Characterization of Commercial Polymer Latexes

Introduction

Polymer latexes are essential components in a broad range of commercial products and formulations such as, paints, cosmetics, coatings, biotechnology, and functionalized supports. Applications are diverse encompassing their industrial use in adhesives, caulks, and sealants, as well as to modify the physical/mechanical properties of cement-based concretes to their exploitation as biomolecule carriers in immunology and as markers in molecular diagnostics.

A common method of industrial production is by emulsion polymerization. The final latex particle is stabilized typically by sulphate and carboxyl groups which are chemically part of the polymer surface resulting from the initiator (such as hydrogen peroxide or potassium persulphate) used in the reaction. In addition, there are physically adsorbed surfactant molecules (from the emulsifier) that have polar groups (ionic or nonionic).

The final product is always contaminated with unwanted biproducts, such as unreacted monomer, oligomers, electrolytic debris, etc., from the polymerization reaction. Although the latex is usually subjected to some cleaning process, such as steam stripping or ion exchange, it is never extensive – we are not talking about NIST traceable standards here! – resulting in variation in the polymer latex. Differences between nominally identical materials because of variations in mechanical and chemical processing methods can influence the performance of any subsequent procedures that use them.

Further, industrial/commercial latexes are often stored for a long time before actual use and they will “age”. An unwanted – and potentially problematic – feature of polymer latexes prepared by emulsion polymerization is the diffusion over time of unreacted monomer from inside the latex particles. This can be obvious from the smell after opening a stored container!

Invariably, the monomer is insoluble in water and will reside at the particle surface, and so will alter the surface functionality of the latex dispersion. The ability to perform a given function (such as binding) will depend on the surface chemistry prevailing *at the time of use*, and thus ensuring that latex dispersions perform as expected is an important step in their manufacturing.

This type of precise quality control (QC) process is how businesses seeks to ensure that product quality is maintained or improved. QC involves testing of units and determining if they are within the specifications for the final expected product. A major function in QC is to verify the product quality against some predefined standard(s), to ensure the quality of all the batches manufactured, at every stage of production. It is well-recognized that high quality products are much more efficient and effective, so QC benefits both the manufacturer and the consumer.

A methodology that is quantifiable, fast, and non-invasive – *without the need to dilute suspensions* – offers practical and economic advantages as a QC tool in contexts where polymer latexes are produced. However, the test must be objective, easy to run, and be predictive – that is, a test that measures *fundamental* characteristics and is neither a function of the instrument nor of the operator. NMR spectroscopy provides such a test.

> “The ability to interrogate latex dispersions without dilution provides a major practical advantage for NMR relaxation over other particle characterization techniques.”

About NMR Relaxation

NMR spectroscopy is one of the most powerful analytical tools used to probe details of molecular structure and dynamics. Traditional devices employing NMR technology require high magnetic fields and, hence, large magnets and related instrumentation. However, the advent of small powerful magnets has allowed instruments such as the Mageleka *M*agno*M*eter XRS™ *R*elaxo*M*eter to be designed that have small footprints and are suited to normal, routine laboratory analysis.

The basic technique used in the *R*elaxo*M*eter is NMR relaxation. The relaxation time is a fundamental intrinsic property of solids and liquids and its measurement provides direct information about the extent and nature of any particle-liquid interface (i.e., suspensions; see Mageleka Technical Note 1 at www.mageleka.com).

What the *R*elaxo*M*eter measures is the extent of molecular motion as protons interact when perturbed by local magnetic fields. The molecular motion of the liquid in contact with a particle surface relaxes much more rapidly than does the rest of the liquid, which is free (i.e., "bulk" liquid). This surface relaxation is typically of the order of microseconds, compared with the NMR relaxation time for the bulk liquid (i.e., in the absence of particles), which can be of the order of seconds. For many dispersions of interest, we can assume that there is a fast, dynamic exchange between the liquid associated with the particle surface and the bulk liquid, so we can measure a dynamic average that reflects the properties of the interface.

NMR relaxation is uniquely sensitive to two important features of any particle-liquid interface. The first, and most obvious, is the extent of wetted surface in a suspension. Here we can include particle size, shape, morphology and, indeed, porosity. A second, and less appreciated feature, is that NMR relaxation is also sensitive to the chemical nature of a particle surface. This would include the fundamental surface charge and, thereby, the type and number of functional groups. Thus, NMR is unique in this respect because, typically, traditional characterization instruments are only sensitive to one of the features – for example, particle size or zeta potential but not both simultaneously.

What does the *R*elaxo*M*eter do?

