e-Polymers **2003**, no. 032.

http://www.e-polymers.org
ISSN 1618-7229

Adsorption of monodisperse polybutadienes on carbon black, 2
Bulk adsorption

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(Received: May 19, 2003; published: June 27, 2003)

Abstract: The adsorption on carbon black (CB) of a series of monodisperse polybutadienes (PBs) with different molecular weights (M_n in the range of 3000 to 120 000) but identical microstructure (1,2-PB content ≈ 80%) was studied in the bulk for different polymer/CB ratios (τ, in the range of 2 to 10 g/g). In this respect we particularly studied the evolution of the amount of polymer, which cannot be extracted from the polymer/filler system upon blending, the so-called bound polymer, and attempted to investigate the conformation of the resulting adsorbed molecules as well as the conditions that control the formation of the polymer/filler network. The conformational transition turned out to depend exclusively on molecular weight, and the networking transition to occur at constant $M_n^{1/2}/\tau$, essentially through an entanglement process of the adsorbed chains.

Introduction

Part 1 [1] of this series of papers reported experimental data on the synthesis of monodisperse polybutadienes having number-average molecular weights (M_n) in the range of 3000 to 120 000, and their irreversible adsorption from solution on carbon black surfaces. Experiments were performed under excess polymer condition, i.e., free polymer chains remained available in solution after adsorption equilibrium was reached. It was recognized that the pertinent variable affecting the adsorption is the polymer concentration in solution. Solid particles concentration (within the range of 2.32 to 46.50 g/l) was found to have no detectable effect on the adsorption process. Two major findings are worth mentioning:

- A *networking transition* that separates dispersion from a coherent three-dimensional network was clearly identified.
    1. It occurs at a fixed polymer/filler ratio and is independent of both polymer/solvent and filler/solvent ratios and chain conformation.
    2. It is associated essentially with a percolation process.
    3. At the transition point the 'functionality' of a solid particle in the network decreases, and chain folding increases with increasing M_n.
    4. Networking most likely results from an entanglement process of adsorbed chains and not from a direct linkage of two particles by a single chain.

- A *conformational transition* occurring at a critical concentration, c_t, was also identified
    1. Below c_t macromolecules adopt a flat conformation while above c_t the polymer is in a coil-like conformation.
    2. These two regimes together with c_t are quite well predicted by the theory for sufficiently high molecular weights.

Both, conformation of polymer molecules adsorbed at the solid/liquid interface and polymer/solid network formation are essential to understand the behaviour of the composite material and its properties. Properties of the adsorbed layer such as thickness and number of attached segments as well as the functionality of the solid particle are easily derived from the conformational side while swelling and deformation of the network are governed by the polymer/solid network formation side.

The highest polymer concentrations that could be used in the previous study were limited because of difficulties related to experimental and practical considerations. In order to explore a higher domain of concentrations one should inevitably perform adsorption experiments in the bulk.

In the present work, the adsorption of monodisperse polybutadiene was studied in the dry state for different:

- polymer/carbon black ratios (τ, from 2 to 10 g/g),
- polymer molecular weight M_n (from 3000 to 120 000 g/mol).

Experimental part

Synthesis

The synthesis of a series of highly monodisperse (M_w/M_n = 1.1) polybutadienes differing in molecular weight and exhibiting identical microstructure (1,2-PB content ≈ 80%, a result confirmed by the fact that all samples exhibit the same glass transition temperature of about -27°C) was presented in previous papers [1,2]. All samples used and their molecular weights are gathered in Tab. 1.

Tab. 1. Polybutadiene samples

Samples	$M_{n\ (eq\ PS)}$
PB3	2800
PB10	9900
PB23	22 800
PB38	37 700
PB67	67 000
PB117	117 300

Compounding

The polymers compounded with carbon black (N110, Degussa) were prepared using a Thermo Haake MiniLab Rheomex CTW5 internal mixer (capacity of the mixing

chamber = 3 ml). Blending was done at 70°C, i.e., well above the glass transition of the polymer, in order to provide a good efficiency of the dispersion. After the polymer was sheared for 5 min at 50 rpm, a specific amount of carbon black (CB) was added progressively within about 5 min, followed by 15 min of shearing under the same conditions, then another 15 min at 100 rpm. Under such compounding conditions all samples were mixed until a constant shearing force and good dispersions were reached. In order to accelerate the adsorption kinetics, the compounded materials were aged in vacuum for 3 weeks at 50°C.

