Supplementary information

Dynamics of particle-covered droplets in shear flow: Unusual breakup and deformation hysteresis

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Materials and methods

Materials

Polydimethylsiloxane (DMPS1M, Sigma-Aldrich) with a viscosity of 1 Pas and density of 0.973 g/cm^3 at room temperature (23^{o}C) is chosen as the droplet phase. Polyisobutylene (Glissopal 1000, Basf) with a viscosity of 15 Pas and density of 0.894 g/cm^3 at 23 ^{o}C is the matrix phase. Silica nanoparticles (Aerosil Rhodorsil R972, Degussa) with a primary particle radius of 8 nm forming fumed aggregates with a size of around 100 nm are used.[1] The density of these particles is 2.2 g/cm^3 and their surface is hydrophobic due to the presence of a dichlorodimethylsilane coating. To study the particle structures at the interface, the standard polydimethylsiloxane was replaced by heat curable polydimethylsiloxane (Sylgard 184, Dow Corning) with a viscosity of 3.5 Pas at 23°C. It was verified that the difference in surface energy between the standard PDMS and the heat curable PDMS is negligible as the standard PDMS has a surface tension of 20.4 mN/m and that of the heat curable PDMS is 19.3 mN/m, as determined by the pendant drop method.

Droplet preparation and visualisation

A 3 wt% suspension of silica particles in PIB was prepared. Thereto, pure PIB and cyclohexane were first mixed for 12h with a magnetic stirrer. Then, the nanoparticles were dispersed in cyclohexane with an ultrasonic probe (UP 400s, Hielscher, Germany) used at 0.5 cycles and 100% amplitude for 2h. The particle-cyclohexane mixture was subsequently added to the PIB-cyclohexane solution and the obtained mixture was further stirred for 1h. Afterwards, the solvent was completely evaporated in a Rotavap (Rotovapor Büchi) at 60°C and 10 rpm resulting in a suspension of 3 wt% silica in PIB. Finally, the suspension was placed in a petri dish and PDMS droplets were injected by means of a home-made pressure driven injection device and kept for different amounts of time. The 3 wt% silica suspension in PIB has a small yield stress, which prevents the droplet from sinking and ensures a uniform coverage of the interface. After different residence times, a single PDMS droplet was taken from the petri dish and the PIB suspension around the droplet was carefully removed by placing the droplet in a neat PIB matrix and gently moving it around. Removal of the adhering PIB suspension was verified optically as remaining suspension around the droplet leads to distortion of the droplet

edge in the microscopy images due to the light scattering by the particles. After removal of all non-interfacially bound particles, the droplet was carefully placed in the glass cup filled with pure PIB in the counter rotating shear device. A schematic of this counter rotating device is shown in Figure S1. As can be seen, a droplet in the stagnation plane can be visualized with a stationary microscope equipped with a camera from either the top (through the prism) or from the side. In the latter case, a correction cup is required to correct for the image distortion due to the cylindrical shape of the cup.

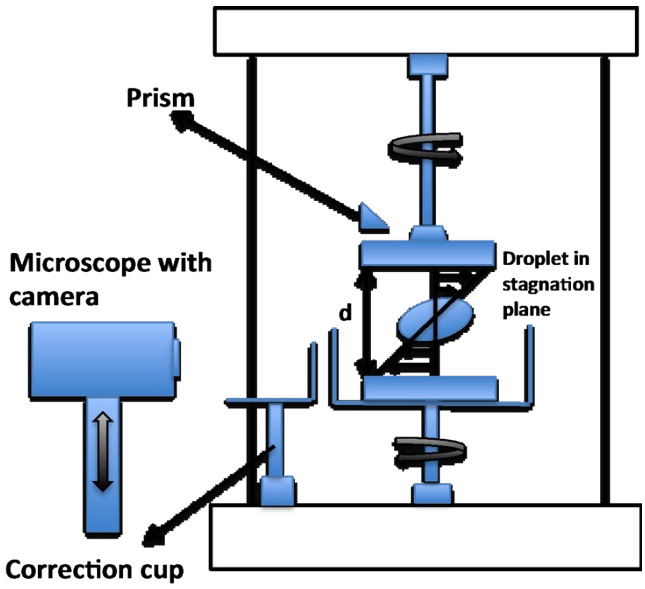

Figure S1. Scheme of counter rotating device.

Preparation of planar silica-covered interfaces for SEM imaging

A layer of heat-curable polydimethylsiloxane is placed in a cup. Subsequently, a layer of 3 wt% PIB suspension, with the same thickness as that used for the droplet preparation is gently poured on top. Hence, the amount of particles is similar to that in the case of the droplets. Then, the system is kept for different amounts of time after which it is cured in an oven (2 hours at 80°C). Finally, the top phase is removed by washing with heptane leaving only the cured polydimethylsiloxane bottom phase and interfacially localized particles.

Preparation of two-layer systems for static multiple light scattering

A two-layer system consisting of a layer (1 cm thickness) of 3 wt% silica-PIB suspension on top of a layer of PDMS (1 cm thickness) was prepared in a cylindrical tube. The particle localization was followed over time by visual inspection and static multiple light scattering.

