# Rapid Payne effect test—A novel method for study of strain-softening behavior of rubbers filled with various carbon blacks

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**ABSTRACT:** In the presented article, the strain-softening process in rubber compounds filled with carbon black is investigated. First people to observe this process were Fletcher and Gent in 1954. Later, Payne did an extensive investigation of the process thus the test is generally known as Payne effect test. Based on the measured data, so-called Payne softening can be calculated. The Payne softening is broadly considered as the measure of the strain-softening. In order to investigate strain-softening behavior of a filled rubber compound several strain amplitudes are imposed during a Payne effect test. In this article, a two-point (rapid) version of the test containing only two strain amplitudes is introduced and verified statistically. This test has shown that for the investigation of the filler network disintegration in filled rubbers primarily the large deformations are important, notwithstanding the strain history of a sample. Moreover, the softening characteristic is observed in 30% of the time of the original test. The new method is exemplified for a study of three different rubbers filled with various carbon blacks. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41976.

## INTRODUCTION

Dynamic-mechanical properties of rubbers are crucial for most rubber industry applications. Rubbers are usually filled with high loadings of fillers such as carbon blacks or silica. Incorporation of active fillers into a rubber compound significantly influences the dynamic-mechanical properties of the rubber compound such as strength and stiffness in general applications and rolling resistance, dry, wet, and snow traction, tread wear and other mechanical properties in tire applications specifically. The reinforcement effect of active fillers is considered to be the main reason for obtaining the required functional properties of the particular compound.[1] The reinforcement phenomenon of carbon black has been studied by numerous researchers and many reviews were elaborated, e.g. by Kraus,[2] Leblanc,[3,4] and Donnet and Custodero.[5] Principal physical mechanisms contributing to this phenomenon are assigned as follows: van der Waals forces among carbon black particles; van der Waals forces between carbon black particles and a polymer; chemical cross-links or the chemisorption of a polymer chain on the fillers' surface; and the mechanical interlocking of a polymer chain on to the filler surface.[1–8]

The monitoring of the evolution of dynamic modulus over a certain range of strain amplitudes is of a major importance for most rubber applications, such as the tire tread.[5] Under the increasing strain amplitude, the dynamic properties of unfilled rubbers display only a little change while the dynamic modulus of filled rubbers decreases substantially. Since the changes of modulus of unfilled rubbers are very small, the effect has been fully attributed to the filler related interactions. The nonlinearity in behavior at small strains is assigned to the gradual breakdown of inter-aggregate adhesion, i.e. filler network disintegration and this is generally known as Payne effect.[9,10] The strain-softening behavior at medium to large deformations under quasi-static loading conditions is termed Mullins effect and is attributed to the detachment of rubber macromolecules from the surface of filler particles.[11] Houwink[12] and later Dannenberg[5,13] explained that the detachment is caused by the slippage of rubber macromolecules over the filler surface. Regardless to the magnitude of applied strain amplitude, Wang *et al*.[10] stated that the Payne effect can serve as a measure of filler networking which originates from filler–filler as well as filler–polymer interactions. Generally, Payne effect test is based

**Table I.** Properties of Incorporated Carbon Blacks as Given by the Provider

| Carbon black grade | Iodine adsorption (mg g$^{-1}$) | STSA (m$^2$ g$^{-1}$) | NSA (m$^2$ g$^{-1}$) | OAN (cm$^3$ 100g$^{-1}$) | COAN (cm$^3$ 100g$^{-1}$) | VV[a] (cm$^3$ 100g$^{-1}$) |
|---|---|---|---|---|---|---|
| N121 | 121 | 114 | 122 | 132 | 111 | 62.8 |
| N220 | 121 | 106 | 114 | 114 | 98 | 55.3 |
| N326 | 82 | 77 | 78 | 72 | 68 | 40.2 |
| N339 | 90 | 88 | 91 | 120 | 99 | 55.7 |
| N550 | 43 | 39 | 40 | 121 | 85 | 49.3 |
| N660 | 36 | 34.8 | 35 | 91.4 | 74 | 43 |

[a] VV – void volume parameter characterizing carbon black structure complexity measured at mechanical compression speed 2 MPa s$^{-1}$ and read at 75 MPa.

on the monitoring of dynamic moduli during increasing strain amplitude applied to a rubber sample. There is not one exclusively correct standard version of the test and the magnitude of applied strain amplitudes and frequency is not strictly defined; they are rather empirical and arbitrary. The basic concept is to design a test simulating the conditions within a mixing chamber, i.e. by the right combination of the magnitude of strain amplitudes and frequency to meet the shear rate generated during the mixing process. Payne[9] applied strain amplitudes from very low 0.001% to 10% at frequency 0.1 Hz to his samples. On the other hand, Böhm and Nguyen[14] used amplitudes from 0.2% to 14% at frequency 1 Hz and Wang et al.[10] worked with strain amplitudes from 0.1% up to 100% and frequency 10 Hz. Understanding of such a complex phenomenon as well as development and improvement of suitable test methods remain an open challenge for research. Here we present a rapid (shortened) version of the Payne effect test of our own design exemplified on the study of a set of model carbon black filled rubber compounds. This investigation was performed in order to prove or disapprove the interchangeability of commonly accepted current test methods and our originally developed shortened version and if possible to introduce the rapid test method to the scientific community and demonstrate a viable substitute to the standard version of the Payne effect test.

## EXPERIMENTAL

### Materials
**Carbon Black.** Six different carbon black grades (Orion Engineered Carbons GmbH, Germany) were used. General characteristics of specific surface area (SSA), i.e. iodine number, statistical thickness surface area (STSA), and nitrogen adsorption (NSA) as well as the oil absorption techniques and mechanical compression investigating the complexity of carbon black structure are presented in Table I.

**Rubbers.** Three various polymer matrices, i.e. natural rubber (NR), styrene-butadiene rubber (SBR), and ethylene propylene diene rubber (EPDM) were used. For the characterization of neat polymers a gel permeation chromatography (PL-GPC 220, Agilent Technologies) was used. Tests were carried at temperature 160°C and trichlorobenzene was used as the solution. Observed data are listed in Table II.

