PROPOSED METHOD FOR CLASSIFYING NATURAL RUBBER FOR USE IN PRESSURE SENSITIVE ADHESIVE TAPES

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Abstract

Natural rubber is used as an important raw material by the pressure sensitive adhesives industry. However, the normal quality variation is relatively high compared to synthetic polymer alternatives.

This paper discusses measurements of the magnitude and nature of this natural rubber quality variation using a special dynamic mechanical rheological tester. Also the paper discusses some of the causes of this variation and the new ASTM Standard (D7050) that describes how effective sorting can be implemented to improve product consistency.

Introduction

More natural rubber is consumed annually than any single synthetic elastomer; yet the quality of this natural product is influenced by many special factors not associated with synthetic rubber production. For example, the Hevea tree clone from which the rubber latex is obtained and the age of the tree can affect natural rubber quality as well as the soil and climate conditions. Natural rubber molecular weight distribution can be bimodal or unimodal. Figure 1 shows three types of natural rubber distributions.

Figure 1.

Type A distribution is a skewed unimodal distribution. Type B is bimodal with the height of the lower MW peak at half or less of the higher MW peak while Type C distribution is distinctly bimodal with the height for the lower molecular weight peak almost equal to the height of the peak for the high molecular weight portion. Bimodal is reported as the most common distribution for latex. Also the magnitude of the molecular weight distribution (MWD) can vary greatly. The $M_W / M_N$ ratio is reported to vary...
between a range of 2.5 to 10 for all types of natural rubber. (Where \( M_W \) is the weight average molecular weight and \( M_N \) is the number average molecular weight. The higher \( M_W/M_N \), the broader the MWD).

In addition, further variation is introduced through the manner in which the natural rubber latex is coagulated, dried, processed and stored. The nature of these conditions can increase the gel content of the rubber (% insolubles in toluene for example). Gel content can vary from 5 to 50%. Some hypotheses to explain this increase in gel are (1) free radical cross-linking or (2) a reaction of aldehyde groups on the rubber molecules with free amino acids or protein molecules which are present in the non-rubber fraction. These increases in gel content are associated with so-called “storage hardening” or rise in natural rubber viscosity while in storage. Sources of natural rubber can differ in their susceptibility to this “storage hardening.” These differences can be associated with processing history as well as being a clonal characteristic of the latex itself.

Mooney Viscosity
Mooney viscometer is probably the most widely used method for measuring the quality of natural rubber. This viscometer was invented by Melvin Mooney, U. S. Rubber Co. in the 1930s and is now used to measure the viscosity of both natural and synthetic rubber worldwide. This method consists of rotating a special serrated rotor while embedded in a rubber sample within a sealed, pressurized, serrated, temperature controlled cavity. The rotor turns at a constant rate of 2.0 revolutions/minute (0.21 rad/s) and the resulting torque is measured. This test imparts a shear rate of only 1 sec^{-1}. The Mooney viscosity results are reported in arbitrary Mooney Units (MU) which are based on torque as defined by ISO 289 and ASTM D1646.

Wallace Plasticity
This method measures plasticity by compressing a small rubber disk between two platens at 100° C for 15 seconds at a fixed thickness of 1.00 mm. After this pre-heat period, the rubber specimen is subjected to constant compressive force of 100 N for 15 additional seconds. The plasticity (Po) is measured as the final thickness at the end of this period expressed in arbitrary units which are equivalent to 0.01 mm. This method is quite rapid; however usually the median of three separate readings is calculated to report the final value. The test also has an extremely low shear rate. This method is described in detail as the International Standard ISO 2007. One important advantage of the Wallace plasticity is its relatively small sample size which is more easily air-oven aged. From this oven aging, the Plasticity Retention Index (PRI) is calculated in accordance with ASTM D3194.

