Characterization of Polyurethane Emulsions for Particle Size and Structure by Field-Flow Fractionation Coupled to Multi Angle Light Scattering

General Information

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Application Polymer
Technology AF4-MALS-DLS
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Introduction

Polyurethanes are widely used in a variety of applications, including paints, coatings, elastomers, insulators, foams, and more. They are considered one of the world's most versatile and widely used polymers [1]. The chemical structure can be varied to achieve many end use properties and this means the emulsion droplets produced from the polymer have a very wide range of sizes, which can make accurate characterization by techniques such batch light scattering inaccurate.

In this Application Note, we present data on separation of three polyurethane emulsion samples using Asymmetrical Flow Field-Flow Fractionation (AF4) coupled to Multi Angle Light Scattering (MALS) and Dynamic Light Scattering (DLS.) A schematic for the AF4 channel is shown in Figure 1. The combination of cross flow and channel flow causes size separation over the course of the analysis, with smaller particles eluting to the connected detectors before larger particles. The MALS data is used to calculate the polymer molecules' radius of gyration (R_g), and the DLS measures hydrodynamic radius (R_h). These two measurements can be combined to calculate the ratio of R_g/R_h, which provides additional information about particle shape and density.

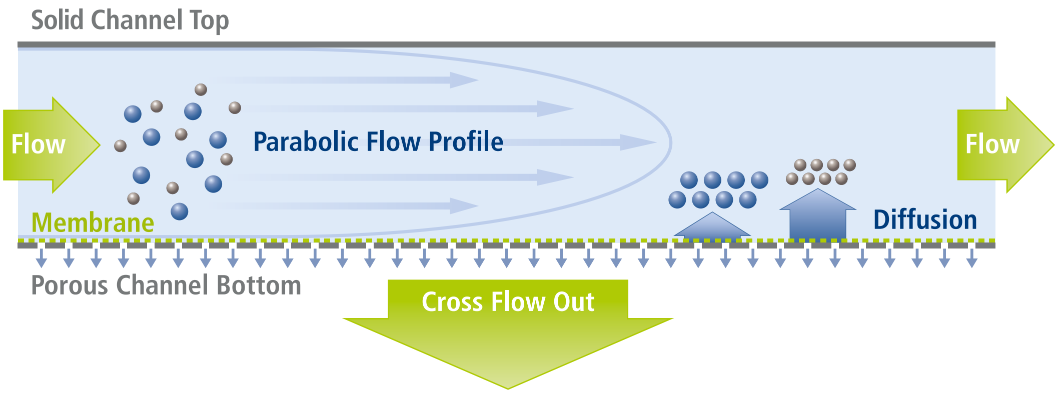

Figure 1: Schematic of AF4 principle.

Experimental Details and Results

Three polyurethane emulsions were diluted from their starting concentrations of 35% by weight to an analysis concentration of approximately 0.1% by weight. To separate by size and characterize the emulsions, an AF4 system (Postnova AF2000) was used with MALS (PN3621) and DLS (Malvern Zetasizer DLS.) An AF4 carrier solution of 3 mM sodium azide at pH 7.3 was used in the experiments, to provide ionic strength for sample stability and to act as a disinfectant for the system.

The MALS response for the three polyurethane samples is shown in Figure 2. The R_g is plotted as dots across each fractogram in Figure 2A, and R_h is plotted in Figure 2B, providing a measure of the molecules' sizes. The three samples increase in size from 1 to 2 to 3. Sample 3 has a secondary peak with sizes around 90-110 nm in R_g and 160-200 nm in R_h. The presence of this small amount of larger particles would falsely increase the reported size of the sample by any batch light scattering technique such as DLS but can be easily separated and identified by FFF. In fact, all three samples have a high polydispersity of sizes and would not yield the correct average size by DLS.

