA samples were prepared at the size of 10 mm wide, 50 mm long, and 80 μm thick. The rheological characteristics were studied using a rotational rheometer (MCR 102, Anton Paar, Germany). The measurement was conducted in a parallel plate geometry with a diameter of 25 mm at 210 °C and was performed at strain rates ranging from 0.01 to 1 s^{-1} . For the rheological test, the analytical specimens were manufactured using an injection molding machine (clamping force 45 ton, Engel, Germany) operating at an injection temperature of 210 °C and a mold temperature of 40 °C according to the ASTM standard.

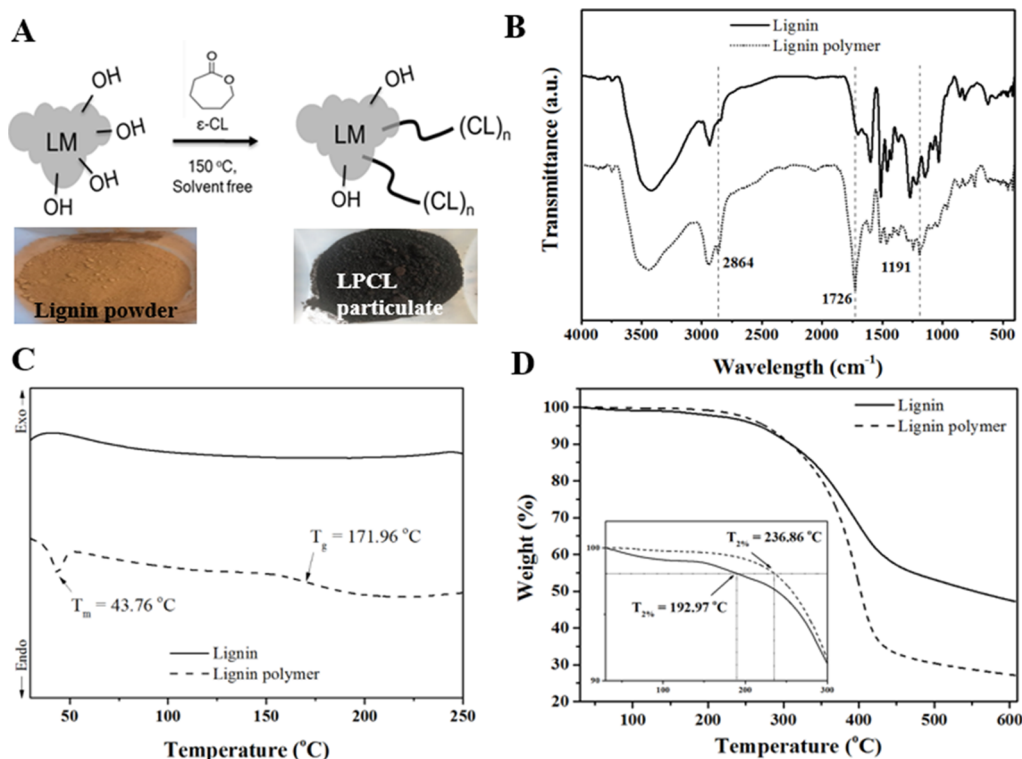


Figure 2. (A) Schematic synthesis route of the lignin-based polymer through the ROP of ϵ -caprolactone. (B) FT-IR spectra, (C) DSC curves, and (D) TGA thermograms of the pristine lignin and lignin-based polymer.

RESULTS AND DISCUSSION

Synthesis of Lignin-Based Polymer. Figure 2A shows that the lignin-based polymer is synthesized by the ROP of ϵ -caprolactone with the hydroxyl groups in lignin molecules, where the DBTDL acts as the initiating agent for the ring opening reaction of ϵ -caprolactone monomers.

