

An Extraction Kinetics Method to Study the Morphology of Carbon Black Filled Rubber Compounds

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ABSTRACT: A method was developed to investigate the kinetics of extraction of the unbound fraction of rubber compounds and to assess the macromolecular characteristics of extracted species. The results obtained show that the extraction kinetics can be modeled with a simple law. For full compounds a correction for nonrubber extractable ingredients must be applied; but it is demonstrated that compounding ingredients do not affect the bound rubber level of a given formulation, providing that the optimum mixing energy level has been achieved during the preparation procedure and that the compound maturation processes have been completed. Macromolecular characteristics of labile rubber species were analyzed versus extraction; and a simple equation, implicitly referring to a Fickian process, is offered to model the observed effects. It is so demonstrated that the polydispersity of labile species varies during the extraction process and that the largest molecular weight fractions are involved in the rubber–filler interaction, as predicted by theory. Experiments on model compounds allow the effect of both the mixing energy and storage maturation to be studied in detail, and a model that takes both effects into account was developed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 959–970, 1997

INTRODUCTION

It was recently demonstrated that the variation of the rheological properties of freshly mixed rubber compounds upon storage is associated with an evolution of the bound rubber content.¹ This indicates that rubber–filler interactions initiated during the mixing operations still evolve in the material at rest. Experimentally it was found that both the bound rubber and the rheological properties vary during the storage period at room temperature according to a simple law in square root of time until a stabilized situation is reached; this suggests that diffusion processes might be involved but the overall physics of these effects is far from being understood.

Bound rubber is an old concept in rubber science,² which is known to be one of the major factors in carbon black reinforcement. [By definition bound rubber is the fraction of polymer that cannot be extracted from an uncured (carbon black) filled compound by a good solvent of the gum elastomer. Above a sufficient filler level (in the 15–20% weight range), a highly swollen rubber–filler gel remains after all the free rubber has been extracted by the solvent.] For a given elastomer, the amount of bound rubber at fixed carbon black content depends, among other factors, on the surface area, structure (or morphology), and surface activity of the filler. Mere thermodynamic considerations suggest that statistically any type of bonding of polymer to a filler particle will preferentially involve the largest molecules. Such a view was initially developed by Meissner in his 1974 theory on bound rubber³ by considering the adsorption of structural units of a polymer on reactive sites

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assumed to exist on the surface of the filler particles. Without any hypothesis regarding the nature of the reactive sites, this theory, further developed in more recent publications,^{4,5} predicts the preferential adsorption of large molecules and the dependence of bound rubber on the molecular weight of the polymer, as indeed was experimentally observed. One notes in recent years a renewed interest in bound rubber, particularly concerning what its contribution to reinforcement is.^{6,7}

Our interest in bound rubber is its relationship with the rheological properties of uncured compounds and the support it gives to a morphological model proposed for carbon black filled rubber materials.⁸ However, the true nature of rubber–filler interactions is not yet elucidated and consequently the very reasons for the coupled evolution of bound rubber and rheological properties of uncured rubber compounds remain unclear, which opens the way to alternative explanations for the observed effect of storage time on properties of unvulcanized rubber stocks.⁹

We report hereafter the development of a method to investigate the *kinetics of extraction* of the unbound fraction of rubber compounds and to assess the macromolecular characteristics of extracted species. Moreover, models are described that allow the treatment of experimental data on a clear physical background, in order to consider not only the effect of storage time, but also the effect of the mixing energy level achieved during material preparation.

EXPERIMENTAL

Test Materials

High *cis*-1,4 polybutadiene (Neocis BR 40 from EniChem S.p.a, Italy, 98% *cis*-1,4 content) com-

pounds as described in Table I were prepared in an internal (Banbury) mixer according to an upside down procedure (first the black and other compounding ingredients, then the rubber). A standard formulation and three model compounds (only rubber and black) were prepared, the latter differing by the mixing energy level achieved. After dump, the compounds were sheeted off on a roll mill and stored at room temperature under a plastic cover. To achieve the complete development of rubber–filler interactions, the full compound (mix 1) was stored for 2 months before performing the extraction experiments described below. After 13 days storage, portions of the three binary compounds (mixes 2A, 2B, and 2C) were remilled 8 min. At various intervals during 2 months, samples of the binary compounds (remilled or not) were taken and tested as described below.

The macromolecular characteristics of the gum rubber were measured by gel permeation chromatography (0.05% THF solution; 40°C) using different columns and detection techniques. As shown in Table II, different results were obtained, but the mean values (i.e., $M_n = 142,000 \text{ g mol}^{-1}$ and $M_w = 493,000 \text{ g mol}^{-1}$) are within the range claimed by the supplier (respectively, 132,000 and 400,000 g mol^{-1}).

Extraction Kinetics Experiments

A special glass device was constructed to perform the swelling of test samples in a fixed quantity of the appropriate solvent (toluene) for well-defined periods (Fig. 1). Essentially, the sample was weighed in a steel wire basket and disposed in the glass vessel with a polytetrafluoroethylene

Table I Formulations

	Mix NR			
	1	2A	2B	2C
Neocis BR 40 ^a	100	100	100	100
N330 black	50	50	50	50
Zinc oxide	5	—	—	—
Stearic acid	2	—	—	—
Dutrex R729 ^b	5	—	—	—
Anox HB antioxidant ^c	2	—	—	—
Mix. energy (MJ/m ³)	1950	460	1480	2420

^a 98% *cis*-(1,4-polybutadiene; ML (1 + 4) 100°C = 43, EniChem Elastomeri.

^b Aromatic oil, Shell Chemical Co.

^c Polymerized trimethyldihydroquinolin, EniChem Synthesis.