### Rubber Compounds
In the experiment 21 varied samples were compounded. The composition and mixing of these compounds were carried out according to the international standard ASTM D3192. However, compounds do not contain a complete vulcanizing system but there is the addition of anti-ageing agents as shown in Table III. Standardized mixing process was executed using the Laboratory mixer (Everplast Machinery, Taiwan).

Overall, 18 filled rubber compounds and three neat matrices, based on a rubber and chemicals without addition of carbon black, were prepared.

### Sample Characterization
Firstly, the dynamic viscosity of three neat matrices containing no carbon black was measured. In the second phase of the experiment, the Standard Payne softening test (SPST) and the shortened Rapid Payne softening test (RPST) were carried out on uncured rubber compounds. All rheological tests were done in triplicate. For the characterization of prepared uncured compounds the rotorless shear rheometer RPA 2000 (Alpha Technologies, Akron, Ohio) was used and all tests were carried out at a constant temperature of 70°C.

Since this article is focused on the properties of uncured samples primarily, reader is referred to the international standard ASTM D6601, which thoroughly describes a test method to study cure and after cure dynamic properties of filled and

**Table II.** Molar Mass Ditribution Characteristics of Used Rubbers

| Matrix | $M_n$ | $M_w$ | $M_z$ | $M_{z+1}$ | $M_p$ | Polydispersity |
|---|---|---|---|---|---|---|
| NR | 132,000 | 329,000 | 2,210,000 | 12,348,000 | 295,000 | 2.5 |
| EPDM | 144,000 | 777,000 | 2,859,000 | 11,964,000 | 413,000 | 5.7 |
| SBR | 70,000 | 532,000 | 2,581,000 | 5,529,000 | 141,000 | 7.6 |

**Table III.** Compounds were Mixed According to ASTM D3192 Recipe

| Ingredients | Rubber compound (phr) |
| --- | --- |
| Rubber matrix | 100 |
| Carbon black | 50[a] |
| 6PPD[b] | 1.5 |
| Ozone wax | 2.5 |
| Stearic acid | 3 |
| ZnO | 5 |

[a] No addition of carbon black was used in the case of a neat matrix sample compounding.
[b] 6PPD denotes N-(1,3-dimethylbutyl)-N'-phenyl-1,4-Benzenediamine, available under the trade name Kumanox 13.

unfilled rubbers, to complete the picture of the behavior of a rubber compound.

**Dynamic Viscosity.** Using the Cox-Merz rule [eq. (1)], which describes the relation between the apparent viscosity $\eta_{app}(\dot{\gamma})$ measured via capillary rheometer and the complex dynamic viscosity $\eta^{*}(\omega)$ measured using an oscillatory rheometer, it was established that the real dynamic viscosity $\eta'$ corresponds to the corrected viscosity measured using the capillary rheometer. Hence, the real part of the dynamic viscosity $\eta'$ was used for the characterization of tested matrices. Samples of matrices were exposed to the frequency sweep from 33.000 to 0.005 Hz at the strain amplitude 7% selected from the area of linear elasticity[15]:

$$\eta_{app}(\dot{\gamma}) = \eta^{*}(\omega) \tag{1}$$

Shear thinning is used for the characterization of non-Newtonian fluids such as rubber compounds. It is described as the decrease in viscosity with increasing shear rate of the sinusoidal strain when the rapidity of the decrease is also important.[15]

**Standard Payne Softening Test**
The Payne softening test (SPST) considered here as a standard one is based on the test designed by Payne.[9] Firstly, a sequence of strain amplitudes in the range from 1% to 140% is imposed to the sample. Then immediately, the strain is relaxed imposing the same strain amplitudes downwards. At this stage, the sample is so-called conditioned and the Payne softening can be measured by the repeated imposition of the defined series of strain amplitudes. The test lasts 15 minutes and the strain frequency is 1.667 Hz.

The dependence of complex dynamic moduli on dynamic shear strain observed for NR-based compounds is illustrated in Figure 1 as an example. This behavior of filled rubber compounds is widely known and published. To name the most significant contributions, work of Houwink,[12] Payne,[9] Mullins,[11] Kraus,[2] Dannenberg,[7] Wang,[10] Donnet,[5] and Leblanc[3,4] should be mentioned.

The Payne softening is calculated as the subtraction of the modulus measured at the highest strain from the initial modulus observed at the small strain amplitude as shown in the following equation:

$$\text{Payne softening} = G_{1\%}^{*} - G_{140\%}^{*} \tag{2}$$

**Rapid Payne Softening Test**
Comparing with the SPST, the shortened, Rapid Payne softening test (RPST) is defined by two strain amplitudes only. Firstly, the sample is conditioned by applying a series of 1, 140 and 1% strain amplitudes following each other. Then, the amplitudes 1 and 140% are imposed to a sample and Payne softening is calculated. This test lasts 4.5 minutes. The calculation of the Payne softening follows the same procedure as described in the above section.

**Repeatability and Two Methods Agreement Assessment Methodology**
Initially, the average $(\bar{x}_i)$ [eq. (3)] and its standard deviation $(SD_i)$ [eq. (4)] were calculated for each sample of $i$-th compound, obtained by either of the two Payne softening test versions in order to present a general overview of experimental data in Figure 3:

$$\bar{x}_i = \frac{\sum_{j=1}^{k} x_{ij}}{k} \tag{3}$$

$$SD_i = \sqrt{\frac{\sum_{j=1}^{k} (x_{ij} - \bar{x}_i)^2}{k-1}} \tag{4}$$

where $j$ indexes specimens within the triplicate measurement and $k$ is the number of specimens measured for each compound (i.e. $k = 3$).