The characterization and analysis of the synthesized lignin polymer are estimated via FT-IR, DSC, and TGA. As can be seen in Figure 2B, several aspects indicate PCL grafting on the lignin. Important finger-print peaks observed in the lignin polymer spectrum were an increased intensity of the peak at 2864 cm^{-1} (C–H stretching), 1726 cm^{-1} (C=O ester), and 1191 cm^{-1} (C–O stretching) associated with an ester linkage between lignin and caprolactone.²³ Figure 2C shows the DSC results of the pristine lignin and lignin polymer. An endothermic peak observed at $43.76\text{ }^{\circ}\text{C}$ is attributed to the melting of the PCL crystalline region in the lignin polymer. In the case of lignin, it is difficult to confirm the glass transition temperature because of the strong hydrogen bonding between the lignin molecules, but T_g of the lignin polymer is observed at $171.96\text{ }^{\circ}\text{C}$. This indicates that the intermolecular hydrogen bonding of lignin was disrupted because the OH groups of lignin were converted into the PCL chain.²⁴ Figure 2D shows that the thermal stability of the lignin polymer is improved compared to the pristine lignin, resulting in the degradation temperature ($T_{2\%}$) of the lignin polymer being increased from 192.97 to $236.86\text{ }^{\circ}\text{C}$. The enhanced thermal stability of the lignin polymer is assumed to be due to the increased molecular weight.²⁵

Particulate Size of LPCL in the ABS Matrix after High-Shear Processing. Figure 3 shows the optical morphology

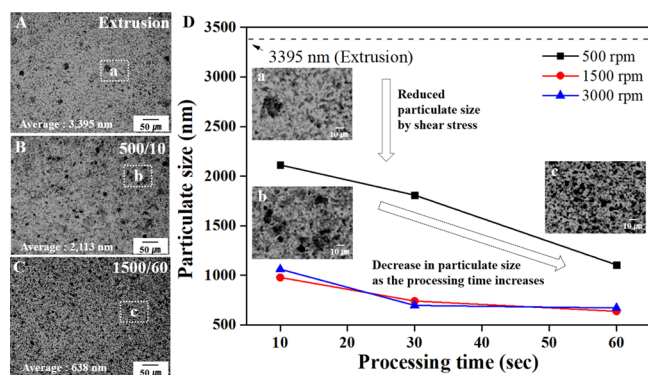


Figure 3. Optical images of the fabricated sample by [(A) a in graph] twin-screw extruder and high-shear processed at [(B) b in graph] 500 rpm/10 s, and [(C) c in graph] 1500 rpm/60 s. (D) Variation of the particulate size according to various high-shear conditions.

and particulate size that reveal the improved dispersibility of the LPCL particulates in the ABS matrix and the decreased size of LPCL particulates. The ABS appears as a gray matrix and LPCL as a black island dispersed in the ABS matrix. The particulate size of LPCL was decreased from 3395 nm (the extruded composite) to 638 nm by high-shear processing at 1500 rpm/60 s. In the ABS matrix, the size of LPCL particulates tends to decrease with increasing processing time and shear rate. In addition, the dispersibility of LPCL in the matrix is improved.

The morphology of the composites were further confirmed by SEM, as shown in Figure 4A,B. SEM analysis was performed

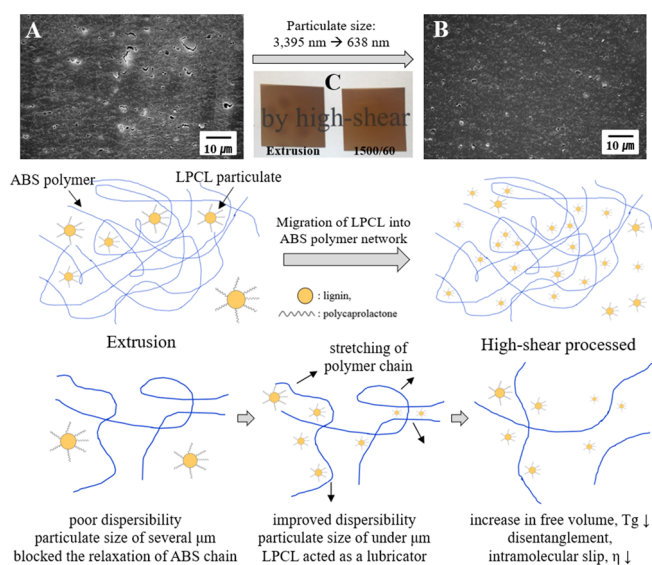


Figure 4. Morphology and camera images of ABS composites containing 10 wt % of LPCL after swelling with acetic acid 25% solution to make the LPCL particulates stand out; [(A) and left of (C)] extrusion, [(B) and right of (C)] high-shear processed at 1500 rpm/60 s. The proposed scheme shows the mechanism of T_g and viscosity reduction by high-shear processing (bottom part).

after LPCL was swollen with 25% acetic acid solution for 20 min to facilitate the distinction between LPCL and ABS.²⁶ In the fabricated LPCL/ABS composite by the twin-screw extruder, the LPCL particulates are of several microsizes and are not uniformly dispersed in the ABS matrix (Figure 4A). On the other hand, the high-shear-treated LPCL particulates show improved dispersibility in the ABS matrix, and the size thereof is reduced to 638 nm (Figure 4B). With the same context, the film of the extruded composite shows heterogeneous dispersion of the LPCL in the ABS matrix; however, the case of the high-shear-processed composite exhibits a homogeneous state (Figure 4C). Thus, the enhanced dispersibility identified through morphological analyses is assumed to be due to the insertion of LPCL and ABS molecular chains into different component regions by high-shear stress.

