Thermodynamic Study of Surfaces of Liquid Polybutadienes and Their Interfaces with Poly(dimethylsiloxane)

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ABSTRACT: Surface tension of liquid polybutadienes (PBD) as well as interfacial tension between them and poly(dimethylsiloxane) (PDMS) were measured in the temperature range from 25 to 150°C. The measured pressure–volume–temperature (PVT) data were used for the determination of reduction parameters of pressure, volume, and temperature in several equations of state for polymers. The reduction parameters were used for the estimates of surface tension and compared with experimental data. Interfacial tensions were used to determine Flory-Huggins interaction parameters using the Roe and Helfand theories for the system PBD-PDMS. The results obtained using both the theories were somewhat different; the difference being the least with the segment chosen as a part of molecule containing 4–5 nonhydrogen atoms.

Modifications of PBD that were investigated increase the density. Maleic ester end groups increase both surface tension and interfacial tension and bring a positive contribution to the Flory-Huggins interaction parameter (to its enthalpic component), whereas the pending maleic anhydride groups have shown the opposite effect; their negative contribution to Flory-Huggins parameters concerns mainly its entropic component. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 169–180, 2009

Key words: polybutadiene; Krasol[TM]; liquid rubber; surface tension; interfacial tension; equations of state; reduction parameter; Flory-Huggins interaction parameter

INTRODUCTION

Surface and interfacial tension of polymers depend on the intermolecular interaction forces, particle concentration, thermal motion and associated entropic effects, and on structure (length, flexibility, and branching of polymer chains). The forces of intermolecular interactions and thermal motion can be characterized by reduction parameters (Prigogine,[1] Patterson and coworkers,[2,3] Sanchez and Lacombe[4,5]) and, for systems with more components, by Flory-Huggins interaction parameters.[6] Changes in phase composition also affect the surface and interfacial tension. One of the ways of expressing the relationship between the pressure–volume–temperature (PVT) data of the material and surface tension is provided by the theory of behavior of macromolecules in concentration gradient and the theory of corresponding states. The measured surface and interfacial tensions make it possible to assess correctness of various models of arrangement in the surface or interfacial region or to determine the values of parameters occurring in these models. The works and results of Dee, Sauer, Walsh, and Ougizawa[7–14] became an initial point and one of the main sources of knowledge for this work.

The aims of the work were to do following with pure and substituted liquid polybutadienes (PBDs):

1. To measure their densities (PVT data), surface tensions, and interfacial tension between them and an easily measurable reference material.
2. To determine reduction parameters by procedures described by previous authors, to evaluate the suitability of respective equations of state, and to compare the selected estimates of surface tension with the measured values of PBDs.
3. To estimate the Flory-Huggins interaction parameters from measured interfacial tensions and to evaluate the influence of used model and its parameters on the obtained results.

4. To evaluate the influence of modifications of PBDs on the aforementioned parameters.

THEORETICAL BACKGROUND, KNOWN FACTS, AND DATA

Equations of state for polymers

Equations of state express relationship between the reduced quantities $\tilde{p}, \tilde{V}, \tilde{T}$ as introduced in Refs. 1 and 15. The simplest commonly used equations of state originates from Flory et al.:[15]

$$\tilde{p}\tilde{V} = \tilde{T}(1 - \tilde{V}^{-1/3})^{-1} - \frac{1}{\tilde{V}} \quad (1)$$

The Prigogine[1] equation was further refined by Dee and Walsh[7]

$$\tilde{p}\tilde{V} = \tilde{T}(1 - \tilde{V}^{-1/3}\delta)^{-1} - 2\tilde{V}^{-2}(A - B\tilde{V}^{-2}) \quad (2)$$

where A and B are geometrical constants of equation for Lennard-Jones potential and δ differs in models.