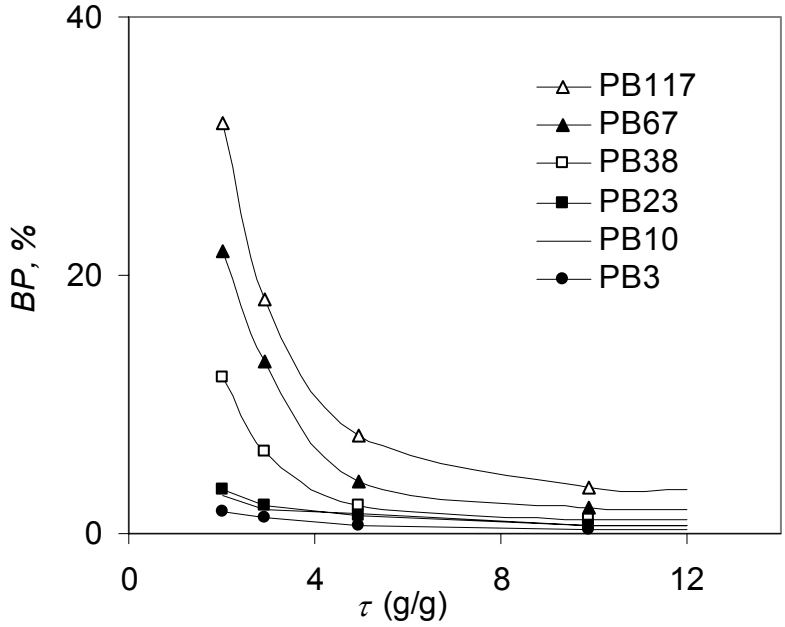

Fig. 1. *BP%* (percentage of bound polymer) obtained for different polymer/filler ratios and polybutadiene samples

A typical solvent extraction was performed as follows: 1 g of compounded sample was maintained in 50 ml of toluene for one week, the solvent being renewed 3 times. After centrifugation at 6000 rpm for 30 min, the residual liquid was drained and the remaining fraction of undissolvable polymer/filler blend was dried at 50°C in vacuum. The amount of adsorbed polymer was determined by microgravimetry after pyrolysis of the sample under inert atmosphere at 900°C. The exact initial polymer content in each blend was also assessed according to the same procedure. For each molecular weight, the polymer/CB weight ratios τ were selected so as to respect the three following limits:

1. τ should not fall below the limit corresponding to a visually coherent blend (too high filler contents lead to the formation of crumbs).
2. τ should have a value such that the amount of remaining solid after blend extraction is high enough to be pyrolyzed and measurable by microgravimetry (at least 0.5 g of solid material).
3. τ should be high enough in order to insure that free polymer chains remain available in the blend after adsorption equilibrium is reached (excess polymer condition).

All conditions but the last one were controlled experimentally during the mixing operation. The excess polymer condition is satisfied if the percentage of adsorbed

polymer (*BP%*, the percentage of bound polymer in the initially mixed polymer phase) does not approach the total amount of the initial polymer compounded in the blend.

It is clear from Fig. 1 that, even at the lowest τ and for the highest M_n, when equilibrium is reached adsorption never exceeds 35% of the total amount of polymer. Consequently, the excess polymer condition is evidently satisfied. It was thus assumed that, after adsorption, the CB surface is completely covered by the polymer.

Results and discussions

Effect of molecular weight

Fig. 2 provides the evolution of *BP* versus M_n for different τ values. It appears clearly that, whatever τ, two regimes separated by a critical molecular weight, M_n^*, can be distinguished:

- for M_n < 23 000, *BP* is independent of τ and independent or slightly dependent on M_n. The corresponding amount of adsorbed polymer is rather low (*BP* is in the 0.02 to 0.05 g/g range) and is as a matter of fact comparable to what was found in the case of adsorption from dilute solution [1].
- for M_n >23 000 g/mol, *BP* increases with molecular weight, the slope of the different lines being inversely dependent on τ.

Since it was assumed that adsorption equilibrium is reached under excess polymer conditions and the coverage of the CB surface by the polymer is complete, the independence (or slight dependence) of *BP* from the molecular weight for M_n < 23 000 suggests that the adsorbed macromolecular chains should adopt a rather flat conformation. It is worth mentioning that according to a naive but relevant calculation (based on a specific surface area of the carbon black equal to 150 m^2/g), the amount of *BP* per unit surface area at the threshold level corresponds to 2 to 4 polybutadiene monomer units per nm^2, which is not an extravagant value for a 100% covering ratio.