The interpenetration of molecular chains leads to the shifted glass transition temperature, which was identified through thermal analysis in the T_g results section.²⁷ The scheme in the bottom part of Figure 4 shows improved dispersion and reduced particulate size of the LPCL in the ABS matrix by high-shear processing. The difference in the particulate size and dispersibility by the high-shear equipment led to the disentanglement of ABS molecules and the increased free volume around the LPCL particulates, resulting in viscosity reduction and T_g decrease of LPCL/ABS composites. Figure S1 of the Supporting Information shows the UV–vis transmittance spectra of the LPCL/ABS composite films. The ABS composite containing the lignin polymer completely blocks light with the wavelength below 400 nm because of the UV absorption capacity of lignin.⁷ The transmittance is directly proportional to the LPCL particulate size at the wavelength above 400 nm. This behavior is related to the total interface area between the filler–matrix within the composite, along with the LPCL particulate size.²⁸

Effect of the High-Shear Process on the Melt Viscosity. The influence of the high-shear process on the

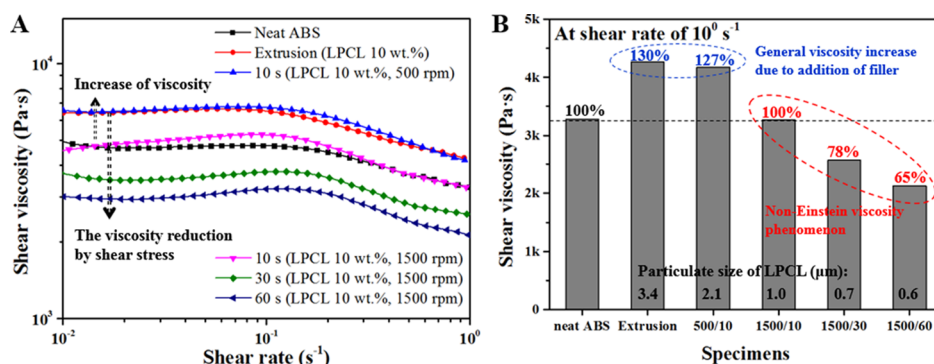


Figure 5. Variation of (A) shear viscosity as a function of shear rate. (B) Comparison of the shear viscosity at a shear rate of 10^0 s^{-1} for neat ABS and LPCL/ABS composites (which is treated with 500 rpm/10 s and 1500 rpm for 10, 30, and 60 s).