During the experiment, repeatability of measurements of the Payne softening of carbon black containing compounds was evaluated for both standard and rapid (shortened) testing methods. Next, the two methods were compared and tested for agreement. Both investigations were performed according to Bland-Altman's statistical method.[16,17] The repeatability of any
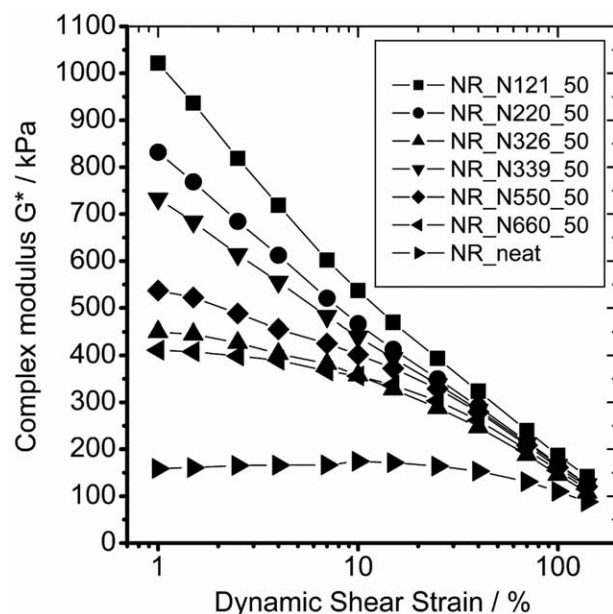
**Figure 1.** Evolution of the complex modulus of NR compounds with increasing dynamic shear strain for SPST.

Payne softening test method is influenced considerably by the rubber compounds' dispersion inhomogeneity in filler because of an imperfect mixing process. The variability between specimens taken from one compound is of significance in rubber research and industry, therefore the estimation of a mean value and its standard deviation obtained from triplicate measurements is usually practiced.[15]

According to Refs. 16–18, the coefficient of repeatability ($CR$) expresses the 95% probability limits for two subsequent readings by the same method to be within $\pm CR$ interval. The narrower the interval the better the repeatability and hence the value of $CR$ can be used for a quantitative comparison between different methods used for measurements of the same quantity. The following equation defines the $CR$ with the use of one-way analysis assuming the normal distribution of the differences between replicates:

$$CR = t \cdot \sqrt{2} \cdot sw \qquad (5)$$

where $t$ is the value of the $t$-criterion for the sample size $n$ (in our case 21 compounds), $sw$ is the within subject standard deviation calculated as the square root from within sample variance ($sw^2$) as in following equation:

$$sw^2 = \frac{\sum_{i=1}^{n} \sum_{j=1}^{k} \left(x_{ij} - \bar{x}_i\right)^2}{DoF \cdot n} \qquad (6)$$

where $DoF$ is the degree of freedom within the sample, i.e. $DoF = k - 1$, where $k$ is the number of replicates (in our case of triplicates $k = 3$), $x_{ij}$ is the Payne softening value measured for $j$-th specimen of $i$-th sample and $\bar{x}_i$ is the average Payne softening value calculated for each data triplet obtained for $i$-th compound.

The agreement between the two methods can be assessed by the use of the Agreement limit ($AL$) which is based on the differences between the values obtained by measurements of the same set of samples by both methods. The mean difference is the measure of the consistent tendency for one method to exceed the other, which is called bias. The variation about this mean is estimated by the standard deviation ($SD$) of the differences. Both the bias and the variability are assumed to be uniform throughout the measurement which is checked graphically in the respective figures. If the differences are normally distributed, 95% are expected to be found within an interval above and below the mean called $\pm AL$ which is actually the definition of the $AL$.[16–18] Following Equation defines the $AL$ with the use of $SD$:

$$AL = t \cdot SD \qquad (7)$$

where $t$ is the value of the $t$-criterion for the sample size $n$ (in our case 21 compounds), $SD$ is the standard deviation of the differences between average SPST and average RPST obtained for each sample, calculated in equation as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(\bar{x}_{iSPST} - \bar{x}_{iRPST}\right)^2}{n-1}} \qquad (8)$$

where the variables have the same meaning as in the equations above, just indexed with SPST or RPST to point towards the used version of the Payne softening test.

It was mentioned above that both the repeatability coefficient and the agreement limit approach to the treatment of the differences are the same, i.e. assume the normal distribution of the foresaid differences. If a relationship is manifest between the difference and magnitude of the measured variable, logarithmic transformation of the data is extremely useful as it can be simply performed prior to data analysis and the obtained $CR$s and $AL$s can be back-transformed and interpreted in direct relation to the original data.[16–18] The repeatability coefficients and limits of agreement obtained from log transformed data as intervals $\pm CR$ log or $\pm AL$ log give backward limits for the ratio of the actual values as the coefficients multiplying the actual value – antilog of $CR$ log or $AL$ log which is higher than 1 for the upper limit and reciprocal value of the antilog of $CR$ log or $AL$ log which is lower than 1 for the lower limit because the antilog of addition and subtractions results into multiplication or division respectively.

Spearman's rank correlation coefficient ($\rho$) was used for evaluation of the statistical dependence of the data. As the independent quantity, any of the physical characteristic of carbon blacks in Table I was chosen ($c_i$) and the related quantity was the value of Payne softening ($\bar{x}_i$). The $\rho$ value was calculated six times for each characteristic, i.e. three sets of samples according to the used type of matrix using values obtained by SPST and RPST. Seven pairs of each of the raw scores $c_i$, $\bar{x}_i$ were converted to ranks $C_i$ and $X_i$, and the Spearman's $\rho$ was calculated according to the following equation:

$$\rho = \frac{\sum_i \left(C_i - \bar{C}_i\right)\left(X_i - \bar{X}_i\right)}{\sqrt{\sum_i \left(C_i - \bar{C}_i\right)^2 \sum_i \left(X_i - \bar{X}_i\right)^2}} \qquad (9)$$

where $i$ ranges from 1 to 7, 8 to 14, or 15 to 21 for the respective type of matrix, and $\bar{C}_i$ and $\bar{X}_i$ are average rank values. To assess the significance of the test, the $P$-values were estimated. Because of small number of observations the $P$-values were taken from critical tables.[19]

## RESULTS AND DISCUSSION

### Dynamic Viscosity of Neat Matrices

The results of dynamic viscosity measurements of the used rubber matrices are presented in Figure 2.

