Rheological Characterization of Forcibly Stored Liquid Paints

Time for Liquid Colors

Liquid colors are still an underestimated alternative to a masterbatch for coloring plastics. There are many advantages to using liquid colors: Homogeneous coloring free of streaks even with small additions and fast color changes with few cleaning cycles. However, shelf life is often seen as a disadvantage. This study evaluates the change in liquid colors over time when stored at room and elevated temperatures.

Liquid colors on the test bench: The SKZ and the company Netzsch investigated the behavior of the colors after accelerated storage. © SKZ/Netzsch

In many areas of consumer goods, color and design are just as important as the function of a component. Color and its processing in the product, for example, convey a feeling, of quality and value. It serves for identification purposes and points out danger, respect, or purity. Due to the increasing demand for color variety, plastic manufacturers directly color the parts during the injection molding process, often using (color) masterbatches.

Liquid colors are a cost-efficient and flexible alternative to masterbatches for coloring plastic components. In comparison to masterbatches, better dispersion of the pigments in the plastics is a major advantage, leading to lower dosing quantity in order to achieve the same color quality as with masterbatches. In addition, the liquid carrier material, that is based, for example, on unsaturated fatty acid esters or natural oils, yields a cleaning effect in the injection molding machine. This enables faster color changes which significantly reduces the scrap rate. Along with possible impacts on processing (e.g., stick-slip phenomenon) and the material properties of the finished part (softening effect on the polymer), the storage behavior of liquid colors is also of great interest for the application.

Coloring with Liquid Colors Is Often More Cost-Effective than Masterbatch

This study investigates whether accelerated aging of liquid colors is possible due to an increased storage temperature and whether this is evident from changed rheological properties:

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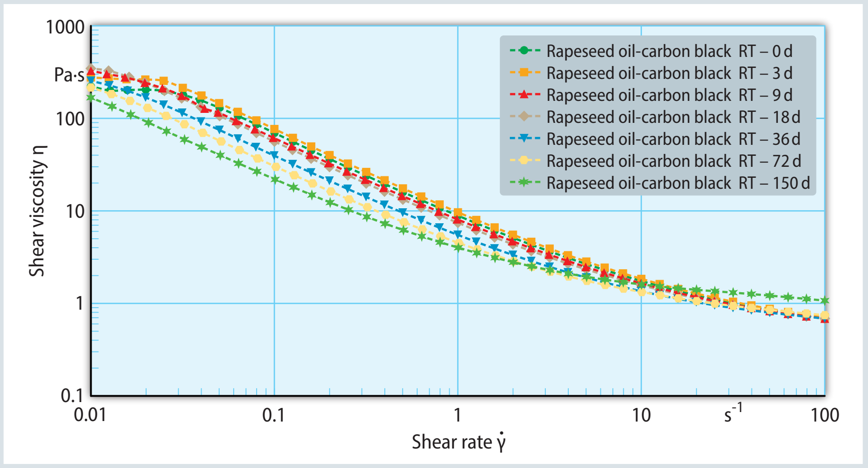

Fig. 1. Comparison of the viscosity curves of the suspensions, stored at room temperature (RT).

Source: SKZ; graphic © Hanser

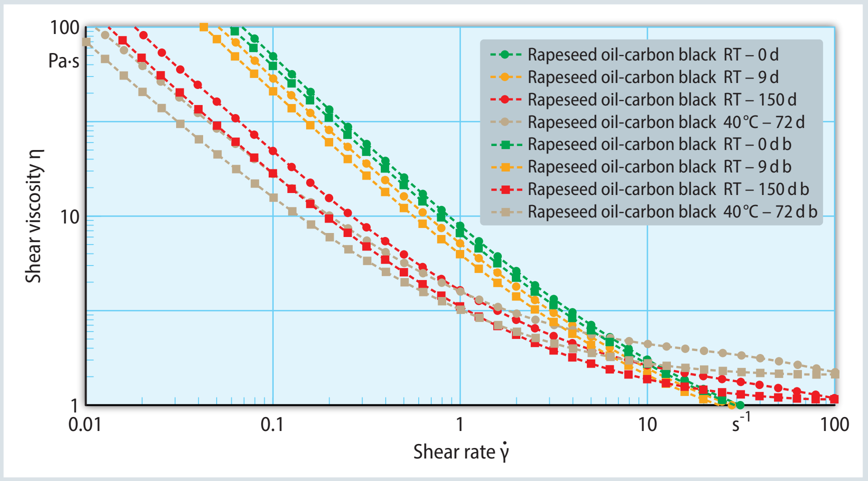

Fig. 2. Comparison of the viscosity curves of the suspensions, stored at room temperature (RT) and 40 °C with increasing and decreasing shear rates (b, back). Source: SKZ; graphic © Hanser