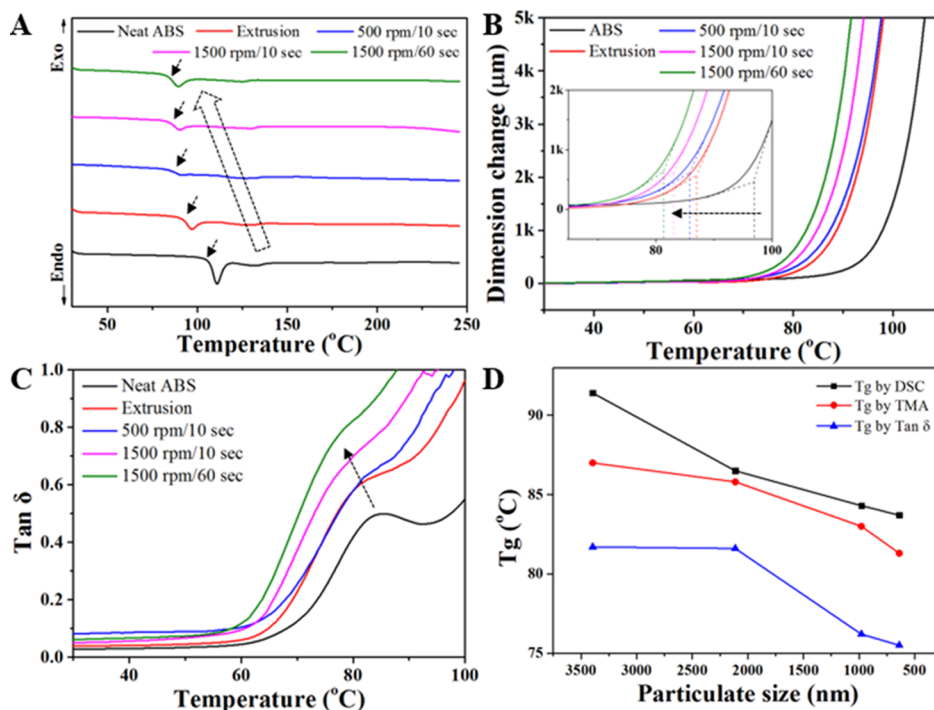


Figure 6. Glass transition temperature characterization of the neat ABS and LPCL/ABS composite through (A) DSC, (B) TMA, and (C) $\tan \delta$ of DMA. (D) T_g results according to each analysis method as a function of the LPCL particulate size.

melt behavior of LPCL/ABS composites was studied by a rheometer. Rheological properties of LPCL/ABS composites can be utilized to understand structure–property relationships.

Figure 5A shows the shear viscosity as a function of the shear rate for the neat ABS and the LPCL/ABS composites filled with LPCL 10 wt %. The shear viscosity of the extruded composite and the high-shear processed composite at 500 rpm/10 s is higher than that of the neat ABS, but it decreases with increasing shear rate and processing time. More specifically, the steady mode results show that the smaller the size of LPCL particulates added to the ABS matrix, the lower the shear viscosity of the composites (Figure 5B), that is, the viscosity of LPCL/ABS composites tends to decrease as the applied shear stress increases. The decrease in melt viscosity of the LPCL/ABS composite after high-shear processing is assumed to be due to the incorporation of LPCL particulates into the ABS polymer matrix and the applied shear stress to composite specimens. The incorporated LPCL particulates can act as a lubricator that promotes the

motion of the chains and cause the non-Einstein viscosity phenomenon.^{14,15} When shear stress is applied to the LPCL/ABS composite, the LPCL particulates can contribute to a decrease in viscosity because of the preferential orientation of the PCL aliphatic chains along the flow direction and the slip between the PCL and ABS chains.^{29,30} In addition, the improved dispersion and reduced particulate size in the matrix by high-shear processing leads to the disentanglement of ABS molecules and the increased free volume around the LPCL particulates, resulting in viscosity reduction as shown in Figure 4.³¹ Thus, the rheological properties, including the non-Einstein viscosity phenomenon, of the LPCL/ABS composites in this study can be expected to improve the processability and productivity, when the immiscible blends are conducted through high-shear processing.

Glass Transition Temperature of LPCL/ABS Composites after High-Shear Processing. The glass transition temperature of a polymer can be explained by the free volume theory of polymer chains.³² T_g of the LPCL/ABS composite is

investigated by DSC, TMA, and DMA analysis to demonstrate the decrease in viscosity due to the increase in the free volume of LPCL/ABS composites.

Figure 6A–D and Table 1 show the T_g results from the three analytical methods, which reveal the same tendency that T_g

Table 1. LPCL Particulate Size and T_g Results from DSC, TMA, and DMA

case	LPCL particulate size (nm, 10 wt %)	T_g by DSC (°C)	T_g by TMA (°C)	T_g by $\tan \delta$ (°C)
neat ABS		107.0	96.9	85.1
extrusion	3395	91.4	87.0	81.7
500 rpm/10 s	2113	84.2	85.8	81.6
1500 rpm/10 s	979	84.3	83.0	76.2
1500 rpm/60 s	638	83.7	81.3	75.5

decreased as the particulate size decreased. T_g of the LPCL/ABS composite significantly dropped with the increasing interface area between LPCL and the ABS matrix because of the decrease of the LPCL particulate size, most likely demonstrating the excellent plasticizing efficiency with ABS. It is assumed that the small molecule LPCLs migrate to the ABS polymer chains, which greatly increases the free volume of the molecular chains, thereby improving the chain mobility of the polymer and apparently reducing T_g . Figure 6C shows that the mechanical damping value of the LPCL/ABS composite increases because of the increased interface area between LPCL particulates and the ABS matrix, through decrease in the particulate size through high-shear processing. The large interfacial contact area between LPCL molecules and the ABS matrix significantly increases the possibility of energy dissipation because of chain vibration and interfacial sliding.³³ Increasing the damping effect due to energy dissipation between filler–filler molecules or filler–matrix molecules can provide benefits of a longer service life of the components and reduction in noise.³⁴