Scanning electron microscopy imaging

The particle layer at the PIB-PDMS interface was imaged by scanning electron microscopy (SEM) obtained with an XL30 FEG using the secondary electrons detector.

Static multiple light scattering

The transmitted and backscattered light through the two-layered system was captured with a Turbiscan MA 2000 profilometer (Formulaction, France). The transmission and backscattering signals were registered after specific time intervals covering a period of 1080 hours.

Results

Interfacial localization

The two-layer system consisting of the 3 wt% PIB-silica suspension on top of pure PDMS after 1080h is shown in Figure S2. It can be seen that the top layer is opaque due to the presence of the silica particles whereas the bottom layer remains transparent, indicating the absence of particles in this phase. The transmitted and back scattered light due to static multiple light scattering of the PIB+silica/PDMS two-layer system is shown in Fig. S3. It can be seen that both transmission and backscattering are around 100% for the PDMS layer. In addition, the results remain unaltered with increasing residence time, which confirms the absence of particles in the bottom PDMS layer.

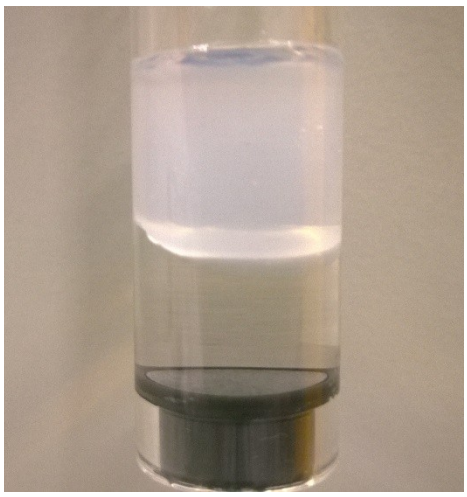

Figure S2. PIB-particle/PDMS two-layer system after 1080h

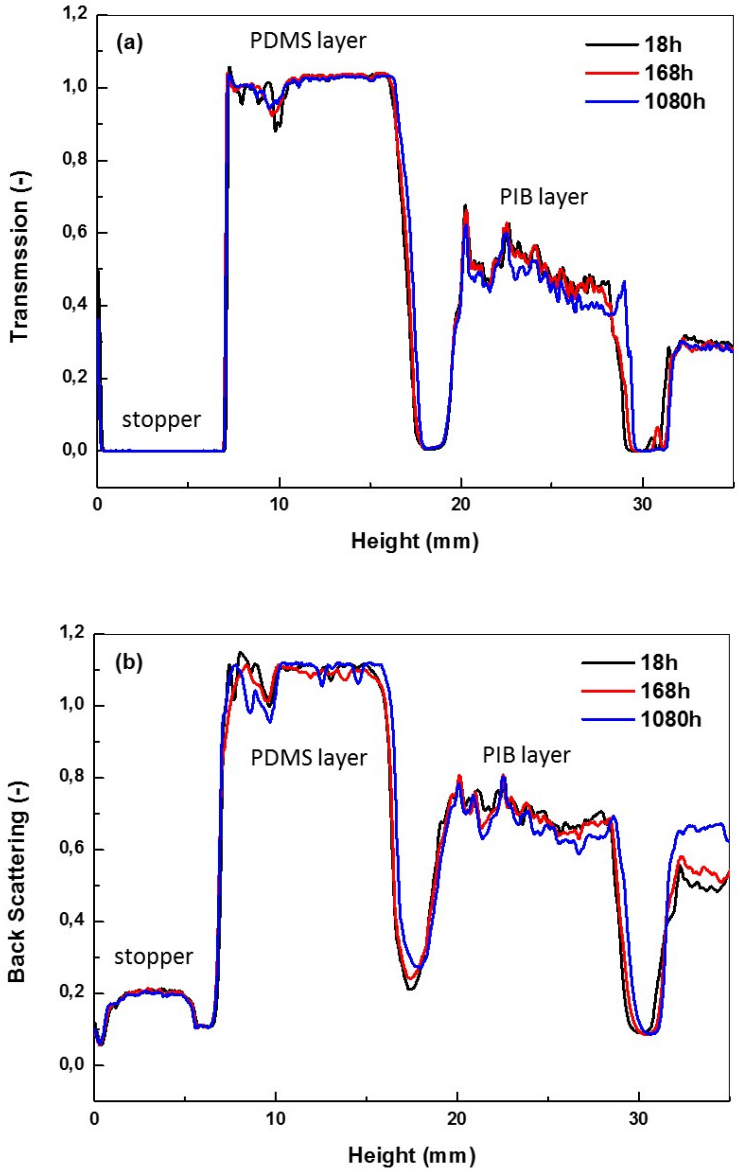

Figure S3. Transmssion (a) and back scattering (b) of PDMS and PIB-particle layers versus sample height at different residence times. Height 0 corresponds to the bottom of the tube.

Movies

Movie ESI 1: Droplet breakup of a particle-covered droplet (corresponding to Figure 4b)

Reference

1. J. Vermant, G. Cioccolo, K. Golapan Nair, P. Moldenaers, *Rheol. Acta*, 2004, 43, 529.