Table II GPC Data on Gum *cis*-1,4 Polybutadiene

GPC Instrument			M_n (g mol ⁻¹)	M_w (g mol ⁻¹)
Type	Detector	Columns (No., Type)		
Waters R410	Refractometer	2; linear ultrastryagel	155,000	624,000
Waters R410	Refractometer	5; microstryagel; 10 ⁵ , 10 ⁴ , 10 ³ , 500, 100 Å	162,000	497,000
Waters 150 CV	Viscometer	4; linear ultrastryagel	109,000	350,000

valve at the bottom. A known quantity of solvent was poured in the vessel and left in contact with the rubber sample; after various periods of time, the solvent (which contained some extracted species) was collected through the valve and another portion of pure solvent was poured in the vessel for a further extraction period. The procedure was repeated until complete extraction was achieved (up to 1 week). The extracts were collected and evaporated under vacuum to assess the extracted quantity of rubber; from the dry residue a 0.05% weight solution in THF was prepared and injected in a Waters R410 GPC with either 2 ultrastryagel linear columns or 5 microstryagel columns (porosity: 10⁵, 10⁴, 10³, 500, and 10² Å) to determine the macromolecular characteristics of the extracted species.

Rheological Measurements

Mooney tests were performed at 100°C according to a standard procedure (ASTM D1646) for rub-

ber viscosity and vulcanization characteristics (Mooney viscometer) on samples of binary compounds taken after various storage periods.

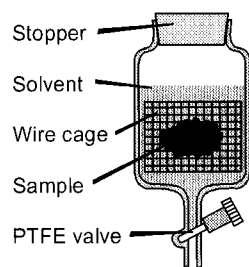
RESULTS

Extraction Kinetics Experiments on Full Compound (Mix 1)

To assess various aspects of the method, extraction kinetics experiments were repeated with samples of either 0.25 or 2 g and following different sequences of extraction periods. The quantities of extracted material after each solvent contact period (i.e., at times t_{i+1} , as sketched in Fig. 1) were cumulated to provide the gross experimental data of Table III.

At any extraction time, the extracted material obviously consists of the extracted rubber plus all the soluble compounding ingredients. Therefore,

Glass device for extraction kinetics



Experimental approach

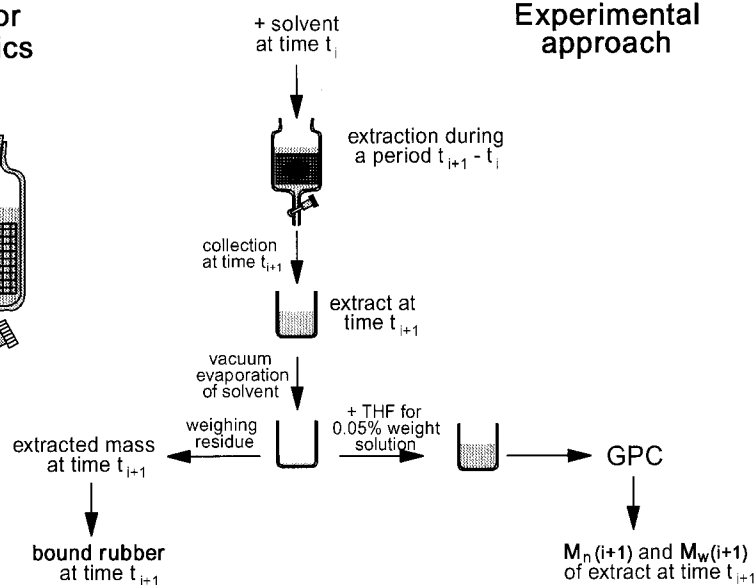


Figure 1 Glass device for extraction kinetics and schematic description of the experimental procedure.

Table III Extraction Kinetics Data on Full *cis*-1,4 Polybutadiene Compound

Extraction Duration (h)	Cumulated Extract (g) Sample; Sample Weight					
	1-1; 0.2505 g	1-2; 0.2502 g	1-3; 2.0052 g	1-4; 2.0067 g	1-5; 2.0053 g	1-6; 2.0082 g
1	0.0123	0.0123	0.1268	0.1315	—	—
2	0.0231	0.0226	0.2303	0.2410	—	—
3	0.0320	0.0322	0.3131	0.3312	—	—
4	0.0405	0.0407	0.3844	0.4008	—	—
5	0.0455	0.0449	—	—	—	—
5.5	—	—	0.4618	0.4754	—	—
6	0.0508	0.0499	—	—	—	—
7	0.0555	0.0542	0.5305	0.5453	—	—
8	0.0605	0.0595	—	—	—	—
8.5	—	—	0.5883	0.6052	—	—
15	0.0877	0.0861	—	—	0.7102	0.7041
17	0.0936	0.0924	—	—	—	—
19	0.0985	0.0968	—	—	0.8106	0.8063
24	0.1031	0.1017	0.8540	0.8690	0.8759	0.8695
27.5	—	—	0.8857	0.9035	—	—
32.5	—	—	0.9088	0.9296	—	—
39.5	—	—	—	—	0.9472	0.9385
48	0.1172	0.1156	0.9425	0.9612	0.9680	0.9599
55	0.1214	0.1202	—	—	—	—
56.5	—	—	0.9510	0.9684	—	—
120	0.1290	0.1291	0.9718	0.9869	0.9913	0.9865
128	0.1301	0.1301	—	—	—	—
168	—	—	0.9776	0.9942	0.9967	0.9928

Note: Data not corrected for nonrubber extractables (stearic acid and oil).