Thermal Degradation of the ABS Polymer in High-Shear Processing. Thermo-oxidative degradation of ABS is a temperature-dependent process. Degradation of the rubbery phase (polybutadiene) in ABS is initiated by hydrogen abstraction from carbon α to unsaturated bonds, producing hydroperoxide radicals, leading to carbonyl and hydroxyl products.³⁵ Thus, it is necessary to confirm that low thermal stability, which is known to be a disadvantage of ABS resin, is

expected to affect the composite properties after high-shear processing.

Figure 7 shows the weight loss and GPC curves for neat ABS and high-shear processed ABS resin. Figure 7A shows that the thermal degradation of ABS3000/60 (specimen of neat ABS resin treated with high-shear at 3000 rpm, 60 s) begins at a relatively rapid rate from 170 °C, compared with the neat ABS and ABS1500/60 (specimen of neat ABS resin treated with high-shear at 1500 rpm, 60 s). This is because of the chain scission of ABS molecules by heat and mechanical shear stress during high-shear processing.³⁶ As confirmed by GPC in Figure 7B, the molecular weight of re-extrusion and ABS1500/60 is similar to that of the neat ABS. On the other hand, the number-average molecular weight and weight-average molecular weight of ABS3000/60 are 38 000 and 83 000 g/mol and are about 37 and 35% lower than the neat ABS, respectively.

Studies on recycling of ABS resins have shown that thermal decomposition does not occur, even if the extrusion process is repeated 4–5 times.³⁷ It is considered that the high-shear processing condition of 3000 rpm/60 s in this study is more severe than the general extrusion conditions. As a result, the thermomechanical degradation of ABS by thermal and shear stresses causes molecular chain scission and reduces the molecular weight.³⁸

CONCLUSIONS

ABS composites containing the lignin-based polymer were fabricated via extrusion and high-shear processes. The LPCL/ABS composite was fabricated by high-shear processing to improve its dispersion characteristics and decrease the particulate size of LPCL in the ABS matrix. The resulting LPCL/ABS composites clearly showed non-Einstein viscosity phenomena, seemingly due to the conformational rearrangement and the increased free volume of ABS molecular chains in the vicinity of LPCL particulates and completely blocked UV rays. Consequently, the non-Einstein phenomenon due to the application of nonspherical LPCL particulates and the size control in this study suggest an interesting plasticization methodology for improving the processability and productivity of high-loading filler/polymer composites and ultrahigh molecular weight polymers.

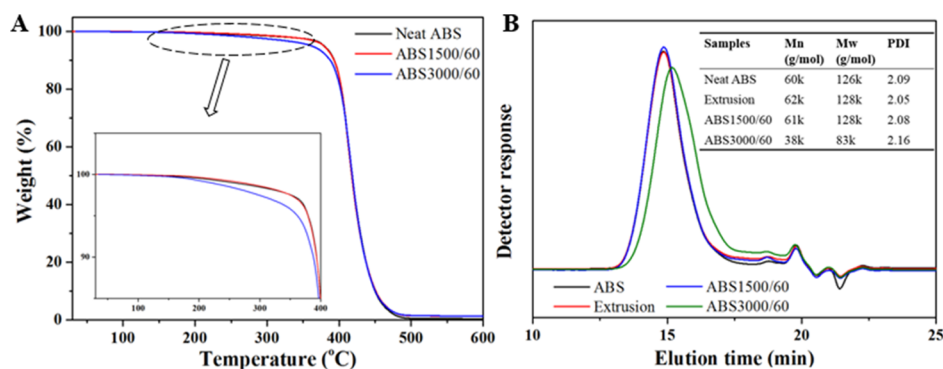


Figure 7. (A) TGA and (B) GPC curves of the neat ABS, extrusion (re-extruded ABS sample W/O LPCL by twin-screw extruder in our lab), ABS1500/60 (high-shear processed ABS sample W/O LPCL at 1500 rpm/60 s), and ABS3000/60 (high-shear processed ABS sample W/O LPCL at 3000 rpm/60 s).

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01043.

UV–vis transmittance curves of the neat ABS and ABS composites containing LPCL 10 wt % fabricated under various conditions (PDF)

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Notes

The authors declare no competing financial interest.

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