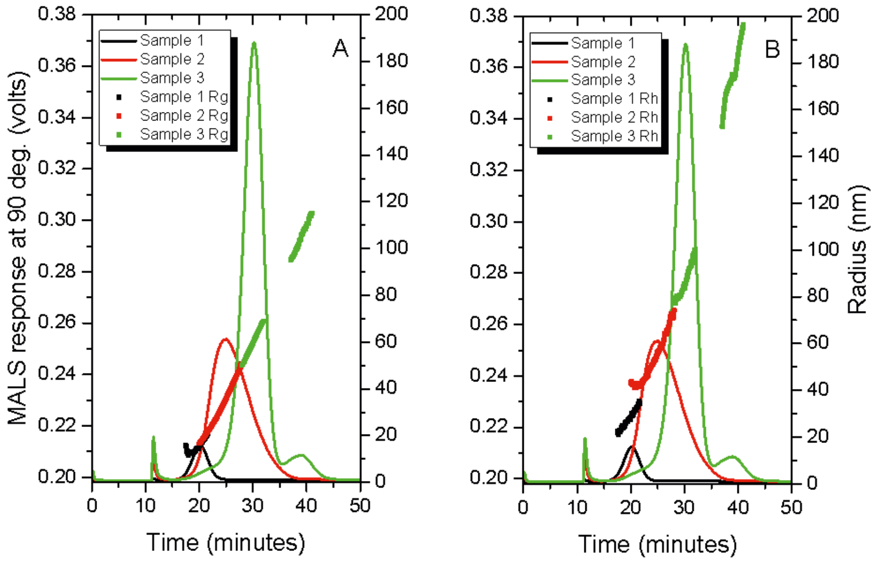

Figure 2. Fractograms with MALS response at 90°, with dots across each peak representing R_g (Figure 2A) and R_h (Figure 2B.)

In Figure 3, the ratio of R_g/R_h is plotted across each peak. This ratio describes the size/density relationship of the particles and can therefore indicate something about the structure. We can see that the ratios for the three samples are somewhat different showing that the samples do not have the same emulsion particle structure which may also indicate that the polymers used are of a different chemical structure.

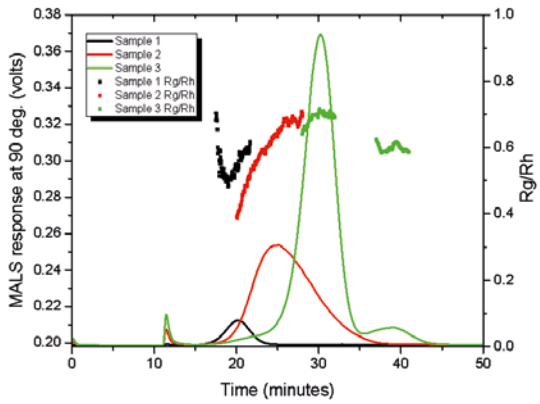

Figure 3. The ratio of R_g/R_h plotted across each peak in the fractogram.

Samples 1 and 3 have a small range of ratios, indicating the structures do not vary much with particle size. On the other hand, sample 2 shows a wide range of ratios from <0.4 at the smallest sizes up to 0.7 at the larger size range. This indicates clearly that the small and large emulsion droplets of this sample do not have the same structure. We can also see in sample 3 that the small amount of large size particles observed at 39 minutes retention time does not have the same R_g/R_h ratio as the main peak. In fact the ratio is smaller, indicating that this is not aggregation of particles from the main peak but is a different particle structure.

Conclusion

From the data presented here we can clearly see that AF4-MALS-DLS can be a powerful tool in the analysis of polymer emulsions and can reveal the true sizes of the particles. In addition, there is much data on the particle structure that can be obtained from the light scattering ratios at each size point.

References

[1] J. Akindoyo, M. Beg, S. Ghazali, M. Islam, N. Jeyaratnam, Y. Ar. RSC Advances, 2016, 6, 114453-114482.

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