a correction must be introduced on the measured extracted quantities. Thermogravimetric analysis on compound samples before and after solvent extraction showed that the nonrubber extractable ingredients are the oil and the stearic acid; obviously the carbon black and the ZnO but also the antidegradant remain in the compound. At the end of the process (i.e., when a plateau in the cumulated extracted quantities was reached) essentially all the oil and the stearic acid had thus been extracted. By considering that at any time t_i , these ingredients are extracted proportionally to the labile rubber, the corrected amount of unbound rubber is obtained from

$$[X_C]_i = [X_A]_i \left(1 - \frac{W_s(P_{Oil} + P_{StA})}{P_{Cpd}[X_A]_f} \right) \quad (1)$$

where W_s is the sample weight (g); P_{Oil} and P_{StA} are, respectively, the oil and stearic acid contents (phr); P_{Cpd} is the overall formulation parts (phr); $[X_C]$ and $[X_A]$ are the corrected and apparent ex-

tracted rubber (g); subscript i corresponds to time t_i ; and subscript f corresponds to the final time of the extraction experiment. For the compound considered, P_{Oil} , P_{StA} , and P_{Cpd} are 5, 2, and 165.25, respectively.

After this correction is made, the results are expressed in percent extracted rubber versus the initial gum rubber content in the compound. Figure 2 shows the extraction kinetics curve obtained when plotting the percent extracted rubber versus the process duration. As can be seen the experimental reproducibility is excellent and a plateau is reached after around 100 h, when practically all the unbound rubber has been removed from the compound.

Modeling Extraction Kinetics

In order to fit the experimental data with a model having some physical sense, we consider that, when an uncured carbon black filled compound is treated with a good solvent of the rubber, the solu-

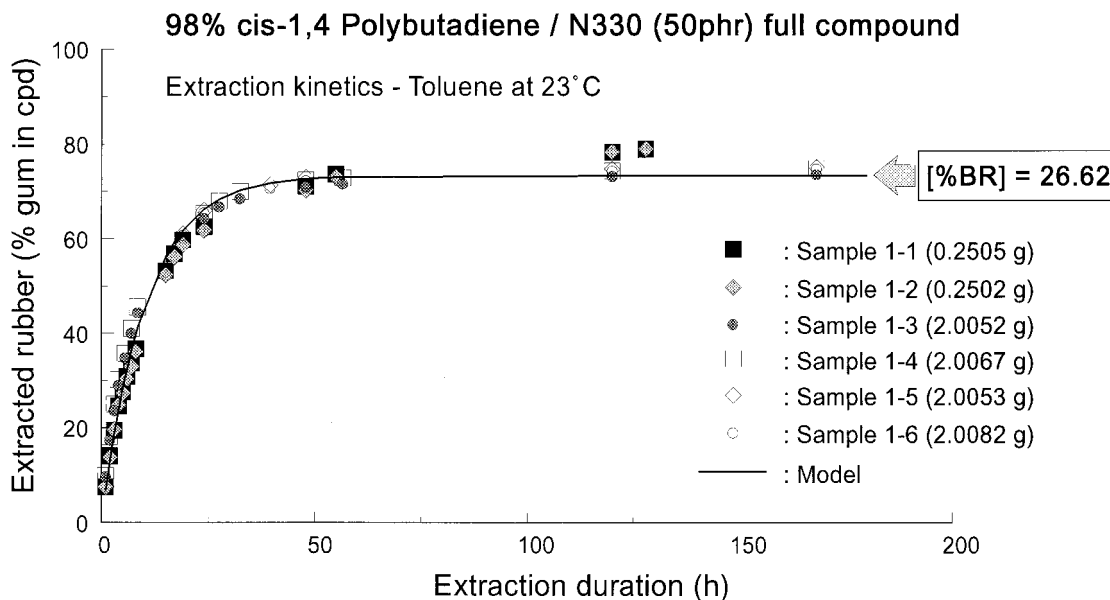


Figure 2 Extraction kinetics: experimental results on a full polybutadiene compound.

ble polymer is removed at a rate that, in a first approximation, is assumed to be proportional to the amount of extractable rubber remaining in the compound; that is,

$$\frac{d[\% \text{extracted}]}{dt} \propto [\% \text{extractable}]$$

or

$$\frac{d[\% \text{extracted}]}{dt} = b[\% \text{extractable}],$$

where $[\% \text{extracted}]$ and $[\% \text{extractable}]$ are, respectively, the quantities of extracted and extractable rubber in percent of the gum rubber content in the compound, and b is a (rate) constant. At any time during the solvent extraction process, however, the following equality holds (note that in this reasoning, the extraction process is assumed to occur in an isothermal condition):

$$[\% \text{extracted}]_t = 100 - [\% \text{BR}] - [\% \text{extractable}]_t,$$

where $[\% \text{BR}]$ is the quantity of bound rubber in percent of the initial gum rubber content of the compound. Obviously $[\% \text{BR}]$ is independent of the extraction duration, but depends on the rubber nature, the type and level of carbon black, the compound preparation procedure, and in general on all the factors that might affect the elastomer–

filler interaction. For a given formulation the term $(100 - [\% \text{BR}])$ is thus a constant that corresponds to the amount of extracted rubber for an infinite time, or at least an extraction duration sufficient for the amount of extractable rubber remaining in the swollen compound to be practically equal to zero; i.e.,

$$(100 - [\% \text{BR}]) = [\% \text{extracted}]_{t=\infty}.$$

It follows that

$$\frac{d[\% \text{extracted}]}{dt} = b([\% \text{extracted}]_{t=\infty} - [\% \text{extracted}]),$$

which through rearrangement and integration yields

$$[\% \text{extracted}]_t = [\% \text{extracted}]_{t=\infty}(1 - e^{-bt}) = (100 - [\% \text{BR}]) (1 - e^{-bt}). \quad (2)$$

By nonlinear regression analysis, this model was fit to the data (see Fig. 2) and yielded 26.62 for $[\% \text{BR}]$ and 0.097 for the rate constant b .