- Is it possible to observe changes in liquid colors during storage by rheology?
- Can the occurring changes be accelerated by increasing the storage temperature and can the behavior of liquid colors be predicted?

Materials and Methods for Measuring Accelerated Aging

Liquid colors are mixtures of substances consisting of a liquid carrier, binder, colorants, and additives. Typical carriers are vegetable oils, paraffin oils and fatty acid esters. In addition to inorganic and organic pigments, dyes can be used as colorants. The additives used in liquid colors may be necessary for the formulation and use of the liquid color (e.g., wetting, and dispersing additives, defoamers, rheological additives), but also for the performance of the finished product, e.g., for improved UV stability or as flame retardants.

A simplified model system without additional additives is investigated. The model system consists of rapeseed oil as a carrier with sorbitan fatty acid esters (Tween80/Span80 blend) as a binder and carbon black as the pigment. The solid mass fraction of the pigment in the model system is 15.5 %. The suspensions were stored at both 20 °C (room temperature) and 40 °C for accelerated aging. In parallel, samples without pigment were aged and analyzed in order to detect possible changes in the carrier system.

The rheological tests were carried out at different times (after 0, 3, 9, 18, 36, 72, and 150 days) of storage. Prior to these tests, all samples were stirred and homogenized at moderate/low mixing rates using a dual asymmetric centri-

Info

Text

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References

You can find the list of references at
www.plasticsinsights.com/archive

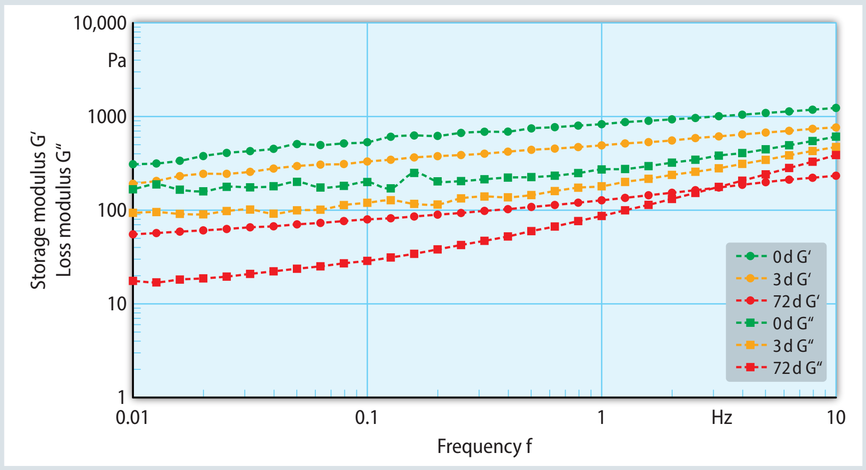

Fig. 3. Course of the storage and loss modulus using a frequency sweep for samples aged for different lengths of time at 40 °C. Source: SKZ; graphic © Hanser

fuge. The samples stored at 40 °C were subsequently adjusted to the measurement (room) temperature for a minimum of 1 hour.

Samples were characterized using rotational rheometers (type: Kinexus Prime ultra+ and Kinexus pro+, manufacturer Netzsch-Gerätebau GmbH) at 20 °C. Preliminary tests have shown that measurements with plate-plate measuring geometries provide comparable results for this material system to those with concentric-cylinder measuring geometries. All samples are investigated with a plate-plate measurement geometry by means of rotational rheology. For the sample stored at 40 °C, oscillatory rheological measurements (frequency sweeps) are also performed. For these tests, a concentric-cylinder was used, enabling larger sample volumes to be tested.