Figure 2(A) shows a log–log plot of the real part dynamic viscosity against shear rate (frequency in radians per second). The most pronounced shear thinning was observed for NR matrix, where the viscosity drop with increasing shear rate is the most rapid among tested matrices. To the contrary, the SBR matrix showed only a gradual decrease of the modulus. This suggests greater macromolecular entanglement of the SBR matrix, since the disturbation of molecular structure occurs at the highest shear rate. The SBR matrix proved the highest viscosity in the mixing area which is generally defined in the range between 10 and 100 rad s$^{-1}$ (e.g. at the shear rate 27.7 rad s$^{-1}$, following viscosities were observed: NR = 666 Pa s$^{-1}$, EPDM = 1090 Pa s$^{-1}$, SBR = 1404 Pa s$^{-1}$). The shear forces generated in the mixer because of the highest viscosity of the SBR matrix are supposed to ensure the highest level of carbon black de-agglomeration and microdispersion (distribution). Besides the
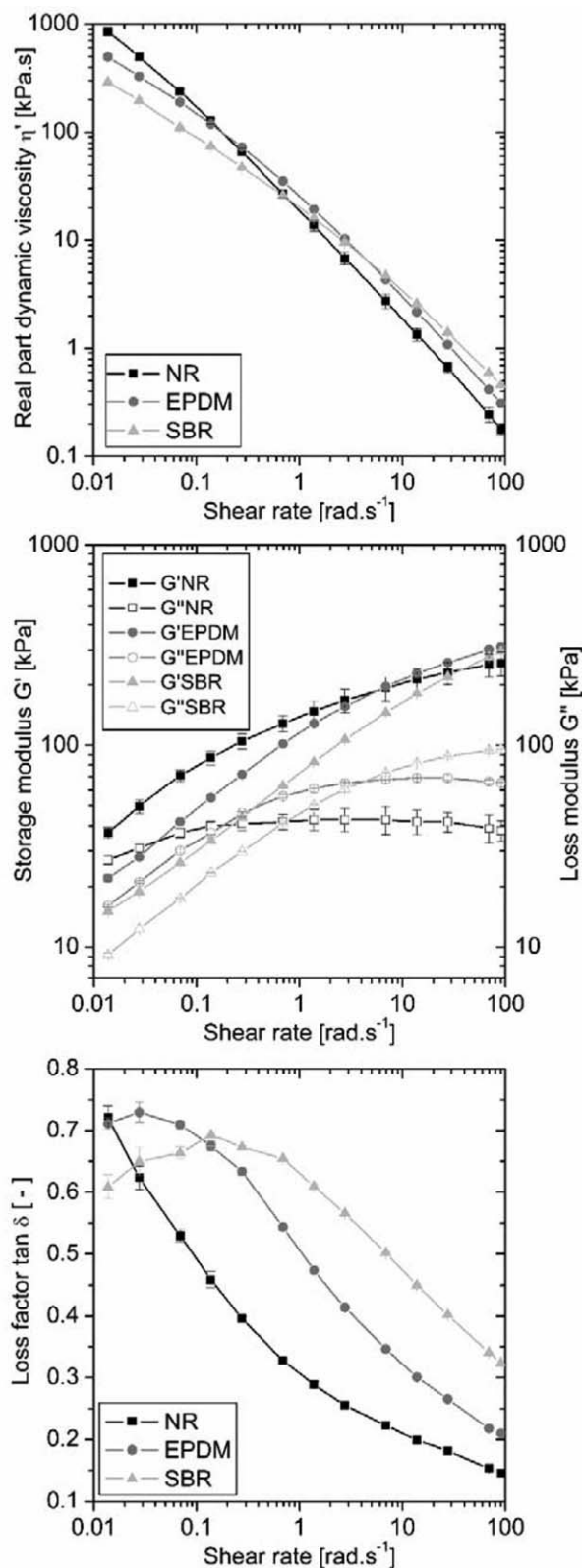
**Figure 2.** Viscosity characteristics. From the upper: (A) Real part of the dynamic viscosity plotted against the shear rate, (B) the dependence of the two parts of dynamic complex modulus on the shear rate, and (C) loss factor tan δ plotted against the shear rate.

highest viscosity the SBR matrix proves the highest loss dynamic modulus ($G''$) in the area of mixing which further contributes to the mixing efficiency because of material flow [see Figure 2(B)].

The development of the ratio between viscous and elastic parts of the dynamic moduli, generally known as the loss factor (tan δ), is shown in Figure 2(C) where tan δ is plotted against shear rate. The significant part of the real dynamic modulus of NR and EPDM matrices ensures a deformation of macromolecules under the shear but not necessarily a flow.

Moreover, Beelen[20] described the shape of the *tan δ* plotted against shear rate may be indicative of the polymer's molecular weight distribution (MWD) and chain branching. Using this approach, the maximum *tan δ* of NR is out of the scale and its shape proves the linear character of macromolecules with a narrow MWD. On the contrary, SBR and EPDM show reduced strain dependence at low strain rates. The maximum *tan δ* for EPDM was observed at shear rate 0.03 rad s$^{-1}$ while the maximum *tan δ* for SBR was observed at shear rate even higher, i.e. 0.2 rad s$^{-1}$. In comparison to the NR a more branched macromolecular structure and wider MWD are suggested for these two materials. For the SBR matrix, the effect of branching and MWD is even more significant which is supported by the GPC analysis summarized in Table II. SBR has the highest polydispersity coefficient which fully corresponds to the conclusion based on the tan δ characteristic. The same trend persists for EPDM and NR, showing moderate and lowest polydispersity coefficients respectively.