Macromolecular Characteristics of Extracted Species

The labile rubber species collected during the extraction kinetics experiments described above

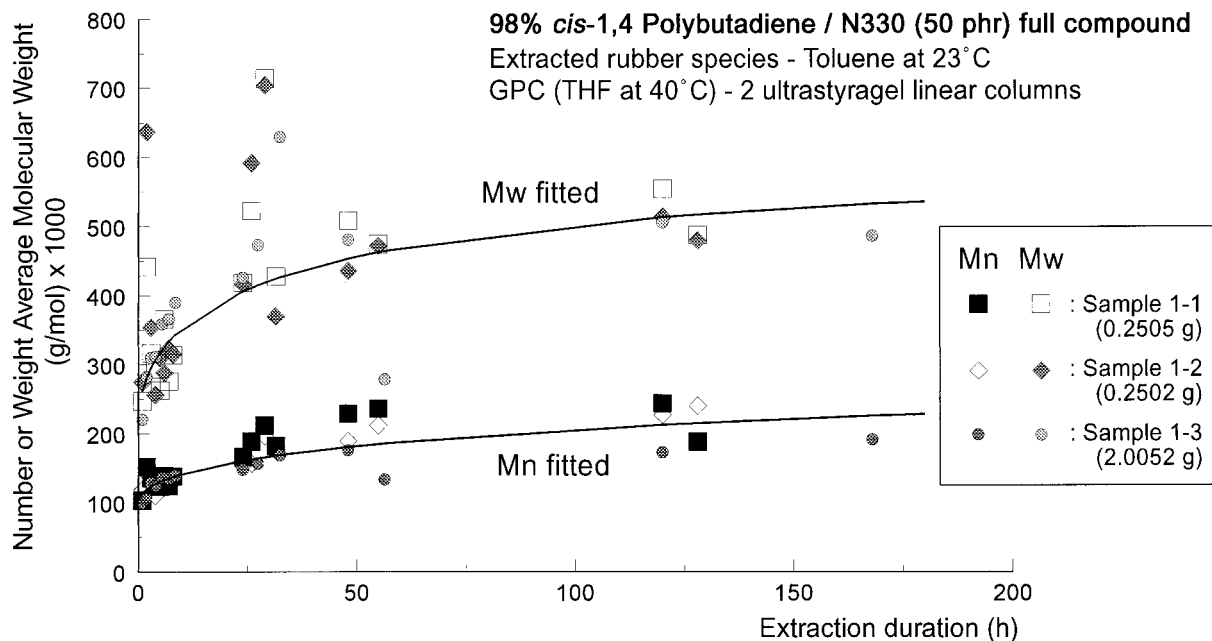


Figure 3 Variation of macromolecular characteristics of extracted rubber species during the solvent extraction process: full polybutadiene compound.

were analyzed for macromolecular weight by GPC. Figure 3 shows the results obtained in terms of number and weight average molecular weights. Despite a certain experimental scatter due to either sample handling or the GPC technique or a combination of both, a clear trend can be seen. Initially shorter chains were extracted (M_n and M_w around 100,000 and 250,000, respectively), then the larger ones. At the end of the process, the extracted species had larger sizes than the average molecular weights of the gum rubber (respectively, 220,000 vs. 142,000 for M_n , and 540,000 vs. 493,000 for M_w). This is a clear indication that the bound rubber essentially consisted of the largest molecular weight fractions.

When the rubber compound was let in contact with the solvent, it started swelling and the process was a complex combination of volume expansion as the solvent permeated the compound and of labile rubber extraction (plus obviously the nonrubber extractable ingredients). With an implicit reference to a Fickian process and with respect to experimental data, we used the following model to fit the data, i.e.,

$$M_t = M_0 + M_\infty[1 - e^{(-a\sqrt{t})}] \quad (3)$$

where M_t is the molecular weight (g mol^{-1} , either M_n or M_w) of the species extracted at time t (h),

M_0 is the size of the first extracted species (g mol^{-1}), M_∞ is the largest chain extracted at the end of the process (g mol^{-1}), and a is the fitting parameter ($\text{h}^{-0.5}$). The curves drawn in Figure 3 were obtained by nonlinear regression analysis that yielded the following parameter for the number average molecular weight,

$$M_{n_0} = 100,267 \text{ g mol}^{-1},$$

$$M_{n_\infty} = 215,790 \text{ g mol}^{-1}, \quad a = 0.067 \text{ h}^{-0.5};$$

and for the weight average molecular weight,

$$M_{w_0} = 208,789 \text{ g mol}^{-1},$$

$$M_{w_\infty} = 376,333 \text{ g mol}^{-1}, \quad a = 0.152 \text{ h}^{-0.5}.$$

One notes that the fitting constant a is 2 times larger for M_w than for M_n . It follows that the polydispersity of the extracted species evolves during the process. By combining the above parameters, a curve describing this evolution was easily drawn (Fig. 4) whose typical shape further supports the view that only the longest rubber chains were involved in the soft bound rubber–filler network. In the early times of the solvent extraction process, most of the extracted species were short and therefore the polydispersity of the recovered un-