Conversely, for M_n > 23 000, *BP* is roughly proportional to $M_n^{1/2}$; adsorbed polymer chains form much more pronounced loops than in the previous regime. Such behaviour has already been reported in the literature for both polybutadiene/carbon black and silica/siloxane blends [3,4], with the establishment of an empirical power law:

$$BP \sim \chi M_n^{1/2} \qquad (1)$$

The power law factor, i.e., 1/2, is a clear indication that Eq. (1) essentially assumes that the chain is just in an unperturbed random coil conformation. However, while ref. [3] points at an increase of *BP* only with filler structure and surface area, refs. [4,5] expect and demonstrate an increase of *BP* with τ conversely to what we actually observe in Fig. 2. In another work [6] related to polybutadiene/carbon black blends, Cohen-Addad and Frebourg expect and observe a decrease of *BP* with τ without any power law with regard to M_n.

The crossover between these two regimes occurs over an astonishingly narrow range of molecular weights (close to 23 000 as obviously observed in Fig. 2). Up to our knowledge, this 'conformational transition' as well as the first regime (for M_n < 23 000) are not mentioned in the literature for polymer adsorptions performed in the bulk. Such a conformational transition is however predicted in the case of polymer adsorption from solution studied as a function of polymer concentration. But even in

this case all molecular weights are predicted to yield a coil-like conformation for large enough polymer concentrations, which was actually reported in part 1 of this series [1]. Only the unusually low M_n range explored in the present work allowed the detection of this conformational transition. Moreover, it is worth highlighting that the exact position of M_n^* on the M_n axis is such that

$M_e < M_n^* < 2M_e$

where M_e represents the entanglement molecular weight of the polymer which is estimated to be 16 000 [7-9].

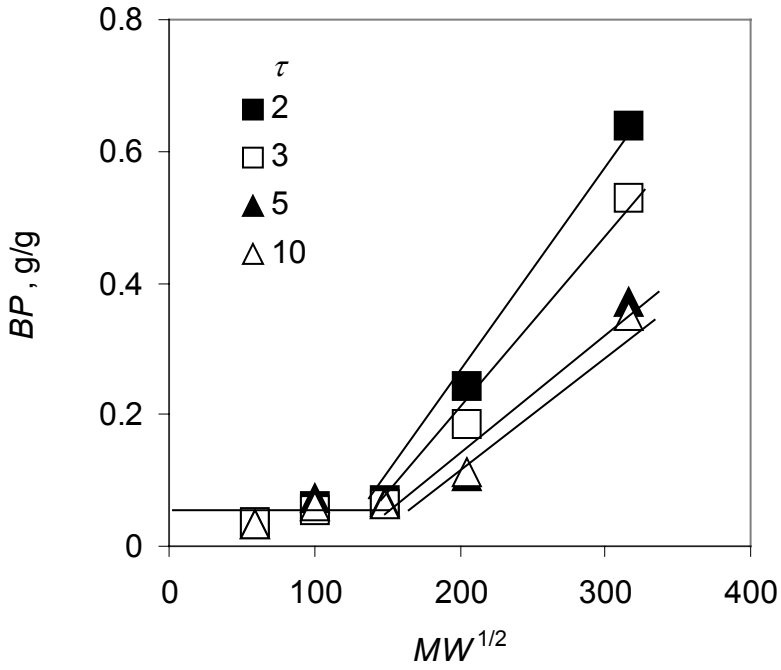

Fig. 2. Bound polymer versus M_n for different τ

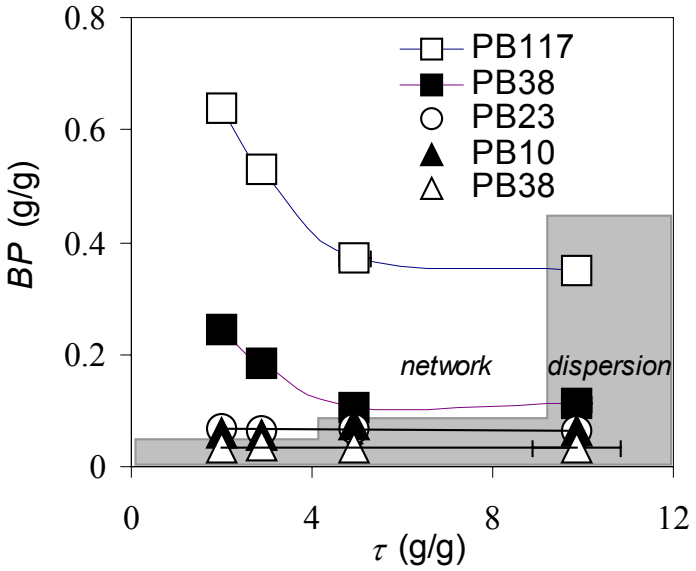

Fig. 3. *BP* versus τ for different molecular weights

Effect of the polymer/filler ratio

Fig. 3 provides the evolution of *BP* as a function of τ for different molecular weights. It is obvious that the general trend is a decrease of *BP* with τ. Such a trend seems however to disappear for lower molecular weights. For sufficiently short chains bound polymer becomes actually independent of τ.

