Precision Associated with Determination of Dirt Content of Natural Rubber

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ABSTRACT: The precision associated with determination of dirt in natural rubber is low even when similar testing procedures are applied. All measurements leading to this estimation involve the use of an analytical balance. For this reason the contribution of associated errors to the ultimate precision of dirt measurements was evaluated using analytical balances of varying degrees of precision. A mathematical model was proposed to estimate the compound standard error associated with dirt measurements, which was found to be ± 0.001 mg. This signifies that, during dirt assay, the masses of test portions, empty sieves, and sieves containing dirt must be estimated to at least 3 significant figures. This error would further decrease with an increase in the quantity of dirt assayed. Prolonged maturation of coagula reduced the length of rubber chains, thus increasing the ease of dissolution of test portions during dirt analysis. Higher molar mass samples were mostly associated with poor reproducibility of dirt and macrogel content determinations. Increasing the mass of test portions improved the precision of dirt measurements, though the recommended sizes of these portions should be a compromise of economic considerations and practical testing conditions. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 957–962, 2001

Key words: natural rubber; dirt content determination; repeatability; standard error; precision

INTRODUCTION

For the purpose of grading, natural rubber of granular form is normally subjected to some specification tests governed by the ISO 2000 standard. Of these tests, the dirt content (that indicates the level of fine impurities) is the primary criterion alongside the resistance of the raw material to thermal and oxidative degradation.[1,2] Nonetheless, research has concentrated on thermo-oxidative behavior as translated by the plasticity retention index (PRI),[3–5] whereas poor processing and handling, which lead to inconsistent and high dirt levels, are responsible for most cases of natural rubber downgrading.[6,7]

The procedure for dirt determination consists of dissolving samples to release dirt particles and eventual collection of insoluble impurities following breakdown of the rubber matrix. Mechanically and chemically induced bond scissions of rubber in solution lead to the formation of free

radicals, which later stabilize by recombining in pairs or on sites along the rubber chains. The presence of oxidation activators reduces the dissolution temperature and also intervenes in the recombination process by reacting rapidly with the free radicals, to give groups that no longer reagglomerate with similar entities.[8–10] Progress has been made over the past 50 years to develop standard procedures and improve the repeatability of this measurement, although poor repeatability is still common, even with the use of similar analytical techniques.[6,11] Although the dissolution method is the most adopted, the error associated with measurements leading up to the estimation of dirt content still has to be determined. This study considers these factors and, from a statistical viewpoint, estimates the compound standard error associated with the analysis.

EXPERIMENTAL

Materials

Different grades of natural rubber processed using different processing methods and covering a wide range of dirt content and molar masses were studied:

1. Two samples were of grade TSR 10 collected in cuplump form, one of which matured for 4 weeks before processing (TSR 10A) and the other for about 16 weeks (TSR 10B). The first case is typical of industrial factory-processing conditions, whereas the second simulates smallholder practice.
2. Two other samples were viscosity-stabilized grades [treated with neutral hydroxylamine sulfate (NHS) to inhibit aggregation phenomena], one of which was artificially latex coagulated using formic acid (TSR 5CV), and the other was collected in cuplump form and treated with NHS before drying (TSR 10CV).
3. The fifth sample was of whole-field ammonia-preserved latex, later coagulated naturally without acid (5 WF).

After factory processing, rubber cakes were compacted into parallelepiped bales and test portions were cut at random and homogenized according to the ISO 1796 standard.

Testing Procedures

Portions of homogenized rubber (about 20 g) were shredded and immersed, respectively, in 400-mL mixtures of white spirit of high aromatic content (bp 155–196°C) and 1.0 g of di-*o*-benzamido diphenyl disulfide (Pepton 22® from Anchor Chemicals) as peptizer. The contents were stored at room temperature for 48 h and then heated at 130 ± 5°C to complete dissolution, and then decanted through 45-μm sieves.[2]

The Wallace rapid plasticity number (P_0) and the plasticity retention index (PRI) were determined in conformity with ISO 2007 and 2930 standards, respectively.

Average molar masses were measured by steric exclusion chromatography (SEC). Separate rubber portions were collected from the homogenized sheet and dissolved in cyclohexane, after which the solutions were centrifuged at 35,000 *g* for 1 h at 17°C. Insoluble fractions were removed after decantation and dried *in vacuo* to constant weight, and the macrogel content was determined. Sol fractions were diluted to 0.2 mg/mL, filtered through a 1-μm filter, and injected into the SEC apparatus, which consisted of a chromatograph with an ERMA ERC-33112 solvent gas remover, a Waters 510 pump (Waters Instruments, Rochester, MN), a Waters 486 UV detector (at 220 nm), an automatic injector, and two PL-GEL 30-cm mixed columns operating at 65°C. Cyclohexane flowing at 0.87 mL/min was used as elutant. The number-average ($\overline{M}_n$) and the weight-average ($\overline{M}_w$) molecular masses were deduced by integrating the area under the molar mass distribution curves. The polydispersity index was estimated as the ratio of $\overline{M}_w$ to $\overline{M}_n$.