Many particle characterization and analysis instruments used in R&D studies are, often, not well-suited for use in a quality control (QC) environment, where rapid assessments are key. In addition to its speed (measurements can be made in a few minutes), the *R*elaxo*M*eter provides complementary information to traditional characterization devices, but it also provides additional interfacial insight not possible with those devices.

A major practical advantage of the *R*elaxo*M*eter is that the measurement is noninvasive and nondestructive. This means that samples can be stored in an NMR tube and re-analyzed at any later date. This allows for investigation of stability, sedimentation, accelerated aging and shelf-storage issues. Furthermore, of practical utility, the *R*elaxo*M*eter eliminates the dilution issues inherent in making measurements using, for example, traditional light scattering techniques. Since dilution is never an innocuous process, wherever possible suspensions or slurries should be analyzed as they are prepared (see Mageleka Technical Note 5). Thus, it is ideal technique for measuring suspensions at high solids loadings; it does not make any assumptions about the size, shape, or concentration of particles, or the liquid in which they are suspended. The *R*elaxo*M*eter can work with suspensions at any industrially relevant concentration. This is especially important for slurries, which can be highly concentrated. Moreover, the simple measurement technique takes only minutes (see Mageleka Technical Note 2).

An NMR relaxation time obtained for a suspension is an average value that is dependent upon the exact composition of the suspension, which includes the liquid phase – whether it is pure, mixed, or contains dissolved moieties. Thus, for a suspension of known composition, prepared by a fixed process, the average relaxation time should – within experimental error – always be the same (see Mageleka Application Note 12). This is somewhat analogous to the zeta potential of a material where the value depends critically upon the exact composition of the dispersion fluid. This makes the *R*elaxo*M*eter's measurement technique ideally suited to QC of polymer latexes because the relaxation time will be affected by variations in mechanical and chemical processing methods, including the presence of unwanted biproducts. Thus, relaxation time measurements can be used to assess the extent to which samples, batches, or lots of polymer latexes differ.

In this Application Note, we will demonstrate how NMR relaxation time measurements can provide insights into differences that can arise during the production of polymer latexes. We present four studies made using three common varieties of polymer latex from different manufacturers, and each example highlights the potential utility of the *R*elaxo*M*eter's measurements in QC and R&D contexts.

Example Study 1

Polyurethane (PU) is used in the formulation of low-VOC ambient-cure and baked coatings in the manufacture of furniture paints, parquet sealing, and printing inks for paper and textiles. Such water-based dispersions reduce solvent emissions and reduce the environmental footprint.

This first example compares a series of different batches of an aqueous PU latex suspension sold commercially under the trade name of BAYHYDROL. Bayhydrol® UH 2952/1 is an aliphatic polyurethane resin dispersion used as a binder for waterborne, air-, and oven-drying basecoats.

The concentration of the PU samples was nominally 40% and samples were measured directly "as received" without any further sample preparation. The relaxation number, R_{no}, was calculated from the measured relaxation time of each sample using a Mageleka *R*elaxo*M*eter. The repeatability of the relaxation time measurements is good (coefficient of variation <0.5%) and so the results are robust, and the batch-to-batch differences found are to be statistically valid. The data are summarized in Table 1.

Table 1. Relaxation Numbers for various batches of Bayhydrol® UH 2952/1 polyurethane.

Batch Number	Average Relaxation Time (ms)	Relaxation Number R_{no}
5264	36.9	65.4
5930	37.0	65.5
4468	37.0	65.5
7565	36.9	65.4
6888	33.4	71.8
5694	41.4	57.7
5263	37.0	65.5
5693	41.1	57.7

Note that the Relaxation Number, R_{no}, is defined as:

$$R_{no} = [R_{suspension}/R_{liquid}] - 1$$

Where, R is the Relaxation rate (= 1/T)

R_{no} is, thus, a useful, *dimensionless* parameter in which the effect of the suspension liquid (which could include dispersants, additives, etc.) is normalized out and so it allows us to rank the strength of liquid-surface interaction.

Figure 1 shows the Relaxation Numbers plotted as a bar diagram.