**Comparison of the Standard and the Rapid Payne Softening Tests**

Figure 3 presents a general overview of the results obtained for all the samples to compare the two methods for assessing the Payne softening. The average results of the RPST for each
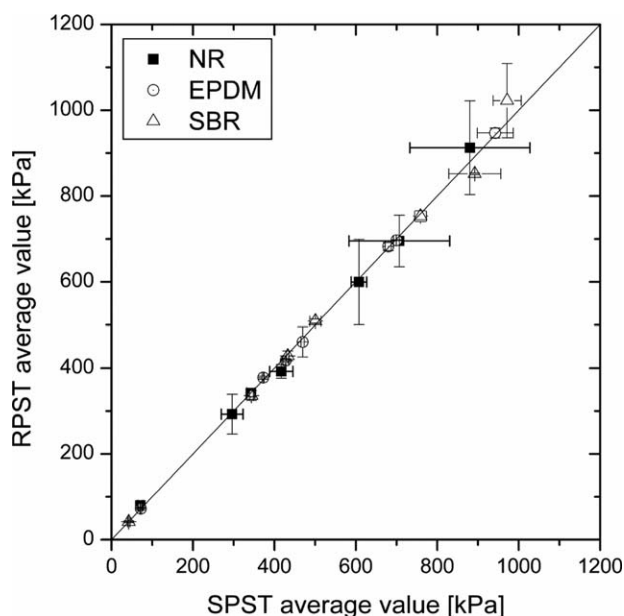


**Figure 3.** Payne softening measured on RPA by SPST and RPST methods with the line of equality.
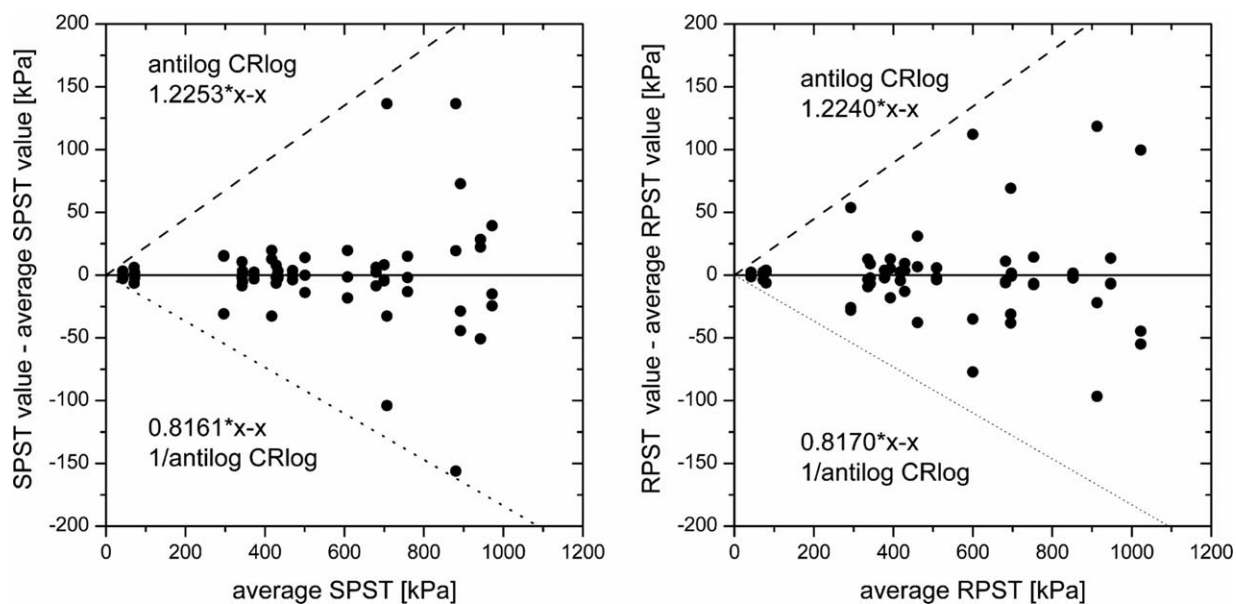
**Figure 4.** The repeatability of the two experimental methods: (A) on the left side is the repeatability of SPST and (B) on the right side the repeatability of RPST.

compound ($\bar{x}_{iRPST}$) were plotted against average results of the SPST ($\bar{x}_{iSPST}$). The error bars show standard deviation of each data triplet ($SD_i$) in $x$ and $y$ axes directions for SPST and RPST method respectively. The graph also shows the line of equality with the slope 1 and there is no apparent bias between the data sets obtained by the two different methods. Next, an increase in variability of differences between actual sample values and their triplet average obtained by either of the two methods can be seen as the magnitude of softening increases. This suggests the type of measurement with constant relative error rather than a measurement with constant error indicating dependence between the differences and magnitude invoking a more sophisticated analysis of repeatability. All these preliminary assessments were studied in more detail and the simultaneous estimation of repeatability and agreement was performed by the analysis of the collected replicated data.

**Repeatability of Both Methods**

The repeatability of each of the two experimental methods can be analyzed with the aid of the graphs in Figure 4, where the differences of replicates' values from mean values are plotted against the average values for SPST [Figure 4(A)] and in Figure 4(B) for RPST respectively. The mean difference between replicates is zero and is plotted by a full line for better clarity. The differences are shown as full circles and it can clearly be seen that in both cases the scatter of the differences increases as the average value of the Payne softening increases. Therefore, a logarithmic transformation of both measurements was performed prior to a further analysis.

The difference versus mean plots for log transformed data is shown in Figure 5 again as full circles for SPST [Figure 5(A)] and in Figure 5(B) for RPST respectively. Two log transformed readings by the same method will be within the interval between lines $\pm CR\ log$ with 95% probability. The within subject standard deviations ($sw_{log}$) are 0.0297 and 0.0296 for SPST and

RPST respectively. It can be seen that the transformation was successful in producing data differences unrelated to the average. Back-transformed limits for the ratio of the actual measurement were obtained as antilog of $CR$ for the upper limit and (antilog of $CR$)$^{-1}$ for the lower limit and they are plotted by dash and dot lines respectively in both graphs in Figure 5. A perfect agreement of the back transformed limits with scattered data resembling an open fan in shape is obvious. One has to keep in mind different scales for $y$ and $x$ axes during intuitive interpretation of the graphs. Repeatability of the two methods can be compared by the use of obtained antilog $CR$s and the values of 1.225 and 0.816 for SPST and 1.224 and 0.817 for RPST can be considered as identical. One source of the fully comparable repeatability in this case is that both methods employ the same apparatus and, indeed, there is no reason for manifestation of any difference resulting from the used machine. The second and more important source of the observed perfect match of repeatability is that the shortened test version is physically relevant as the standard version and that it is still sufficient from the point of the collected data quality although it is three times faster than the standard one (both at the frequency 1.667 Hz).