Statistical Analyses

Analysis of variance was conducted to determine the significance of the different factors studied. Coefficients of correlation characterizing the intensity of the linear relationship between dirt content and chain-length parameters were performed separately for each sample. These relationships, which highlight the suitability of chain-length variables for describing the precision associated with dirt content measurement, were also analyzed using the principal component analysis

Table I Effect of Precision of Balance on Variability in Dirt Content Analyses

Grade	Heating Time (min)	e = 0.1 mg		e = 1 mg	
		Dirt Content (% w/w)	Coefficient of Variation (%)	Dirt Content (% w/w)	Coefficient of Variation (%)
TSR 10	90	0.0120	17	0.010	12
	150	0.0099	19	0.010	10
	150	0.0067	6	0.005	29
TSR 5	210	0.0055	22	0.006	29

technique.[12] Correlation matrices were used to produce principal component bands (PCs). These were linear combinations along orthogonal axes, featuring the direction of maximum variance (PC1) where most spread in the scatter plots were observed, whereas the other axes described variance in data not already described.

RESULTS AND DISCUSSION

Effect of Precision of Analytical Balance

Tests were conducted to investigate the effect of extent of rubber contamination on the reproducibility of dirt content measurements using balances of different precision. All test portions were previously swollen in white spirit for 48 h prior to heating. The results, summarized in Table I, showed an apparent increase in dispersion at lower dirt levels, especially when a balance of lower precision ($e = 1$ mg) was used.

If the uncertainty (relative error) associated with dirt content measurement is given by the expression in eq. (1), where $M_2 - M_1$ is the mass of dirt, and M_0 the mass of the test portion, then the associated error depends exclusively on the quantity of dirt T.

$$\frac{\Delta T}{T} = \frac{\Delta(M_2 - M_1)}{M_2 - M_1} + \frac{\Delta M_0}{M_0} \qquad (1)$$

For a precision of $\pm 0.001\%$, therefore, the absolute dirt should be at least equal to

$$M_2 - M_1 = \frac{\Delta(M_2 - M_1)}{\Delta T} T \qquad (2)$$

with $\Delta T = 0.001\%$, $T = 0.005\%$ (clean rubber), $(M_2 - M_1) = 0.5$ mg; hence, $M_2 - M_1 = 2.5$ mg. This demonstration acquires significance when we consider that, for a sample of 0.005% dirt content, a 50-g sample is needed for a $\pm 0.001\%$ precision, and that the mass of the test portion should decrease as contamination increases (for equivalent levels of precision).

Estimating the Error Associated with Dirt Content Determinations

The law of propagation of errors qualifies the different errors associated with measurements leading to the estimation of a variable. For the estimation of dirt content T, three mass measurements are involved: M_0, M_1, and M_2, the respective masses of test portions, the sieves, and sieves containing insoluble dirt. The law of propagation of errors for this function is given as

$$U_c^2(T) = \sum_{i=1}^{n} \left[\frac{df}{dX_i}\right]^2 U^2(X_i)$$

$$+ 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \left[\frac{df}{dX_i}\right]\left[\frac{df}{dX_j}\right] U(X_i, X_j) \quad (3)$$

where U_c is the compound standard error associated with T and $U(X_i)$ is the error associated with estimating the X_i entry. The last term of eq. (3) is mostly taken into consideration when magnitudes that intervene in the compound error are correlated as $U(X_i, X_j)$ represents the covariance associated with the variables X_i and X_j. In dirt content determination, measurements of M_0, M_1, and M_2 are treated as independent quantities; hence, the covariance term could be ignored. Equation (3) simplifies to the form

Table II   Coefficients of Principal Component Analysis for Dirt Content and Molecular Mass Data

(a) Pearson Correlation Coefficients

Rubber Grades	$\bar{M}_n$	$\bar{M}_w$	Macrogel Gel	Polydispersity Index	PRI[a]
TSR 10A	−0.29	−0.50**	−0.04	−0.50**	−0.17
TSR 10B	−0.21	−0.43*	−0.52**	−0.04	0.22
TSR 5CV	0.26	−0.36*	−0.14	−0.47*	0.42*
TSR 10CV	0.01	−0.17	0.39*	−0.20	−0.41*
5 WF	0.15	0.22	0.17	−0.12	0.24