Correlation Between Mooney Viscosity and Wallace Plasticity
Both Mooney Viscosity and Wallace Plasticity are used to specify different grades of natural rubber in accordance with ASTM D 2227. Conceptually, viscosity and plasticity are opposites in their meaning. While plasticity relates to ease of flow, viscosity measures a polymer’s resistance to flow. Also, a high Wallace plasticity number (Po) for a given natural rubber sample indicates it has a low plasticity and a high viscosity. Therefore Wallace plasticity and the Mooney viscosity should be correlated to each other in theory. In reality, however, these two properties do not correlate perfectly. Some of the reasons for this statistical scatter are as follows. First, the repeatability of the rapid plasticity procedure is not perfect which can introduce some scatter in the correlation. Secondly, variations in gel content for different sources of natural rubber may affect Wallace plasticity Po values more than Mooney viscosity values. Thirdly, Bristow reported that some of the scatter between Wallace plasticity and Mooney viscosity is the influence of thixotropy. With a normal Mooney viscosity test, thixotropic effects are practically eliminated (for an ML 1+4 test) while the Wallace plasticity Po is actually measuring an “initial viscosity” which is affected
much more by thixotropy. This theory is supported by better correlations obtained between Po and the initial Mooney viscosity (not the final viscosity).17

**Purpose**

The American Society for Testing and Materials, Committee D11 on rubber, has been investigating new methods of effectively characterizing and testing natural rubber. For this purpose, the subcommittee D11.22 on Natural Rubber, formed the Definitive Testing Task Group to investigate new methods for characterizing NR. A new instrument which was included in this study was the RPA 2000® rubber process analyzer. The RPA is a special versatile dynamic mechanical rheological tester which was introduced in 1992 and is now used worldwide. The purpose of this study was to determine how effective this new test instrument would be in characterizing natural rubber and its feasibility as a quality control instrument.

**Experimental**

The ASTM D11.22 Task Group for NR Definitive Testing evaluated several submitted samples of natural rubber. These samples were submitted by the ASTM committee members. These different natural rubber samples represented “good processing” vs. “poor processing” as determined from their behavior in their process equipment. They also reported traditional test results, such as Mooney viscosity and Wallace plasticity results, which many times showed these samples to be “the same.”

The RPA is designed to measure the dynamic properties of raw polymers, uncured compounds and final cured compounds. The RPA strains a sample in shear by oscillating the lower die sinusoidally. Oscillation frequency can be set from 0.1 to 2000 cycles per minute (cpm). The magnitude of the lower die movement can be set by the angular oscillation of the lower die or by the required strain on a sample. The lower die can oscillate from ±0.05 degrees of arc to ±90.00 degrees of arc. This angular oscillation corresponds to strains of ±0.7% to ±1256%. Testing at high strain is possible because the RPA uses a unique sealed, pressured cavity to test the rubber specimen at a pressure of at least 400 psi. The RPA can be used easily in a quality assurance environment as well as in R&D because of the ease in which a sample is placed in this instrument. A cross section of the die design is shown in Figure 2. Temperature can be rapidly dropped at a rate of 1°C per second by a forced air cooling feature.

![Alpha Technologies RPA 2000](image_url)
The RPA is designed to measure both elastic and viscous properties of elastomers and compounds. The upper die is attached to a torque transducer to eliminate noise from the lower die drive system and to measure the torque transmitted through the sample. This torque is called the complex torque or $S^*$ and it is not in-phase with the applied strain due to the viscoelastic nature of rubber. The $S^*$ torque signal is reduced by the RPA computer into an elastic ($S'$) component (in-phase with strain) and a viscous ($S''$) component (90 degrees out-of-phase with strain) by applying a Fourier Transform to the $S^*$ signal. The Fourier Transform also improves the signal to noise ratio of the test. $S^*$, $S'$ and $S''$ are shown in Figure 3.

![RPA Torque Response](image)

Figure 3.