While the rotational rheological investigation was mainly used to detect changes in material behavior, the frequency sweeps were intended to obtain information about changes in viscoelastic behavior.

Results and Discussion

The viscosity curves of suspensions stored at room temperature are shown on the left in **Figure 1**. In these measurements, the shear viscosity is determined under increasing shear rates. The results clearly show, that the shear viscosity is decreasing with increasing shear rates, indicating a shear-thinning behavior. As liquid colors are suspensions, the shear stress applied leads to the particles aligning in the shear direction, resulting in lower flow resistance. Additionally, at shear rates below 10 s^{-1}, a decrease in shear viscosity is observed with increasing storage time. This can be interpreted as structural degradation occurring over the storage time. In addition to the measurements shown, rotational measurements were carried out on the rapeseed oil tween-chip samples in respective time periods. Comparison of the particle-free samples over time revealed both newtonian behavior and no age-related change in shear viscosity. The method of storage, at room temperature as well as at 40 °C, has no effect on the shear viscosity measured and the flow curve of the particle-free samples. It can therefore be assumed that a change in shear viscosity of the suspension is not affected by the pure rapeseed oil system. With increasing shear stress (> 10 s^{-1}), the shear-thinning effect decreases due to the gradual arrangement of the particles in the flow field. As a result, the difference between the samples at different time intervals (age) also decreases and the measurement curves typically exhibit a similar result.

Temperature and Storage Time Influence Shear Viscosity

After 150 days at room temperature and after 72 days at 40 °C, the samples show a deviating tendency, particularly in the higher shear rate range (**Fig. 2**). An increase in shear viscosity can be observed around 10 s^{-1} compared to the younger samples. As this behavior is already evident after 72 days for the sample stored at 40 °C, it can be assumed that the storage time could be reduced by about half for the same » changes in the rheological behavior investigated.

As shown on the right in **Figure 2**, a similar tendency can be observed for the suspension stored at 40 °C for 72 days. This can be interpreted by hydrodynamic effects like flow-induced liquid immobilization [1] becoming more significant with increasing storage time and the associated possible structural changes.

Along with the investigation of the dynamic shear viscosity, a frequency sweep measurement was carried out on the suspensions by means of oscillation. This enables mapping of both the elastic and viscous properties, known as the storage and loss modulus.

Figure 3 depicts the frequency spectrum between 10 Hz and 0.01 Hz. In line with the shear viscosity measurements already discussed, a decrease in rheological parameters with increasing storage time can again be observed. The storage modulus (G') is generally higher than the loss modulus (G''), illustrating a solid-dominated material behavior under the conditions tested.

It should be emphasized, however, that a crossover of the storage and loss modulus is observed for the suspension stored at 40 °C for 75 days and that the loss modulus dominates at frequencies > 3 Hz. This can be interpreted as a possible viscosity-dominated behavior for this sample under the given measurement conditions and may indicate that the storage stability of the suspensions is limited. For all suspensions stored for shorter times, however, the loss modulus is lower than the storage modulus over the entire frequency range analyzed.

Summary and Outlook

The rheological investigations presented have shown that the liquid colors exhibit shear-thinning behavior. In addition, it could be observed that the flow behavior of the rapeseed oil-carbon black suspensions change with increasing storage time such that the values of the rheological variables investigated decrease. This change can be observed both in the shear viscosity and in the frequency-dependent storage and loss modulus.

By increasing the storage temperature, aging was accelerated in the rapeseed oil-carbon black suspension. However, it should be noted that other aging mechanisms may be dominant due to the elevated temperature which should be clarified by further investigations.

Focus of these investigations was to characterize the rapeseed oil-carbon black suspensions. In addition, from an applicational point of view, the processability of liquid colors, stored at room temperature and at a temperature of 40 °C, during injection molding is of particular interest.

The investigations were carried out on a model system. Finally, it needs to be clarified whether different temperature-time dependencies can be observed for various systems of liquid colors. This will help to determine if different temperatures are relevant for artificial aging. It may also be possible to identify classes of liquid colors with comparable aging behavior. Further investigations should also include the determination of the maximum temperature at which artificial aging can be carried out. ■