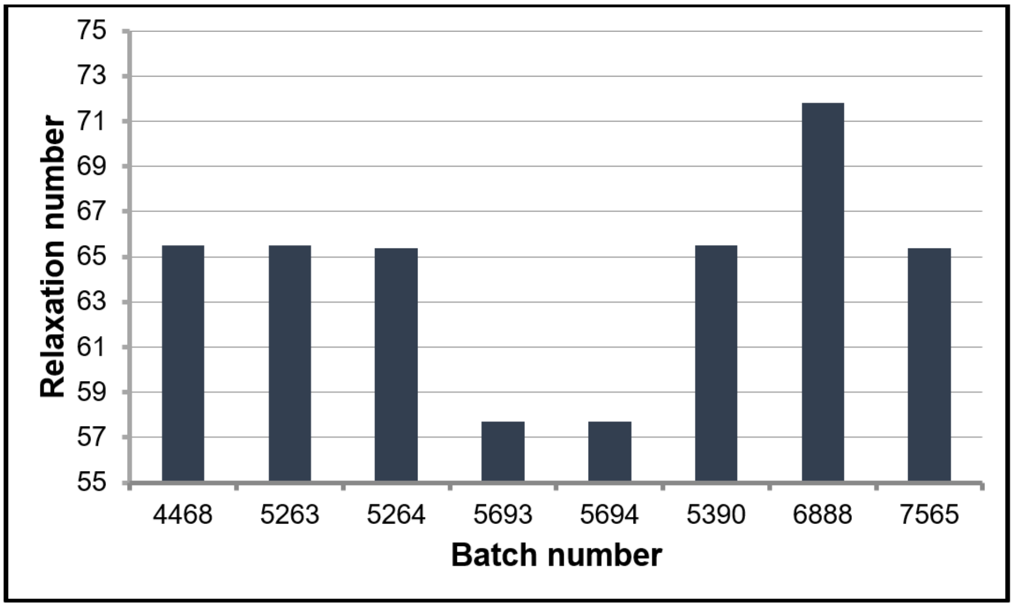

Figure 1. Relaxation Numbers for various batches of Bayhydrol® UH 2952/1 polyurethane (using data from Table 1)

The data in Table 1 and Figure 1 clearly show variation in batches of a polymer latex product that were assumed to be identical. Moreover, additional insight can be found when the data are screened in light of a control value. Control values are used routinely in QC contexts to determine whether a product passes or fails for a particular parameter. Thus, if we arbitrarily set upper and lower control values at 60 and 70, respectively, it is seen that three of the PU batches (5693, 5694, 6888) would be out-of-specification. Hence, this example shows how the *R*elaxo*M*eter's measurements can provide information useful about polymer latexes, including applications relevant to QC.

Example 2

A similar study was made using samples of different batches and lots also of a PU sold commercially under the trade name of LIOPUR. Liopur® PFL 1964 is an aliphatic polyurethane dispersion based on a polycarbonate and is used as a binder; after air-drying, coatings form soft and elastics films.

The concentration of the PU samples was nominally 38% and samples were also measured directly "as received" without any further sample preparation. The reproducibility was good (coefficient of variation <1.0%). The data are summarized in Figure 2.

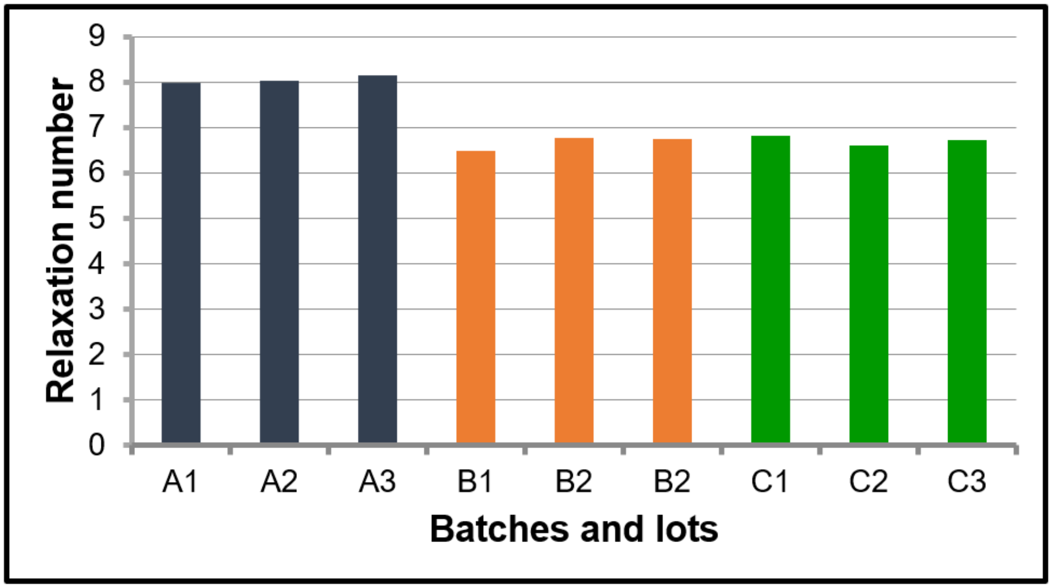

Figure 2. Relaxation Numbers for various batches of Liopur® PFL 1964 polyurethane

Although small variations can clearly be seen within each batch, lots of PU in the two batches B1-B3 and C1-C3 are almost the same and clearly differ from the lots in Batch A1-A3. Of course, more studies and method development would be needed before implementing changes to a QC protocol for these materials based on this information. But the data from this example and the one above demonstrate that using NMR-based measurements from the *R*elaxo*M*eter are an ideal tool for routine QC purposes.