$\tan(\delta)$ is calculated from $(S''/S')$. Torque values ($S$) are directly converted to the shear modulus ($G$) by multiplying with the appropriate die form factor and dividing by the strain. This procedure provides the storage modulus $G'$ and the loss modulus $G''$. Also dynamic viscosity calculations are also performed where dynamic real viscosity $\eta'$ is calculated by dividing loss modulus $G''$ by applied frequency in radians per second $\omega$. These calculations are automatically performed by the computer system.18, 19

**Results and Discussion**

From the comparative testing, it was found that the highest statistical test sensitivity for discerning real differences in processing was achieved with high strain measurements with the RPA. (The method used for measuring statistical test sensitivity or signal to noise ratio is described in ASTM D 6600).

**Case Studies**

In a three year period, the ASTM D11 Definitive Testing Task Group engaged in three case studies involving “problem lots” of natural rubber which were reportedly causing factory problems. These case studies are reviewed below.

**Case Study Number 1**

A large tire producer reported a specific natural rubber lot as being excessively “sticky.” Mooney testing did not show any significant difference between this “problem” lot and a lot that processed normally. Also
the RPA frequency sweep in Figure 4 showed no significant differences between the problem lot and the normal lot when measured at 7% strain (well within the linear viscoelastic region).

![Comparison of TC10 Natural Rubber Frequency Sweep](image1)

**Figure 4.**

However, RPA high strain testing in Figure 5, clearly shows a significant and repeatable difference in the elastic torque $S'$ response at high strains in the non-linear viscoelastic region. Possibly the higher strains disentangle NR molecular chains and relate more effectively to what is happening in the mixing process.

![Comparison of TC10 Natural Rubber High Strain Sweep](image2)

**Figure 5.**

**Case Study Number 2**

A second large tire producer also submitted to the Task Group samples from three different lots of natural rubber. Two of these lots reportedly did not break down in factory mixing while the third lot mixed well. It is interesting that the Mooney viscosity for one of the “bad” lots was very close to the Mooney viscosity for the “good” lot (ML 1+4 of 93 vs. 94). Table 1 gives a description of these three lots.
Figure 6 shows very good separation of the “good” vs. the “bad” lots of natural rubber when comparing the uncured tan δ at high strain test conditions.

Case Study Number 3
A large American non-tire rubber company also submitted samples to the ASTM Task Group. This company was purchasing natural rubber on a regular basis from one plantation until it became tight in supply. To avoid supply problems, this company started evaluating a second source. They performed gel permeation chromatography on both the original source (NR #1) and the proposed alternate source (NR #2). They found that NR #2 had a broader molecular weight distribution with a $M_W/M_N = 4.5$ for NR #2 vs. $M_W/M_N = 3.15$ for NR #1. This broader MWD natural rubber source was found to have a faster black incorporation time than other sources with narrower MWD. Differences in MWD will affect the RPA frequency responses at 7 % strain (one-half of the critical strain). Figures 7, 8 and 9 show the viscoelastic
differences from the uncured storage modulus $G'$, the loss modulus $G''$, and the $\tan \delta$ from an RPA frequency sweep which reflect these differences in MWD. Also from non-linear viscoelastic testing with the RPA, the uncured $\tan \delta$ for NR #2 was 11% higher than the NR #1 when tested at 50 degrees arc strain and 20% higher than NR #1 at 50 degrees arc in a second back-to-back high strain test. (Sometimes two back-to-back high strain sweeps can improve test sensitivity in that the first high strain test disentangles some of the NR molecular chains).²⁰

Figure 7.

Figure 8.
ASTM Actions Resulting from Case Studies

From the discovery that higher strain testing is better for predicting the processing performance differences among different bales and lots of natural rubber, a higher strain test option was added to ASTM D6204, Method B, now allowing either 100% or 200% strain with the RPA. This new Method B can be used for more effective quality assurance of natural rubber over the traditional Mooney and Wallace Plasticity testing, which is less sensitive than the RPA.²¹

Also, RPA trial studies were performed at a tire plant to determine the nature of the normal variation for natural rubber from bale-to-bale or from lot-to-lot.²²

From is study, it was found that the statistical range (6 • Coefficient of Variation) for TSR 20 natural rubber was typically 50 percent as shown below in Figures 10 for RPA elastic storage modulus and Figure 11 for RPA tan δ (viscous to elastic ratio).
Figure 10.