The equations of state of Sanchez and Lacombe[4,5,16] have a different form and is based on differently defined reduction parameters and considering the chain length r:

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T}\left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \quad (3)$$

A comparison of applicability of these equations of state was made by Dee and Walsh.[7] Dee and Sauer and coworkers described the calculation procedures in detail.[8–10]

The review of equations of state for polymers were presented by Rodgers.[17] Other models or model modifications were published by Somcynsky and Simha,[18] Murakami,[19] and Panayiotou and Vera.[20]

Determination of reduction parameters

Especially with limited PVT data,[21] the procedure of determining reduction parameters from thermal expansion α and isothermal compressibility β according to Flory et al.[15] can be used; it is based on the fact that $\alpha^* = 1/T^*$, $\beta^* = 1/p^*$ and $\tilde{a}\tilde{T} = aT$. Equations and description can be found in Refs. 2,4, and 15.

Exact calculation is made by the three-parameter nonlinear regression from PVT data,[7] which can use the result from the aforementioned procedure as an "ansatz" value for calculation.

Surface tension estimations

A review of the surface tension of polymer melts presented by Dee and Sauer[14] describes sev-

eral approaches to express surface or interfacial tension.

One of the ways to predict surface tension is based on parachor, which can be calculated using group contributions, density, and molar mass of mer.[2,22,23]

$$\gamma = \left(\frac{P}{V_M}\right)^4 = \left(\frac{P\rho}{M_S}\right)^4 \quad (4)$$

The density gradient model published by Cahn and Hilliard[24] provides the way to express the surface or interfacial excess quantity, the dependence of which on composition in concentration gradient can be completely described. Its use for determination of polymer surface tension was described by Dee and Sauer,[11] who modified the Cahn–Hilliard equation to express the surface tension from the Helmholtz energy per volume unit (a), density (ρ), and constant κ. In reduced form for $\tilde{\gamma} = \gamma/\gamma^*$, where $\gamma^* = (p^{*2}T^*kc)^{1/3}$, this equation is

$$\tilde{\gamma} = 2\int_{\tilde{\rho}_v}^{\tilde{\rho}_1} [\tilde{\kappa}\Delta\tilde{a}]^{\frac{1}{2}}d\tilde{\rho} \quad (5)$$

Subscripts l and v denote liquid and vapor phases, respectively. Poser and Sanchez[16] found for their case $\tilde{\kappa} = 0.5$. The $\Delta\tilde{a}$ is to be evaluated from an appropriate model together with the corresponding equations of state.

Patterson and Rastogi[2] derived for reduced surface tension an equation

$$\tilde{\gamma} = \left\{-\left(m.\tilde{U}(\tilde{V})\right) - \tilde{T}\ln\left[\frac{\tilde{V}^{1/3} - 0.5\delta}{\tilde{V}^{1/3} - \delta}\right]\right\}\tilde{V}^{-2/3} \quad (6)$$

which becomes

$$\tilde{\gamma} = \left\{\frac{m}{\tilde{V}} - \tilde{T}\ln\left[\frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1}\right]\right\}\tilde{V}^{-2/3} \quad (7)$$

for Flory equation of state and

$$\tilde{\gamma} = \left\{m.(2\tilde{V}^{-2} - \tilde{V}^{-4}) - \tilde{T}\ln\left[\frac{\tilde{V}^{1/3} - 0.5\delta}{\tilde{V}^{1/3} - \delta}\right]\right\}\tilde{V}^{-2/3} \quad (8)$$

for Prigogine equation of state (2) [originally used b or b_{PR} used in Ref. 25 replaced here by δ consistently with eq. (2)].

Dee and Sauer[13] presented a discrete interface cell model (DICM) based on the works of Prigogine and Saraga and of Patterson and Rastogi.[2] They obtained an expression for reduced interfacial tension (cited and used from Ref. 25 for supposed misprint in Ref. 13):

$$\tilde{\gamma} = \frac{\gamma}{\gamma^*} = \left\{\frac{m}{\tilde{V}} - \tilde{T}\ln\left[\frac{b\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1}\right]\right\}\tilde{V}^{-2/3} \quad (9)$$

where m is the geometric factor described later, b is a packing factor, reported to produce a good fit for its values about 2.