98% *cis*-1,4 Polybutadiene / N300 (50 phr) full compound

Extracted rubber species - Toluene at 23°C

GPC (THF at 40°C) - 2 ultrastragel linear columns

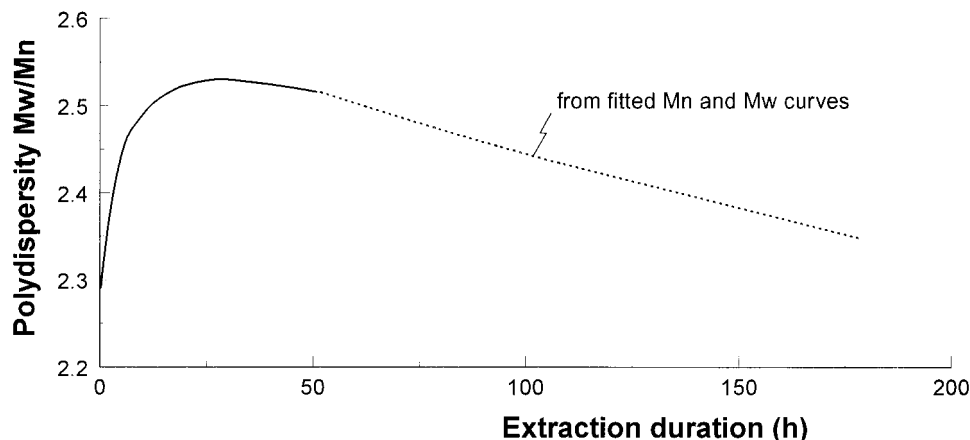


Figure 4 Variation of the polydispersity of extracted rubber species during the solvent extraction process: full polybutadiene compound.

bound rubber was relatively low. Then as the test sample was swollen by the permeating solvent, longer but unbound chains were extracted and hence the polydispersity index increased. The maximum observed in Figure 4 is likely to correspond to the highest swelling of the compound that in this state could be viewed as a coherent network of carbon black aggregates connected by extended bound rubber chains. Beyond this point, the extraction process essentially reached its completion, as shown by Figure 2. The extracted fractions were consequently becoming very low, and the apparently decreasing polydispersity index observed in Figure 4 could just reflect a mathematical artifact. It is nevertheless possible that as the extraction process reached its completion, the only chains that were yet removed by the solvent were the ones that were entangled with the bound rubber.

Extraction Experiments with Binary Compounds

Table IV gives the Mooney test data measured within 1 h after the binary compounds (mixes 2A,

Table IV Mooney Viscometer Data

Mix	Mixing Energy (MJ/m ³)	Mooney Test at 100°C	
		Peak	ML (1 + 4)
2A	460	169.0	144.0
2B	1480	161.0	126.4
2C	2420	144.6	99.0

2B, and 2C) were dumped from the mixer. The expected effect of mixing energy level is seen but, with respect to the Phillips dispersion scale,¹⁰ all mixes were found to be sufficiently dispersed, i.e., rating 5–6 for mix 2A and 7–8 for the others.

Figure 5 shows the extraction kinetics of two samples from mix 2B (1480 MJ/m³ mix energy) after either 12 or 54 day storage at room temperature. As can be seen, the storage did not significantly affect the extraction kinetics; accordingly the model described above was fit to the data by nonlinear regression analysis. The parameters are [%BR] = 25.65 and $b = 0.248$. When compared with similar data obtained for the full compound, it appears that the percent bound rubber was practically the same and hence not much affected by the compounding ingredients. However, the extraction kinetics were 2.5 times faster for the binary compound. One would conclude that the compounding ingredients do not affect the rubber–filler interaction but are likely to promote entanglements between the extractable chains and the bound rubber; consequently the extraction kinetics was slower with full compounds.

The variation of labile rubber species size during the extraction process is illustrated in Figure 6 with data obtained on a sample of mix 2B after 54 days of storage at room temperature. Two GPC analyses were performed with different columns to confirm the trend in the earlier period of the extraction process. The model presented above was used to fit the data; fitting parameters are

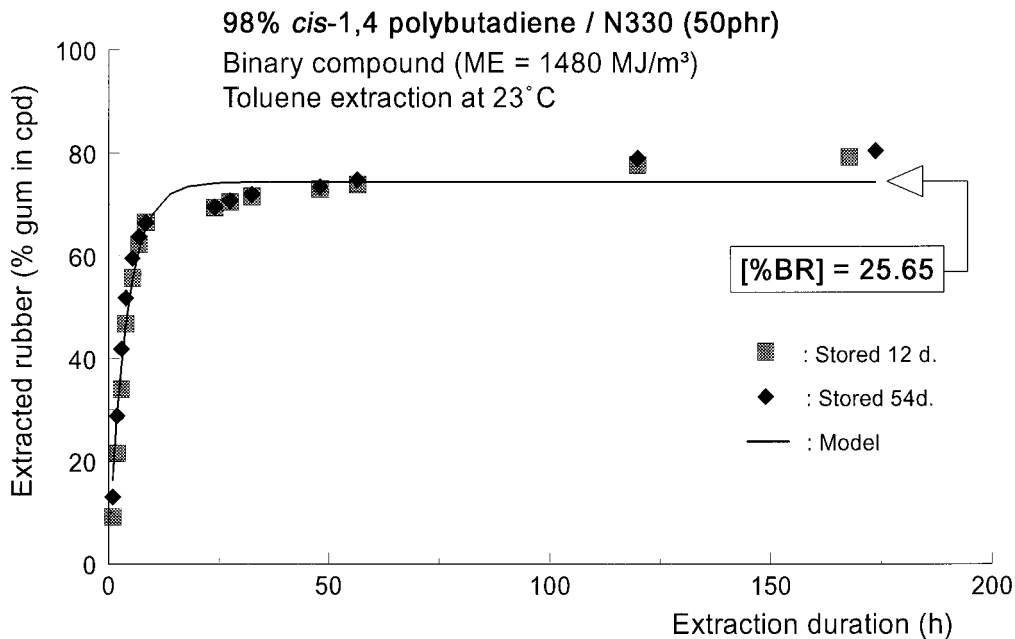


Figure 5 Extraction kinetics: experimental results on a model binary polybutadiene/carbon black compound.

given in the figure. Despite the experimental scatter, comments similar to those made in the case of the full compound can be offered. Using the fitting parameters for the variation of M_n and M_w with extraction duration, a curve with a maxi-

imum similar to Figure 4 was also obtained when plotting polydispersity versus extraction duration; however, the maximum occurred in a shorter period (around 5 h), which reflected the faster extraction kinetics with the binary compound.