Example 3

In this third example we measured relaxation time measurements of a poly ethyl acrylate (PEA) that were different ages. PEA is widely used as a “plasticizer” or “binder” because the polymer is soft and can easily film-form when warmed and allowed to dry (“cure”). Here, we compare a “fresh” sample of a PEA – straight out of a laboratory bench-scale reactor but nominally cleaned – with a sample that had been left to age over an extended time period (> 6 months). The concentration was approximately 25%, and the high reproducibility (coefficient of variation <0.5%) indicates that differences were statistically robust. The results are shown in Figure 3.

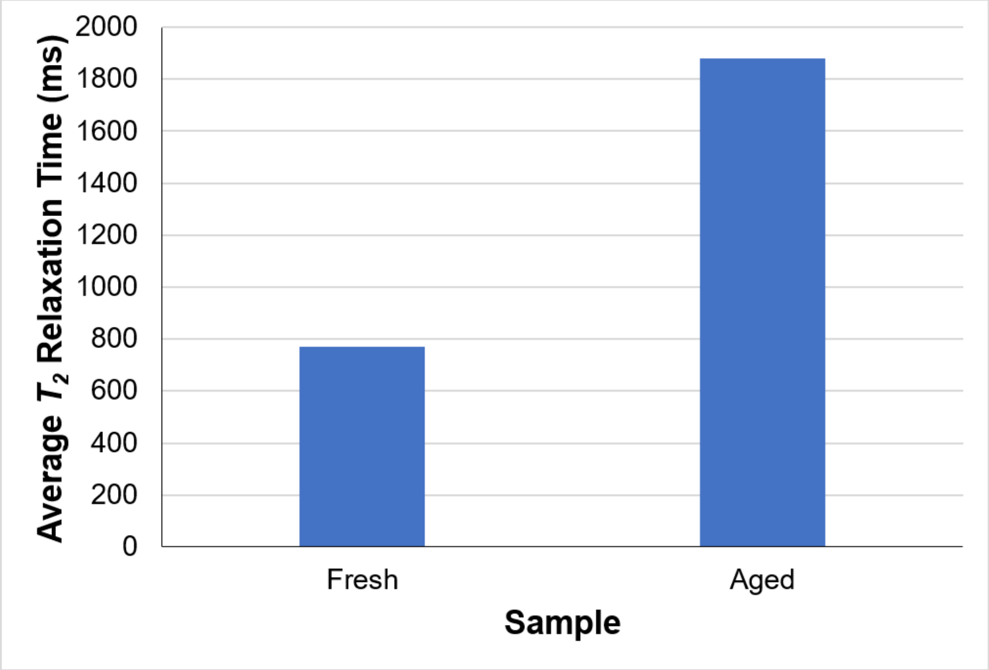

Figure 3. Comparison of the relaxation time for fresh and aged samples of poly ethyl acrylate.

The significant increase in relaxation time arises, in part, from a reduction in surface wettability (an increase in "hydrophobicity" because of diffused monomer) but could also reflect a decrease in available wetted surface area (owing to an increase in particle size arising from aggregation). Regardless, the results clearly show that six months of aging produces differences in the surface chemistry of this particular PEA, and that the *R*elaxo*M*eter detected that difference simply and quickly.

Example 4

In this final example, we examine two samples of styrene-isoprene-styrene (SIS) block copolymers. SIS are high performance thermoplastic elastomers with a combination of high strength, low hardness and low viscosity for easy thermoplastic processing as a melt or in solution. They exhibit both the elasticity and resilience of natural rubber and the ability of polystyrene to be molded and shaped under the influence of heat. SIS block copolymers are widely used in sealants, gasket materials, hotmelt and pressure sensitive adhesives, rubber bands, toy products, shoe soles and in bitumen products for road paving and roofing applications. An important application is in the manufacture of condoms.