**Two Methods Agreement Analysis**

The repeatability investigated in the above section dealt with two single readings by each method. To suppress the variability of the results for each subject, an average of the replicate measurements was calculated. Three measurements on samples from each tested compound were introduced already by Payne in his pioneering version of the softening effect test. The same number of replicas was also used in our rapid version. Averaging removes some of the measurement errors and improves the precision of obtained results. We assume that although single measurements can be performed, the customary use of average of the three measurements together with the identical
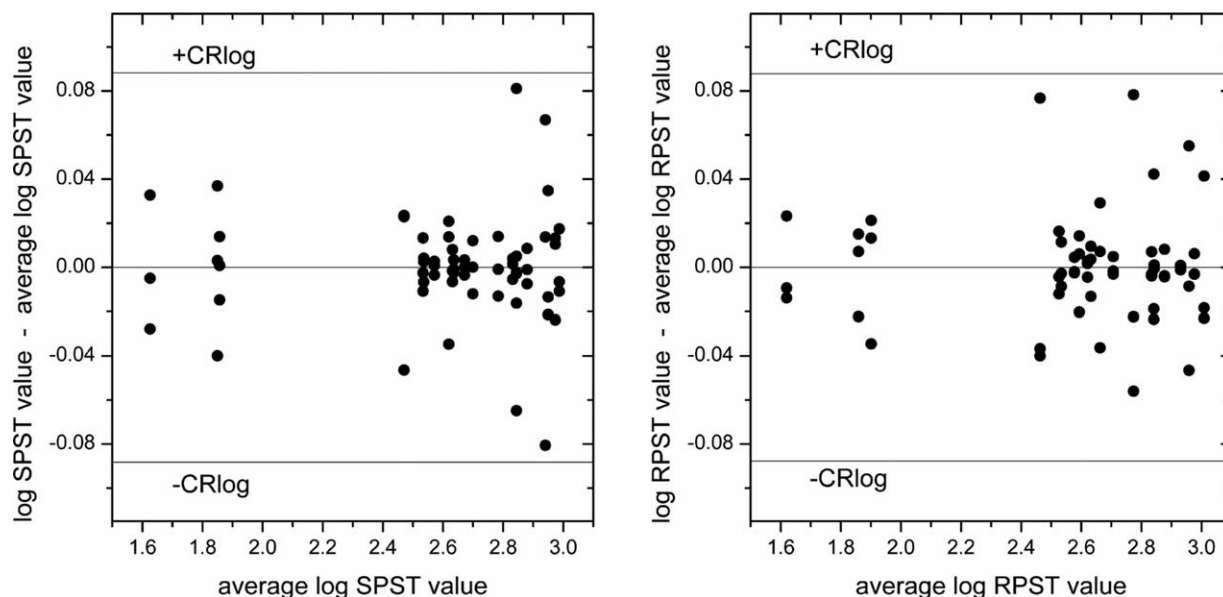
**Figure 5.** The difference versus mean plots for log transformed data of both methods bounded by the lines of coefficient of repeatability; SPST on the left side and RPST on the right side.

repeatability of the two methods justifies their comparing on the base of average results obtained on triplicates only. Figure 6(A) shows the Bland-Altman plot with 95% limits of agreement based on the assumption that the differences are normally distributed.

The $t$ value is 2.1 for sample size of 21 compounds and the standard deviation is 19 kPa, therefore the width of the interval is $\pm AL = 2.1 \times 19$, i.e. 38. The mean of differences 0.7 kPa is negligible with respect to the width of the interval and no bias between the data obtained by the two methods is manifested. There is no tendency of the differences to one or other direction in dependence on the mean value of the average SPST and

average RPST. Therefore, the agreement between the two methods can be considered as very good if the triplicate measurement is used and the average value is calculated in both tests for each examined compound.

Although the differences looked uniform at the first sight, a slight increase in their scatter with increased measured value can be observed. This becomes more visible after plotting the agreement limit bands in Figure 6(A). It seems that averaging cannot fully suppress the deterioration of repeatability with increasing value of softening. Therefore, the data were log transformed and back transformed similarly as in the repeatability study. The log transformation safely removed the slight
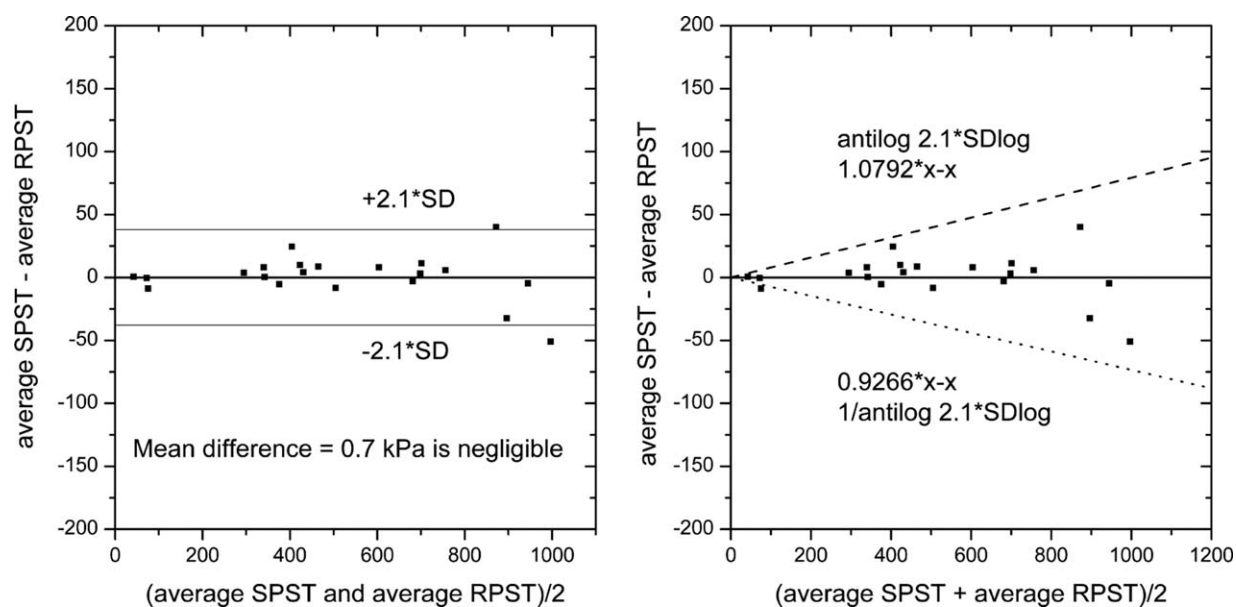