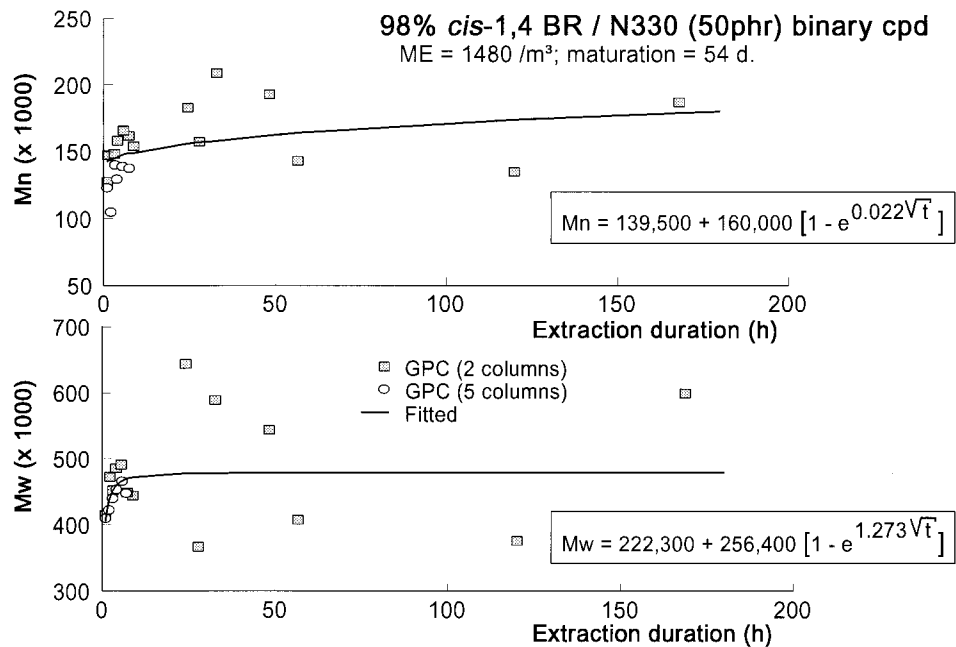


Figure 6 Variation of macromolecular characteristics of extracted rubber species during the solvent extraction process: model binary polybutadiene/carbon black compound.

98% *cis*-1,4 Polybutadiene / N330 (50 phr) binary compound

Banbury mixer 3.1 l. ; upside down mixing

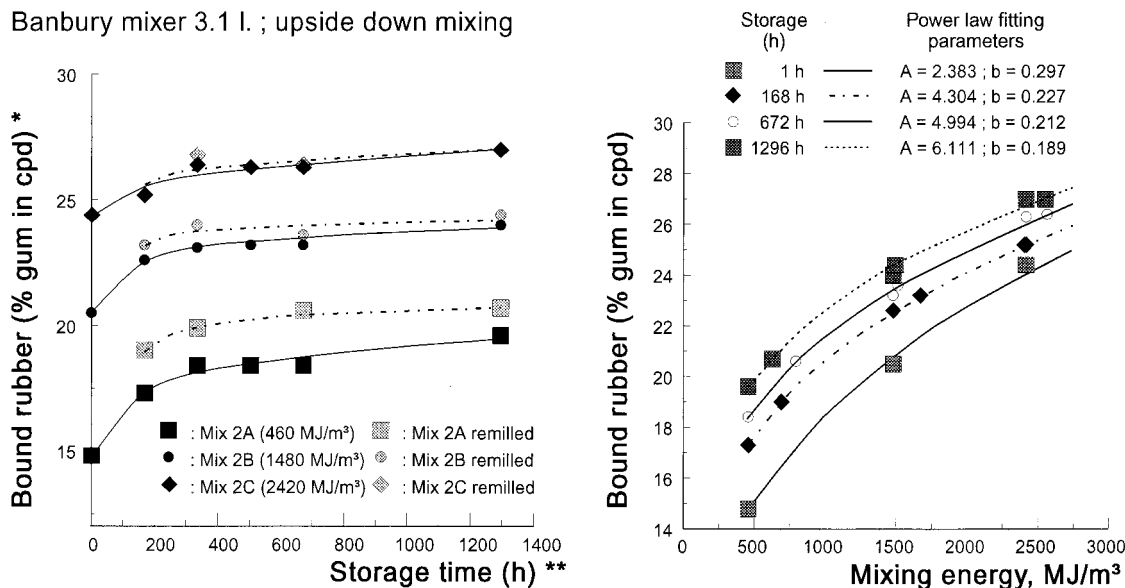


Figure 7 Effect of mixing energy and storage time on bound rubber content in a model binary polybutadiene/carbon black compound.

Effect of Mixing Energy on Bound Rubber

As shown on the left part of Figure 7, the bound rubber evolves with maturation time until a plateau is reached. In addition, a significant effect of the mixing energy level on the maximum bound rubber was noted, which corresponded well with similar observations on styrene-butadiene rubber compounds.¹¹ Through remilling a further evolution of bound rubber was obtained, particularly significant for the two compounds with the lowest mixing energy (mixes 2A and 2B). Therefore, it can be inferred that the optimum bound rubber for a given compound is obtained when nearly all carbon black agglomerates have been split down into aggregates, because in such a case the available filler-specific surface for bound rubber formation is maximum. For any formulation, there is thus a level of mixing energy for optimum rubber–filler interaction. For the binary compounds studied here, this optimum would be around 1900–2000 MJ/m³. However, even when the mixing energy was above this optimum level, there was yet a storage effect and the bound rubber plateau was obtained only after 20 days. Through remilling a further slight evolution of bound rubber was obtained but not enough to reach the optimum. One would conclude that remilling does not break down agglomerates further but accelerates the mechanism (likely to be chain conformation modification) involved in bound rubber maturation.