Funke et al.[26] presented a modification of Patterson's extension of FOV theory where the equation becomes

$$\tilde{\gamma} = \frac{\gamma}{\gamma*} = \left\{ (1 - W^3) - 3\tilde{T}\tilde{V} \ln\left[\frac{\tilde{V}^{1/3} - W}{\tilde{V}^{1/3} - 1}\right] \right\} \tilde{V}^{-5/3} \tag{10}$$

where W is an adjustable parameter reported to be about 0.8 for copolymers.

Theory of interfacial region

There are several groups of theories describing interphase. A representative of those based on analogy to the diffusion equation is the theory of Helfand, Tagami, and Sapse.[27–29] Another approach represented by the lattice theories of interphase, which are described in detail, e.g., by Helfand[30] and Roe,[31,32] was used in this work. The chain consisting of r segments is placed in the lattice, where each cell has z neighbors; of them, mz is in each of the adjacent layer and lz is in the same layer. The entropic component of Gibbs energy is expressed using a possible number of polymer chains configurations in the lattice distributed in layers, and enthalpic component is expressed by the Flory-Huggins interaction parameter χ. The concentration profile is given by the condition of the minimum Gibbs energy of the system, expressed by a series of equations for composition of respective layers, which can be solved by the method of successive approximations.[31]

Analogously to the Cahn–Hilliard procedure,[24] the surface tension is determined by the summation of Gibbs energies, but the summation is discrete here, through individual layers.

Roe found that the concentration profile can be well approximated by hyperbolic function.

$$\varphi_1 = \frac{1}{2}(\varphi_1^A + \varphi_1^B) + \frac{1}{2}(\varphi_1^A - \varphi_1^B)\tan h(qx) \tag{11}$$

This function contains, in addition to the volume fraction of component 1 in bulk phases A and B, only one parameter—the effective concentration gradient (slope) q. This parameter is determined by the substitution of function (11) into equations for concentration profile. The effective thickness d is defined

$$d = (\varphi_1^A - \varphi_1^B) \Big/ \left(\frac{\partial \varphi_1}{\partial x}\right)_0 \tag{12}$$

in the medium layer, and for the cited model is $d = 2/q$.

Roe derived simplified formulae to express the relation between interfacial tension and χ parameter in special cases: vicinity of critical point [eqs. (35) and (36) of Ref. 32], sufficient distance from the critical point ($\chi - \chi_c > 2$) [eq. (21) of Ref. 32], where the effective thickness d is given only by the distance of layers in the lattice, and for the infinite chain length,

$$\frac{\gamma a}{kT} \approx \frac{4}{3} \cdot 2^{-1/4} m^{1/2} \chi^{3/4} \tag{13}$$

From Helfand's works, we have used the formula

$$\gamma_{12} = \frac{kT}{2a}(m\chi)^{1/2}\left[1 + (1 + \chi)\chi^{1/2} \text{arctg } \chi^{1/2}\right] \tag{14}$$

simplified version of which, neglecting the nonlocal energy effect (expressed by the term with second derivation in the equation for interfacial profile), uses value 1 instead of term in brackets.

Flory-Huggins interaction parameter can be estimated by means of solubility parameters, recent model is presented by Lindvig et al.[33] This work estimates them from measured interfacial tension using models described in this section.

Known data of surface tensions and densities

The calculation of surface or interfacial tension requires, in addition, the knowledge of densities of the measured substances, which are determined usually dilatometrically,[34,35] for polymers with higher melting points.

The measured surface tension and density values of poly(dimethylsiloxane) (PDMS) can be found in the literature.[36–41] As to liquid PBDs, only data for roughly similar ethylene–propylene rubber[42] or for solid samples[43] were found, and the only work found investigated related system PDMS/PBD.[44]

MATERIALS AND METHODS

Materials

Liquid rubbers

PBDs Krasol[TM] are liquid rubbers produced by Kaučuk, a.s. (Kralupy nad Vltavou, Czech, Republic)[45] (now Sartomer Czech). Their use as compatibilizers of polyolefin blends was investigated in the Institute of Macromolecular Chemistry.[46] Their density and surface tension data were needed, and this is why they were chosen for this study also. The tested liquid rubbers differ in end and pending groups. The rubbers have the following formulae:

Krasol™ LB, LBH, and LBM
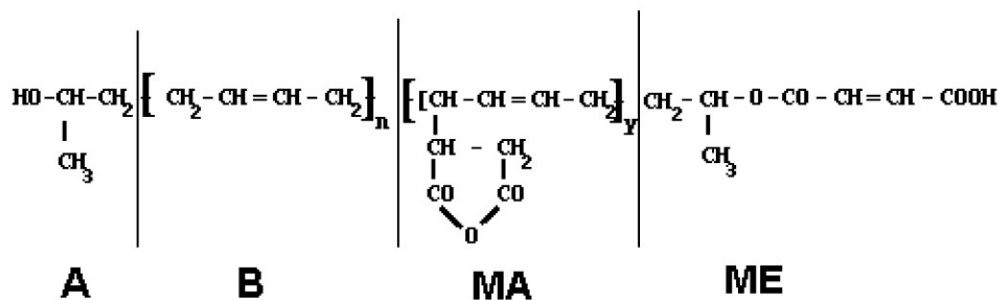
Krasol™ LBD
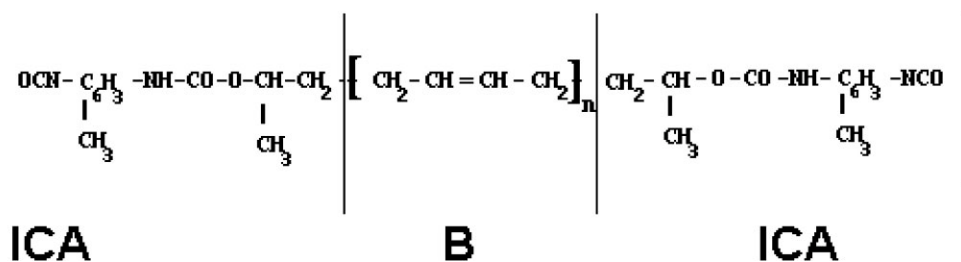
Krasols™ LB, LBH, and LBM 3000 are liquid low-molecular-weight polymers of butadiene, produced by anionic polymerization. They are statistical mixtures of different microstructures: 15% of *cis*-1,4-, 25% of *trans*-1,4-, and 60% of 1,2-PBD. Properties of the samples are listed in Table I. The name Krasol™ LBM is alternatively used for maleinized Krasol LBH.

Poly(dimethylsiloxane)

PDMS Aldrich (Milwaukee, WI) 18,183-8 was used. Its weight-average molecular weight is 137,000.

Density measurements at atmospheric pressure

Polymer densities were measured in a U-shaped dilatometer[34] with a removable vessel in a range up to 230°C for maleinized samples up to 170°C. Dilatometer with the melted and degassed polymer sample was filled in vacuum with mercury up to the scale. The measured temperature dependences of density were used as necessary complementary data for surface tension measurement.

PVT data measurements

Complete PVT data of PBDs were measured by Dee et al. using the method described in this work[12] in the range from 0 to 200 MPa and from room temperature to 225°C.

Surface and interfacial tension measurements

Surface and interfacial tensions were measured using the pendant-drop method[47–50] in argon atmosphere.

TABLE I
Properties of Used Polybutadienes

PBD	M_n	M_w	Structure	Additives	Viscosity (Pa s)			pH	COOH[a] (mmol/g)	COOH[b] (mmol/g)	COOH number per molecule
					25°C	30°C	80°C				
LB	2430	2845	H-B$_{45}$-H	None	8.51	5.74	0.3[c]				
LBM 1b	2730	3070	A-B$_{46.6}$-ME	None	34.47			4.3	0.405	0.338	0.92–1.10
LBM II	2880	3320	ME-B$_{47.5}$-ME	None	61.35			2.9	0.787	0.665	1.9–2.3
LBM III	3160	4040	ME-B$_{51.3}$-MA$_{0.5}$-ME	None	50–70			3.4	1.10	1.01	3.2–3.5
LBD	3500	4500	ICA-B$_{(44–57)}$-ICA	Antioxidant		70–90[c]	1.8[c]				

[a] By titration (phenolphthalein).
[b] By titration (methyl red).
[c] Value for given type of PBD indicated in the catalog.