**Figure 6.** The Bland-Altman plot showing differences between the two methods of ±38 kPa.
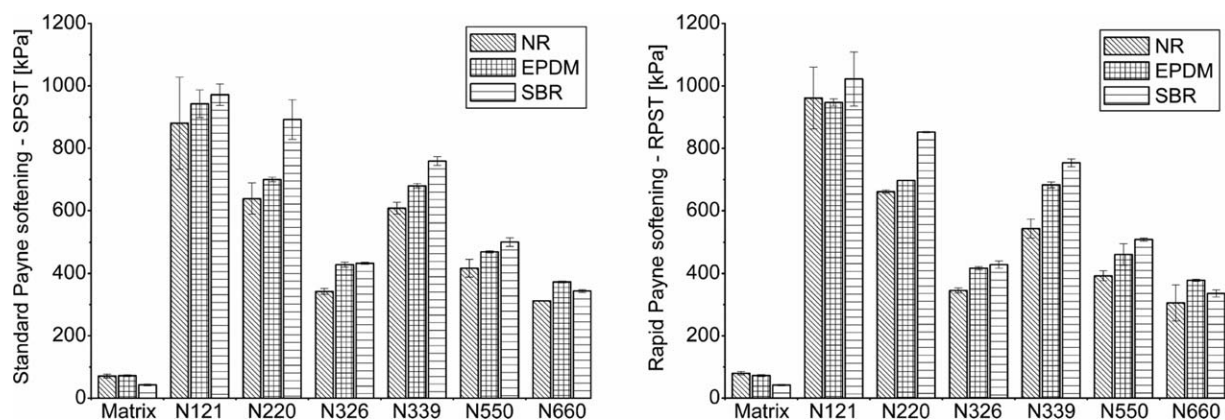
**Figure 7.** Payne softening characteristics observed by the two experimental methods: (A) SPST on the left and (B) RPST on the right side.

relationship between the variability of the differences and the average value of the Payne softening measured by the two methods. Quite narrow relative limits 1.079 and 0.927 were obtained as antilog of $2.1^*SD$ for the upper limit and (antilog of $2.1^*SD)^{-1}$ for the lower limit after back transformation and they are plotted by dash and dot lines respectively in the graph in Figure 6(B). This method seems to be more appropriate to the observed increasing variability of results with an increase in the measured value for each test method which is obviously manifested in their comparison. With regard to this, the agreement between the two methods can be assessed as excellent and the 95% limit of the agreement is more reliable even for small measured values of the Payne softening where the former approach overestimates largely the uncertainty. It can be seen, that the agreement of the two methods is excellent as the measurements by the two methods agreed very closely on average with negligible bias. Another advantage of this data treatment as opposed to the one using raw data without transformation is that it produces data which can be compared to the CRs obtained in the repeatability study where the transformation was perceived as more urgent. The width of the AL suggests how good the agreement between the methods for individuals is. The AL can be compared with CRs. It is more than 2.5 narrower limits than the repeatability for two single readings by each of the methods which is because of their reinforcing by triplication and because of presence of no other factor lowering the agreement between methods.

To summarize, both methods can be used for the Payne softening investigation giving statistically the same results in terms of both, the value and its variability (standard deviation). Furthermore, both methods are fully comparable, have the same level of precision and they can be used interchangeably.

**Results and Discussion of Payne Softening Tests**
Based on the previous section, the discussion of observed Payne softening phenomena with respect to the carbon black grades and used matrix type persists for the results obtained by both methods without any loss of relevance. Considering the fact that results are measured using a series of strain amplitudes in the case of the standard test and using two-point softening in the rapid test, these results are rather surprising and show on

the fragility of the filler network formed by carbon black in rubber melts. Graphical representation of the Payne softening values obtained for all uncured compounds by the SPST and RPST are shown in Figure 7(A,B) respectively. Even here, the interchangeability of the two test methods can be followed. Note that in the case of neat rubber matrices, the measure of rubber mastication is shown rather than the softening.

The influence of the two key parameters on the Payne softening can be evaluated in the framework of the experiment, i.e. influences of a rubber macromolecular structure and carbon black grades, respectively. Referring to the appearance of the bar graphs in Figure 7, there are two effects differing in magnitude and significance. First, the Payne softening value strongly depends on the used carbon black. The differences between compounds with the same matrix and different fillers are much larger than standard deviations of the compared values. Next, there is an observable, relatively weak and less clear but still pronounced dependence of the Payne softening values on the nature of the polymer matrices. The Payne softening values increase with the change of the matrix from NR through EPDM to SBR for fillers N220, N339, and N550, while such effect is unconvincing for N121 as it is buried in the scatter of measured values. On the other hand, neat matrix compounds have nearly opposite behavior. The materials with N326 and N660 might show possibly transient behavior between these two trends. It is evident, that the matrix does not contribute linearly to the observed effect. Therefore, the multiple regression analysis is not suitable for the analysis, or if used, it would show very high error for the parameter bound with the matrix properties. However, the low number of used matrices and large standard deviations limits the possibility of evaluation of these effects by any other quantitative method.