Figure 11.
Compared to a similar study of synthetic rubber variation (SBR 1712), the variation measured in natural rubber is about ten times greater than what is measured for synthetic rubber which is in the neighborhood of only 5% (reference Figure 12 and 13 for raw synthetic rubber variation from bale-to-bale).²³
Because of this greater bale-to-bale variation experienced with natural rubber vs. synthetic raw rubbers, ASTM Subcommittee D11.22 on natural rubber developed a new sorting procedure for natural rubber bales using RPA test criteria. This information is given in the new ASTM D 7050 Standard Practice. Figure 14 shows the RPA elastic modulus $G'$ which is used to separate “tough” rubber from “soft” rubber.
This way, the “tough” or “hard” natural rubber can be more effectively used in the mixing of rubber compounds that possess very fine particle size, low structure carbon blacks. Tough rubber is needed here because it will provide higher shear forces in mixing to achieve better carbon black dispersion than what would be achieved with soft natural rubber. On the other hand, the “soft” rubber can more effectively be used in so called “soft” stocks, which are based on larger particle sized fillers.

Relevance to Pressure Sensitive Adhesive Applications

This work conducted for the ASTM D11 Committee on Rubber has relevance to the pressure sensitive adhesives industry as well.

Measuring and dealing with natural rubber variation is not just a problem for the rubber industry. It is also a problem for the pressure sensitive adhesives industry as well. Many pressure sensitive adhesive applicators use both natural rubber as well as other synthetic polymers as their base. Many pressure sensitive adhesive producers have complained about the inherent variation of the natural rubber and the fact that they cannot predict the solvation time of the natural rubber in solvents. Some PSA fabricators are now starting to use the RPA to make these predictions.

By using ASTM D 6204 Part B (at 100 % strain) and incorporating the new ASTM D7050 Standard Practice for sorting bales of natural rubber, the PSA industry could realize some of the same advantages that the rubber industry is enjoying.

Conclusion

The following conclusions were drawn from the ASTM studies described in this paper.

- RPA high strain measurements are very sensitive to subtle natural rubber differences in molecular chain entanglements and gel content (much better than low strain measurements).
- Wide frequency sweeps of natural rubber at low strains are more sensitive to molecular weight distribution differences
- The magnitude of variation of natural rubber is inherently great even if the technically specified rubber (TSR) is in compliance with ASTM D2227 or ISO 2000.
- Implementing an RPA testing program using ASTM D6204 Part B at 100 % or 200 % strain is much better and faster in characterizing natural rubber than the older, Mooney and Wallace tests that are not very effective.
- Using a sorting procedure based on ASTM D7050 using ASTM D6204 Part B methods should be effective for sorting natural rubber for PSA applications.

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TECH 31 Technical Seminar Speaker

Proposed Method for Classifying Natural Rubber for Use in Pressure Sensitive Adhesive Tapes

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John S. Dick has more than 30 years of experience in the rubber industry, first with BF Goodrich and Uniroyal Goodrich Tire Co. and then to Monsanto's Rubber Instruments Group (now Alpha Technologies) as a senior marketing technical service specialist. Dick has authored over 70 journal and magazine publications and four books on rubber technology. He is a fellow in the American Society for Testing and Materials (ASTM) receiving the Award of Merit in 1990 and Distinguished Service Award in 2005. Also he has represented the United States as a delegate to the International Standards Organization (ISO) for the last 24 years. He was appointed in 1992 to be leader of the U.S.A. delegation to ISO TC-45 on rubber. Dick received his B.S. degree from Virginia Polytechnic Institute and M.A. from the University of Akron.