During remilling compounds received an unknown increment of mixing energy that can be estimated with respect to the observed relationship between the latter and bound rubber content. Indeed a simple power law was found to perfectly fit bound rubber versus mixing energy data for the three mixes considered, as shown in Table V. From the bound rubber data obtained on the remilled compounds, the overall mixing energy absorbed during the mixing and the remilling is obtained from

$$ME_{\text{mix}} + ME_{\text{remill}} = \left(\frac{[\%BR]_{\text{remill}}}{A} \right)^{1/b}, \quad (4)$$

where ME_{mix} and ME_{remill} are, respectively, the energy absorbed during internal mixing and remilling, A and b are the power law parameters, and $[\%BR]_{\text{remill}}$ is the bound rubber content of the remilled stocks as measured after the various storage periods. Results are given in Table VI. When taking into account the mixing energy absorbed during remilling, the bound rubber versus mixing energy data coincide at a given storage period, as shown in the right part of Figure 7.

The above data demonstrate that the bound rubber content of a given sample depends on the mixing energy absorbed by the compound and the storage period (at room temperature) before

Table V Power Law Relationship Between Bound Rubber and Mixing Energy

Mix	Mix. Energy (MJ/m ³)	Storage (h)					
		1 % BR	168 % BR	336 % BR	504 % BR	672 % BR	1296 % BR
2A	460	14.8	17.3	18.4	18.4	18.4	19.6
2B	1480	20.5	22.6	23.1	23.2	23.2	24.0
2C	2420	24.4	25.2	26.4	26.3	26.3	27.0
Power law: [% BR] = A · ME ^b							
Parameter A		2.383	4.305	4.951	4.994	4.994	6.112
Exponent <i>b</i>		0.297	0.227	0.213	0.212	0.212	0.189
SD <i>r</i> ²		0.997	0.999	0.993	0.996	0.996	0.994

bound rubber is measured by the solvent extraction technique. Assuming that the bound rubber measurement is performed at optimum solvent extraction conditions, it follows that

$$[\%BR] = f(\text{ME}, t).$$

As shown above, the bound rubber content of a sample after a given storage period depends on the mixing energy according to a power law. The parameter *A* in eq. (4) thus has the meaning of a (theoretical) bound rubber content that would be obtained when the mixing energy is equal to 1 MJ/m³. The data at the bottom of Table V show that both *A* and *b* evolve with storage time, and the likely origin of this variation suggests that fitting versus \sqrt{t} would give acceptable results. As illustrated in Figure 8, the following equations, whose coefficients were obtained by nonlinear regression, appear satisfying.

$$\begin{aligned} A &= A_0 + A_1\sqrt{t}, \\ b &= b_0 + b_1\sqrt{t}, \end{aligned} \quad (5)$$

when $A_0 = 2.675$, $A_1 = 9.945 \cdot 10^{-2}$, $b_0 = 0.282$, and $b_1 = -2.888 \cdot 10^{-3}$. Such parameters are obviously typical of the system studied, but it follows that the effect of the mixing energy and the storage time on bound rubber can be expressed by the following relationship:

$$[\%BR]_t = (A_0 + A_1\sqrt{t}) \text{ME}^{(b_0 + b_1\sqrt{t})}, \quad (6)$$

as demonstrated in Figure 9 by plotting calculated versus measured bound rubber data.

Bound Rubber and Rheological Properties

As previously demonstrated,¹ there is a relationship between bound rubber variation upon storage and rheological properties, most appearing when the latter directly address the soft rubber-filler network. In other words, start-up flow tests are more sensitive to compound maturation than stabilized steady flow tests. Figure 10 shows Mooney peak data versus maturation time for the three binary mixes; and, indeed, the higher the mixing energy, the lower the initial Mooney peak

Table VI Overall Mixing Energy Adsorbed by Remilled Compounds

Mix (Remilled)	Storage (h)							
	168		336		672		1296	
	BR (%)	ME (MJ/m ³)	BR (%)	ME (MJ/m ³)	BR (%)	ME (MJ/m ³)	BR (%)	ME (MJ/m ³)
2A	19.0	694	19.9	680	20.6	797	20.7	628
2B	23.2	1673	24.0	1636	23.6	1513	24.4	1496
2C	25.2	2408	26.8	2745	26.4	2567	27.0	2554

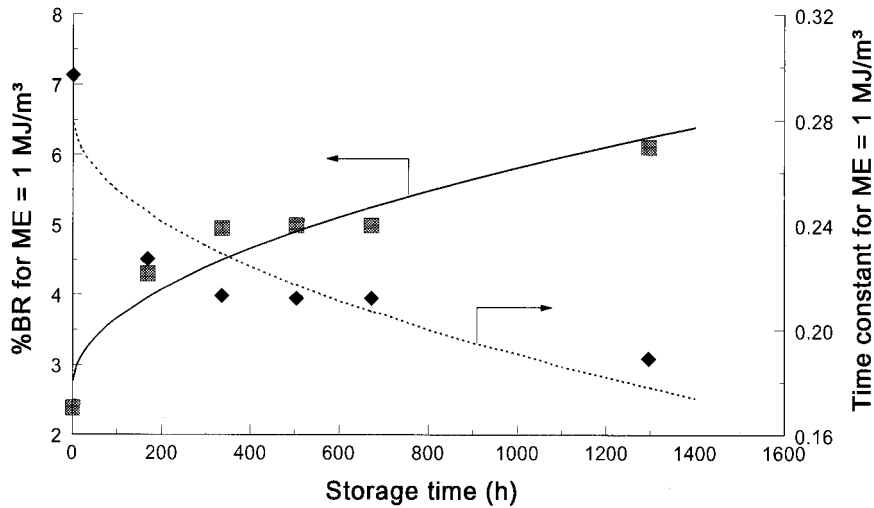
98% *cis*-1,4 polybutadiene / N330 (50phr) binary compound

Figure 8 Modeling the effect of storage time on parameters describing the dependence of bound rubber on mixing energy: model binary polybutadiene/carbon black compounds.