Considering the strong influence of carbon black grade, the highest Payne softening was observed for compounds containing N121 grade. N121 has the highest structure as presented by oil absorption techniques and the highest SSA also. Observed values of the Payne softening were tested with the use of Spearman's rank correlation coefficient where the Payne softening values were correlated with characteristics of carbon blacks indicated in Table I. The use of this relatively robust and

nonparametric test is based on the assumption, that the Payne softening value measured for each compound depends monotonously on the properties of the used carbon black filler but the dependence function is not known (most likely nonlinear). The level of correlation between different parameters and the Payne softening value can be compared simply by comparison of the coefficient's value. The relationship is better as its value approaches unity. The test was always performed for all compounds and strong correlation of the Payne softening to all carbon black type characteristics was found but there was no difference between the three matrices observed. Furthermore no difference between results obtained from SPST or RPST was obtained. The physical characteristics can be divided into three groups ranked according to the $\rho$ value. All three SSA characteristics employed as independent variables gave the same $\rho$ value about 0.96 with $P$-value in the range of $0.01 > P > 0.001$ indicating almost perfect correlation. The next characteristic was COAN with $\rho = 0.93$ and $P$-value in the range of $0.01 > P > 0.001$, which is almost as good as the SSA. The worst score was found for OAN with $\rho = 0.82$ with $P$-value in the range of $0.025 > P > 0.01$.

The excellent correlation of the Payne softening with SSA characteristics of carbon blacks can be explained as the manifestation of the microphysical reinforcing effect related to the specific surface size well known for nanocomposites. The larger the surface area available for polymer–filler interactions, the greater is the reinforcement effect. This fact was proved for example in the work of Wang[10] where the increasing amount of a specific carbon black grade resulted in the enhanced reinforcement effect of a rubber compound. Kraus[2] carried out experiments on bound rubber, investigating interactions between filler and polymer and came out with similar conclusions. Detailed discussion of reinforcement by carbon black can be found in the Refs. 4,5,21. The accessibility of the carbon black surface to polymer matrix macromolecules is dependent on the carbon black de-agglomeration achieved during mixing which is theoretically best characterized by COAN. This parameter, by the ASTM D3493-13 definition, describes carbon black structure obtained after the compression at 24,000 psi four times (24M4) simulating the de--agglomeration during mixing. On the other hand, OAN characteristic which describes carbon black structure before (without) mixing, shows lower correlation with the in-rubber property.

The shape of tan $\delta$ curves revealed that the polymer matrices differ in their molecular weight distribution and branching. GPC supported this fact by results of the polydispersity parameter. The highest level of polydispersity was found for SBR = 7.6 and the lowest for NR = 2.5 while the moderate value belongs to EPDM = 5.7. The molar mass distribution as the leading microphysical parameter ($M_n$, $M_w$, etc. and polydispersity) correlates well with the results of the dynamic viscosity test. The higher the polymer viscosity, the more power is required to mix the compound and higher shear forces are generated during mixing process. For neat matrices it is obvious that the largest Payne softening is observed for the material with the lowest viscosity, ceteris paribus. Payne effect was measured at the frequency 1.667 Hz which corresponds to the shear rate of

approximately 4.5 rad s$^{-1}$. In Figure 2(B), the moduli of NR and SBR are both higher in this shear rate area than the modulus of SBR which predominates towards the higher shear rates. From the dependence of tan $\delta$ in Figure 2(C), it can be observed that the NR shows the highest storage modulus at the given frequency which leads to the most enhanced Payne softening. Whilst for the SBR showing the lowest storage modulus the smallest Payne softening was observed. The lower the tan $\delta$ at a given frequency, the higher is the elastic part of the dynamic modulus. Tan $\delta$ equal to zero would mean the material is completely elastic.[15]

Then, the situation changes in case of filled compounds. Shear forces directly affect the quality of carbon black incorporation into the compound. Gerspacher et al.[22] stated that during the carbon black incorporation, agglomerates are de-agglomerated to aggregates by shear forces and the subsequent mixing ensures the distribution of liberated aggregates through the polymer matrix. It also means that the compound with the most viscous matrix should have the best dispersion and distribution of carbon blacks and should show the highest reinforcing effect. This effect can be expected to be stronger for carbon blacks with higher structure rather than for those of lower structure. Mutual action of these two material predispositions (high matrix viscosity and high filler structure) results in a complimentary effect. On the other hand, it means that the same compound with the highest reinforcement should be the most sensitive to the strain applied during the Payne softening test as it has the strongest tendency to disrupt any network of the carbon blacks already developed within the material volume. The incorporation of carbon black in SBR should be the most efficient according to viscosity results and, indeed, the Payne softening was the most pronounced for SBR matched with high structure carbon blacks in our material selection. The highest reinforcing effect was measured for the compound constituted by the SBR matrix and N121 carbon black grade filler.

## CONCLUSIONS

In this article the Rapid Payne softening test (RPST) was introduced and successfully established. It was shown that this shortened approach can replace the Standard Payne softening test (SPST). It was found that the rapid test obtains the same measure of the filler network disintegration as the standard version of the softening test. Furthermore, since the same results were observed using only one large strain amplitude instead of a series of strain amplitudes, the time of the rapid test is shortened to less than 30% of the standard test. The interchangeability of the test methods was demonstrated on 21 different uncured rubber compounds. Repeatability of the two methods was tested using triplicate repeats and was found to be identical. Also, there is no bias between the two methods, so they give principally the same values on average and, the agreement limits are quite narrow because of the use of averages obtained from the triplicates. However, the full acceptation of the yet developed RPST by the scientific and professional community will require more extensive studies to confirm its reproducibility and applicability to the large spectrum of possible carbon black-rubber matrix combinations.

Furthermore, based on the results of strain-softening tests, it can be concluded that compounds containing carbon blacks with high SSA and high structure, so-called hard carbon blacks, showed high Payne softening. On the contrary, compounds containing soft carbon blacks (with low SSA, low structure) showed systematically lower Payne softening. The correlation between SSA or COAN and Payne softening was found to be highly significant. With respect to that, the influence of the rubber matrix seems to be a less significant. However, a synergy between the structure of carbon black and matrix microphysical parameters through their mutual interaction during mixing was demonstrated.

## ACKNOWLEDGMENTS

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