Two samples of SIS block copolymer aqueous latex suspensions (nominally 30%) were obtained from TOPLUS Sciences. Both samples were measured as received and then serially diluted using distilled water. Figure 4 compares plots of relaxation rate as a function of volume ratio of the block copolymers. To calculate a volume ratio from concentration, the polymer latex density was assumed to be 1.15 g/cc. Note that in a relaxation experiment, liquid molecules in a dispersion can undergo rapid exchange between the bound state and highly mobile free state. The linearity of the plots demonstrates the validity of this assumption of fast exchange.

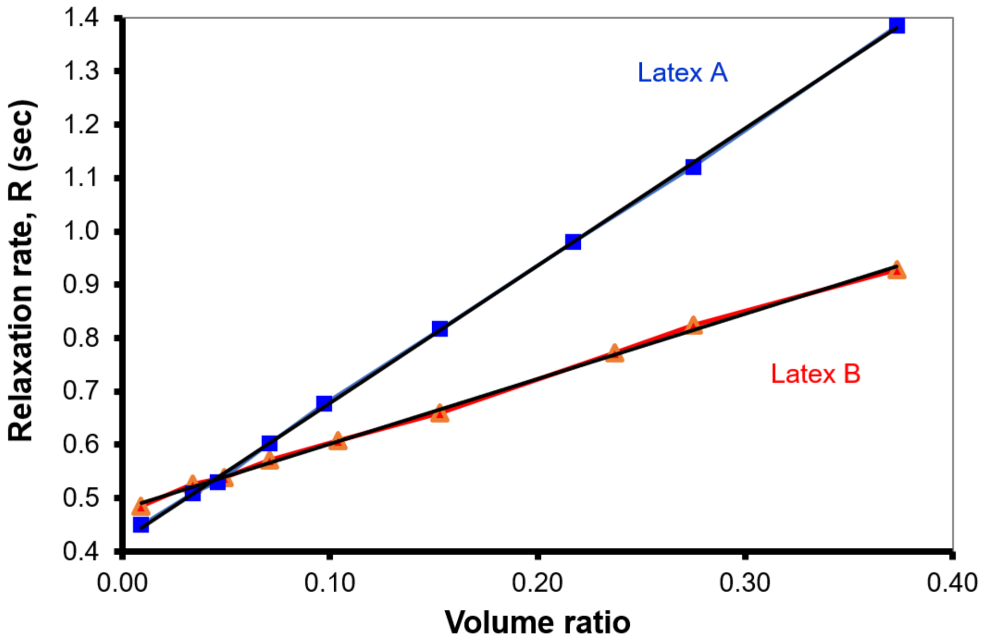

Figure 4. NMR relaxation rates for TOPLUS Latex Copolymer dispersions as a function of volume ratio.

The relaxation rates for the concentrated (30%) latex suspensions are markedly different. The larger relaxation rate for the SIS block copolymer sample A is indicative of a better quality of dispersion with a larger wetted surface area. This is a consequence of not only true variations in the particle size/size distribution of the dispersion, but also the copolymer surface chemistry, which is a function of the polymerization reaction and subsequent cleaning (e.g., steam stripping).

At zero volume ratio, the two lines intersect at *R* values of 0.418 s^{-1} and 0.462 s^{-1} for the Latexes A and B, respectively. This translates to T_2 relaxation times of 2390 ms and 2165 ms. The average T_2 relaxation time of the distilled water used as the diluent in this study was 2108 ms. The observed difference arises because the “dispersion medium” of the latexes cannot be pure water but is “water+dispersant/excipients” (e.g., remnants from the polymerization process).

In Conclusion

The NMR relaxation data presented above demonstrates how the Mageleka *M*agno*M*eter *R*elaxo*M*eter can quantitatively discriminate between dispersions of commercial polymer latexes. It is a fast, simple tool for QC of batch-to-batch and lot-to lot variations in manufacture, and it provides intelligence on the differences in nominally identical latex materials that can then be used to improve product performance.

The ability to interrogate latex dispersions without dilution provides a major practical advantage for NMR relaxation over other particle characterization techniques (especially particle sizing by light scattering methods). Based on the above and other data, the Mageleka *R*elaxo*M*eter could be used to help improve the following aspects of the polymer latex manufacturing process:

1. Investigate the efficiency (and reproducibility) of cleaning processes
2. Determine the efficacy of the charge modifying agents (emulsifiers) used.
3. Review the relative advantages of initiators.
4. Study shelf-storage stability and factors improving resistance to coagulation.

For more information, to send samples, to arrange a demonstration of the MagnoMeter at your facility, or to talk to one of Mageleka's technical applications specialists, please email roger@mageleka.com