As a first approximation, the decrease of τ (i.e., the increase of the carbon black content) should result in a decrease of the inter-aggregate distance in the blend, and thus in an increase of the probability to have two particles of filler linked by the same chain. Such a 'polymer sharing' effect would be expected to decrease the *BP* value. Our experimental results (Fig. 3) appear therefore to be in contradiction with this hypothesis.

Four interpretations can be proposed to explain the decrease of *BP* with τ:

- Increase of the surface accessible to the polymer [10]

It was shown that carbon black disaggregating in blends is more efficient for higher filler contents and higher molecular weights, a process which was associated with an improved shearing upon filler loading increase. Thus, *BP* should increase with surface accessibility.

Such an effect should overcome polymer sharing so as to explain our results. We estimated that surface accessibility should more than double to justify the increase of *BP* upon reducing τ for the highest molecular weight as observed in Fig. 3. However, no experimental evidence whatsoever was found to justify such a surface increase.

- Modification of chemical reactivity [11]

High shear at high filler content might increase the chemical reactivity of the filler surface because of the creation of new active sites and/or polymer chains upon homolytic scission and formation of very reactive free radicals. Both mechanisms would lead to the formation of a very strong surface/polymer chemical bonding and to an increase of *BP*. Such mechanisms were proposed many times but have not been recognized as being major factors in the formation of bound polymer.

- Desorption of chains during the extraction [12]

For a given molecular weight involved in the polymer sharing process, the lower is τ, the higher would be the probability for one chain of exchanging multiple links with two particles and thus to resist solvent extraction. This implies that the effect of solvent extraction on specimens obtained at high ratio τ is to clear, in some way, the surface of the filler.

This hypothesis is inconsistent with the fact that the blends were prepared under excess polymer conditions and thus the carbon black surface exhibits a 100% covering ratio. In addition, a chain that is not involved in polymer sharing still can exhibit multiple adsorptions with the same particle and consequently cannot be extracted. Moreover, as it will be shown hereunder, networking is not the result of a direct polymer sharing process but rather of an entanglement of adsorbed chains.

- Entangled polymer [13,14]

One can assume that a fraction of the polymer in the interfacial region may be trapped through entanglements within the adsorbed chains. Such a process should increase with polymer molecular weight and filler content. This polymer fraction would then become unextractable, either because of an extremely long reptation time or

because of its immobilization under the effect of long-range interactions with the solid surface.

Dispersion/network transition

Fig. 3 (shadowed area) shows the range of M_n's and τ's for which the extracted blends yield a dispersion of insoluble polymer/filler particles, while all other M_n's and τ's yield three-dimensional coherent polymer/filler networks. The puzzling point is the fact that such an experimentally detected transition is not associated with a particular change of the *BP* value over the whole range of τ's. Such a result suggests that the filler/polymer network formation would most likely result from an entanglement networking of the bound polymer, rather than from the direct polymer bonding of several filler particles by one macromolecular chain (if this was the case, *BP* would be expected to decrease with the amount of filler).

Networking is clearly dependent on both molecular weight and τ. However, if we consider τ^* as the polymer/filler ratio at which this transition occurs, the variable $M_n^{1/2}/\tau^*$ seems to be fairly independent of M_n as shown in Fig. 4.