(b) Eigenvalues

Axes	Eigen Values	Variance (%)	Total (%)
PC1	4.0388	67.3	67.3
PC2	1.3934	23.2	90.5
PC3	0.3724	6.2	96.7
PC4	0.1370	2.4	99.1
PC5	0.0547	0.9	100.0

(c) Eigenvectors and Coefficients of Variables in Linear Equations of Principal Axes

Parameters	PC1	PC2	PC3	PC4	PC5
$\bar{M}_n$	−0.427	0.382	0.302	−0.024	0.690
$\bar{M}_w$	−0.483	−0.055	0.366	0.042	−0.057
Macrogel gel	−0.417	0.331	−0.474	−0.653	−0.255
Polydispersity index	−0.114	−0.809	−0.074	−0.430	0.374
PRI[a]	−0.436	−0.156	−0.631	0.614	0.110

[a] Plasticity retention index.
* $P < 5\%$; ** $P < 1\%$. Figures with no asterisk were not significant at $P < 5\%$.

$$U_c^2(T) = 100^2 \left\{ \left[\frac{dT}{dM_2} \right]^2 U^2(M_2) \right.$$

$$\left. + \left[\frac{dT}{dM_1} \right]^2 U^2(M_1) + \left[\frac{dT}{dM_0} \right]^2 U^2(M_0) \right\}$$

which rearranged gives

$$U_c^2(T) = \left(\frac{100}{M_0} \right)^2 \left[U^2 M_2 + U^2 M_1 \right.$$

$$\left. + U^2 M_0 \left(\frac{M_2 - M_1}{M_0} \right)^2 \right] \quad (4)$$

Measurements of standard errors (on a 0.1-mg precision balance) gave values of $U_2(M_0)$ of 1.9977 $\times 10^{-8}$, $U_2(M_1) = 1.25 \times 10^{-9}$, and $U_2(M_2) = 1.25 \times 10^{-9}$. The extended error ($U$), estimated as the product of the compound standard error $U_c(I)$ and an enlargement factor K, allows for the associa-tion of a margin to the calculated error values. The value of K is generally given as 2, which corresponds to the 95% confidence threshold required for the calculation of T. Based on our results, $U_c^2(T) \approx 2.407 \times 10^{-7}$, which gives $U_c = \pm 0.001$. Hence, mass measurements for the estimation of dirt content should be estimated to at least three significant figures.

Relationship Between Macromolecular Mass Parameters and Dirt Content Determination

Coefficients of principal component analyses for dirt content and molecular mass data are presented in Table II. The first part of the Table contains a matrix that characterizes the intensity of the linear correlations between macromolecular chain-length parameters and dirt content for the samples studied. No significant correlations were obtained between $\bar{M}_n$ and dirt content,

whereas significant correlations existed for TSR 10 grades (of inherently higher dirt contents) between the latter and $\overline{M}_w$. A significant negative correlation was also obtained between macrogel content and the quantity of dirt in some TSR 10 grades (TSR 10CV and that subjected to prolonged maturation, TSR 10B). Considering that the amount of insoluble matter in rubber should influence the precision in dirt measurement (for aggregates above 45 μm), reactions that promote the formation of insoluble fractions would therefore decrease the precision of dirt measurements. The polydispersity index was significantly correlated to dirt content for rubber of low dirt content (5CV) and highly correlated for the TSR 10A of more extended maturation. The poor correlations between dirt content and polydispersity index for the TSR 10B of prolonged storage, that treated with crosslink inhibitor (5CV), and the 5 WF indicate that, unlike factors that influence molecular chain length, those affecting the molecular mass distribution of natural rubber are unlikely to have a significant effect on the reproducibility of dirt content measurement.

Prolonged maturation and storage of natural rubber is mostly translated as a denaturation or deactivation of naturally occurring antioxidants, and crosslinking and/or branching of rubber chains. Table II(a) shows a significant relationship between PRI and dirt content for samples treated with a stabilizer (5CV and 10CV), highlighting the effect of crosslinking and storage on the ease and reproducibility in the dissolution of rubber.