(in fact measured within 1 h after dump). After a sufficiently long storage period, however, all three compounds exhibited the same peak value.

CONCLUSIONS

An extraction kinetics method is thus in hand that allows interesting data to be obtained about the morphology of carbon black filled rubber compounds. The method is such that most of the tedious operations involved in the method could be

automated, a project that is currently being considered for further work.

Data obtained show that the extraction kinetics can be modeled with a simple law based on the very basic hypothesis that the extraction rate of labile species is proportional to the amount of extractable material remaining in the compound. For full compounds a correction for nonrubber extractable ingredients must be applied; but it was demonstrated that compounding ingredients do not affect essentially the bound rubber level of a given formulation, providing that the optimum

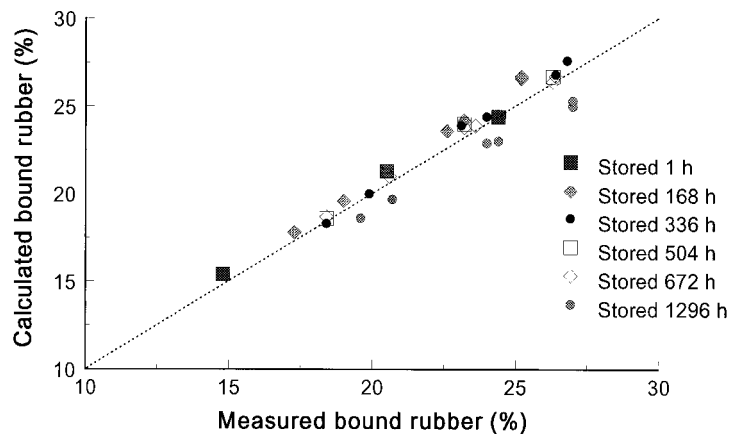
98% *cis*-1,4 polybutadiene / N330 (50phr) binary cpd

Figure 9 Modeling the combined effect of mixing energy and storage time on bound rubber content in model binary polybutadiene/carbon black compounds.

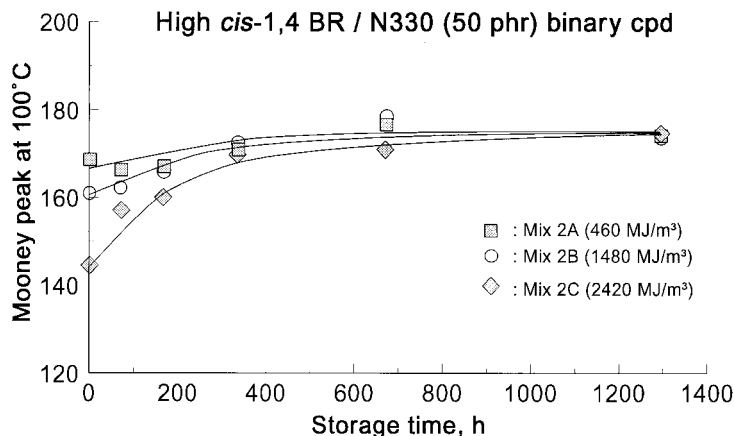


Figure 10 Effect of storage time on Mooney peak of model binary polybutadiene/carbon black compounds.

mixing energy levels have been achieved during the preparation procedure and that the compound maturation processes have been completed.

The analysis of the macromolecular characteristics of extracted rubber species versus extraction duration provides an original insight on the rubber–filler interaction. First, there is an effect of extraction duration that is easily modeled with a simple equation implicitly referring to a Fickian process. This allows the large experimental scatter, due either to sample handling or to GPC techniques, to be compensated for on an acceptable physical background. Second, it was demonstrated that the polydispersity of labile species varies during the extraction process and passes through a maximum whose position on the time scale depends on the complexity of the formulation. The experimental data proved that the largest molecular weight fractions are involved in the rubber–filler interaction, as predicted by theory.

Experiments on model compounds allowed the effect of the mixing energy and storage maturation to be studied in detail, and a model that takes both effects into account was developed. For a given formulation, there is a definite mixing energy level that must be achieved for optimum filler–rubber interaction to be obtained, notwithstanding the effect of storage maturation. Although reduced for optimally mixed compounds, the latter still exists.

The work reported here opens important perspectives for further works. First, the experimental approach described must be applied to other types of rubber compounds to confirm its validity and to prove the models developed for the extraction kinetics and the variation of molecular size

of labile species during the extraction process. In the meantime, the experimental procedure should be automated with respect to its tedious aspects. Second, the information obtained allows us in principle to calculate certain quantitative aspects of rubber–filler morphology, a subject we will develop soon. Third, the observed effects of the mixing energy must receive further attention owing to their considerable practical importance. And last, the relationship between bound rubber and rheological properties must be further considered by focusing on such techniques that directly address the soft rubber–filler morphology, i.e., essentially flow start-up techniques that are presently not common in rubber science.

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