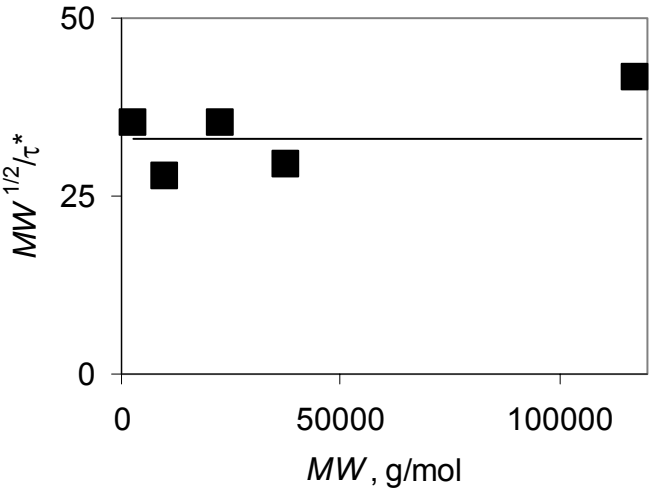

Fig. 4. $M_n^{1/2}/\tau^*$ vs. M_n

This result means that, regarding network formation, there is equivalence between polymer molecular weight and filler content ($1/\tau^*$), i.e., the formation of the three-dimensional network can occur either when polymer chains are long enough or when particle concentration is high enough. Such behaviour reflects a purely geometrical construction. On the one hand, the filler content defines somehow an inter-particle distance, *a*, with a fairly homogeneous solid distribution in space. *a* can be easily estimated from a simple cubic organization:

$$a = R\,[(4\pi/3\ \phi)^{1/3} - 2] \qquad (2)$$

$$R = 3/S_p\,\rho \qquad (3)$$

with particle size $R \approx 10$ nm, considering S_p (specific surface area of the filler) ≈ 150 m^2/g and ρ (filler density) ≈ 2 g/cm^3, ϕ being the filler volume fraction. On the other hand, the polymer molecular weight defines a characteristic distance above which the

macromolecules are long enough to link two particles; this distance is essentially proportional to $M_n^{1/2}$, thus to the radius of gyration, R_g:

$$R_g^2 = 1/6 \langle r^2 \rangle \quad (4)$$

where $\langle r^2 \rangle$ is the mean-square value of the chain end-to-end distance.

Fig. 5 provides the evolution of the characteristic distance between particles at the networking point (a^*) as a function of the polymer radius of gyration. It is clear that the experimental results obey quite well a simple proportional fit, at least for the low molecular weights, viz.:

$$a^* = 2 R_g \quad (5)$$

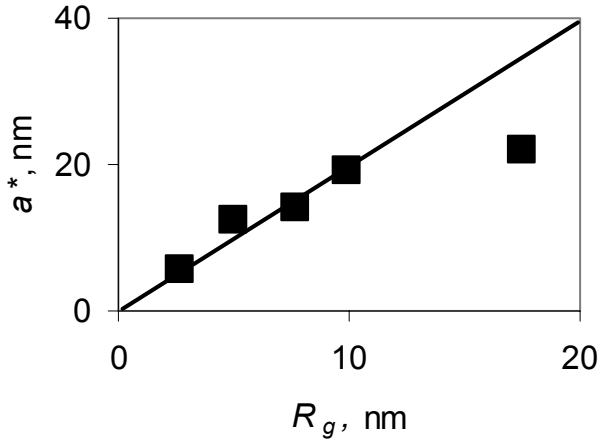

Fig. 5. Characteristic distance between particles, a^*, as a function of R_g

Given the fact that networking may occur when the average adsorbed macromolecules are in a flat unfolded conformation (see sample PB23 at τ < 4 g/g in Fig. 3), we may conclude that the only conditions to form a particle/polymer network is to have few chains in their random coil conformation and the characteristic distance between particles not exceeding twice the radius of gyration. These results confirm the observation made in the previous section concerning the network formation as resulting essentially from an indirect 'entanglement' process.

The highest molecular weight (117 000) is clearly deviating from the proportional fit (Eq. (5)). This is a clear indication that the polymer chain at the networking gel point adopts a flatter conformation than a random coil; therefore, a higher particle content is needed (i.e., a lower a) to form the network.

Conclusion

Adsorption of monodisperse polybutadienes on carbon black shows that polymer conformation on the surface depends essentially on the molecular weight. Low molecular weight polymers adopt a flat conformation with a low *BP* value. High molecular weight polymers are in a coil-like conformation. The transition between the two regimes occurs for M_n values somewhere between M_e and $2M_e$. At high M_n and/or high filler content, a fraction of *BP* results from polymer chains entangled

within the adsorbed chains in the interfacial region without being necessarily in direct contact with the solid surface.

Networks are more likely to be formed by entanglements rather than by direct particles bridging. The network/dispersion transition occurs for a constant $M_n^{1/2}/\tau^*$ ratio, if, at least, few chains are in their random coil formation and the characteristic distance between particles does not exceed twice the radius of gyration.

Acknowledgement: The authors wish to express their thanks to Dr. Friedrich (Materials Research Centre, Freiburg im Breisgau, Germany) for providing an internal mixer.

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