Table II(b) shows five output eigenvalues corresponding to respective input axes. A rapid decrease in eigenvalues was observed from about 4.04 for PC1, to 1.39 for PC2, and to only 0.05 for PC5, indicating a high degree of correlation in the original axes. The eigenvalues show that most of the total variance was in the first three PCs (96.7%), which were therefore used for classification of dirt content relative to the other parameters studied. The PC1 versus PC2 correlation axes shown in Figure 1 indicate that $\overline{M}_n$, $\overline{M}_w$, and the polydispersity index were very well represented on the principal plan ($R^2 > 0.90$). The macrogel content and PRI were also well represented (0.80 $< R^2 < 0.89$), whereas the dirt content was averagely represented ($R^2 = 0.50$). Apart from $\overline{M}_n$ and macrogel content, all other variables were in the direction opposite to that of dirt content, indicating the decrease of dirt as they increased. Taking
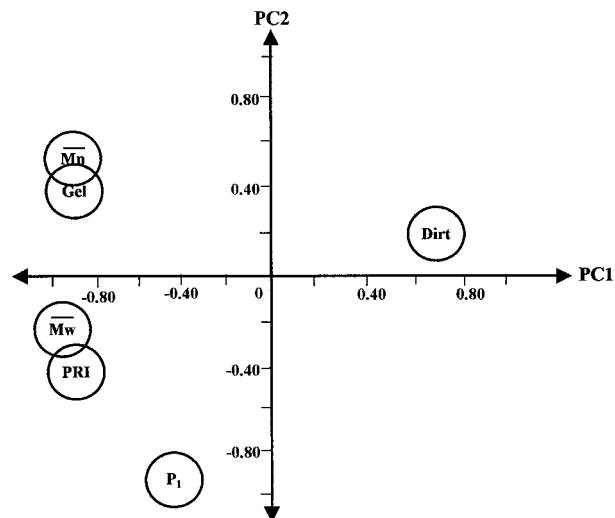
Figure 1 Circle of correlation coefficients. Axis 1 is the horizontal (abscissa) and axis 2 is the ordinate (vertical). P_1 is the polydispersity index.

the absolute values of the eigenvectors [Table II(c)], PC1 was dominated by the weight-average molecular mass variable ($\overline{M}_w$), PC2 and PC4 by $\overline{M}_w/\overline{M}_n$, PC3 by the PRI, and PC5 by $\overline{M}_n$.

CONCLUSIONS

The most adopted procedure for determination of natural rubber dirt content is associated with poor repeatability. Constraints linked to the production of natural rubber persuade producers to adopt practices that modify the chain length of rubber molecules and even increase their dirt content. All measurements leading to the determination of dirt content in natural rubber involve the use of a balance. The precision of dirt measurements was rather insensitive to the relative precision of the analytical balance but varied significantly with the quantity of dirt assayed, whose coefficient of variation decreased as dirt content increased. A model to estimate the associated compound standard error, expressed in terms of the law of propagation of errors, indicated that this error was ± 0.001 mg. Hence, all measurements during the dirt assay (i.e., mass of test portion, mass of empty sieve, and that of sieve containing dirt) must be estimated to at least 3 significant figures. Principal component analyses showed that most spread in dirt analyses were associated with variables that describe molar

mass and its distribution, especially for samples with high dirt content levels.

REFERENCES

1. Loke, K. M. ASTM Spec Tech Publ 1974, 553, 56.
2. ISO 249. Determination of Dirt Content of Raw Natural Rubber; International Organization for Standardization: Geneva, 1987.
3. Watson, A. A. J Rubber Res Inst Malaysia 1969, 22, 104.
4. Sambhi, M. S. J Nat Rubber Res 1988, 3, 107.
5. Bonfils, F.; Laigneau, J. C.; de Livonnière, H.; Sainte-Beuve, J. Kautsch Gummi Kunstst 1999, 52, 32.
6. Nair, S.; Kwong, L.; Mun, L. Standard Malaysian Rubber and Its Control; Rubber Research Institute of Malaysia: Kuala Lumpur, 1972.
7. International Rubber Study Group (IRSG). Audit Report on Natural Rubber Quality: Contaminants; International Rubber Study Group: Wembley, UK, 1991.
8. van Essen, W. J. J Rubber Res Inst Malaya 1950, 12, 262.
9. Bristow, G. M.; Watson, W. F. in Chemistry and Physics of Rubber-like Substances; Bateman, L., Ed.; Maclaren & Sons: London, 1963; p. 417.
10. Wolman, Y. in Chemistry of Functional Groups; Zabicky, J., Ed.; Interscience Publications: New York, 1970; p. 670.
11. Nkouonkam, B.; Ehabe, E. Interlaboratory Crosschecks for Rubber Quality Control in Cameroon; IRAD Ekona Center: Cameroon, 1995.
12. Onywere, S. M.; Opiyo–Akech, N.; Gaciri, S. J.; de Wit, M. J. Afr J Sci Technol Sci Eng Ser 2000, 1, 56.