The device was built essentially according to the literature.[51] Samples were degassed in only slightly increased temperature below 100°C to avoid other chemical changes due to increased temperature.

The drop images were acquired using an optical device consisting of objective Anaret 4,5/105 mm, tubus ca. 25 cm long, and CCD camera Elvia OS-458. The image was taken through a Matrox IP-8 frame grabber with resolution of 768 × 576 pixels at 256 gray levels. Dimensions were calibrated by the cylindrical body according to Girault et al.[52] The drop contour was primarily established using gray level threshold by tracing according to Pavlidis,[53,54] where the arithmetic mean of both peaks in a gray histogram was used as brightness threshold, and refined using the maximum brightness gradient and partial edge smoothing with polynomials.[55] The contour was further processed by the multiple-selected-planes method.[56] Tables of the dependence of $1/H$ on the respective S_k were calculated and, analogously to the interpolation equation for one plane of Misak,[57] an equation for remaining planes was found,[58] which precisely interpolates this dependence. Surface tension was then calculated from the shape and size data and from the polynomial density–temperature data from own measurements.

RESULTS AND DISCUSSION

Experimental results

Measured densities

The dilatometrically measured densities were expressed by the equation

$$\rho = \sum_i \left[\rho_i (T - T_r)^i \right] \qquad (15)$$

and used to evaluate surface tensions by the pendant-drop method. The coefficients for reference temperature $T_r = 25°C$ for PBDs and PDMS are summarized in Table II; since the comparison of results was made for calculations for 350 K, densities for 350 K are also presented. The measured values are shown in Figure 1. Density of PDMS is within limits reported in literature, density of both PDMS and nonfunctionalized PBD by 1% higher than that found by Anastasiadis et al.[44]

The complete PVT data of PBDs were measured by Dee and coworkers.

Measured surface tensions of PBD and interfacial tensions between PBD and PDMS

Both surface tensions of PBDs and interfacial tensions between PBD and PDMS were measured in the range from room temperature to ca. 150°C. The measured surface tensions are presented in Figure 2, and the interfacial tensions in Figure 3. The

TABLE II
Fit of Measured Temperature Dependence of Physical Quantities of PBD and PDMS

| Material	Density							Surface tensions					Interfacial tensions PBD/PDMS			
	Range (°C)	ρ (298 K) (kg m^{-3})	ρ_1 (kg m^{-3} K^{-1})	ρ_2 (g m^{-3} K^{-2})	ρ_3 (mg m^{-3} K^{-3})	ρ (350 K) (kg m^{-3})	Range (°C)	γ (298 K) (mN m^{-1})	γ (350 K) (mN m^{-1})	γ_1 (mN m^{-1} K^{-1})	Range (°C)	γ (298 K) (mN m^{-1})	γ (350 K) (mN m^{-1})	γ_1 (mN m^{-1} K^{-1})
Krasol LB	20–230	892.1	−0.586	0.09		861.9	25–150	33.6	29.9	−0.071	25–150	3.41	3.59	0.0034
Krasol LBM Ib	20–170	918.5	−0.621	0.19		886.8	25–160	34.2	30.9	−0.063	25–150	4.05	4.11	0.0010
Krasol LBM II	20–170	928.9	−0.550	−0.32		899.5	25–140	34.1	30.6	−0.068	50–150	(4.71)	4.33	−0.0072
Krasol LBM III	20–170	936.3	−0.597	−0.06		905.2	25–140	33.9	30.2	−0.071	30–150	(4.53)	3.89	−0.0012
Krasol LBD	20–200	929.1	−0.320	−1.46		908.5								
PDMS	20–250	971.4	−0.907	0.93	−3.27	926.4	25–250	20.3	17.2	−0.048				

Values in parentheses are extrapolated values.
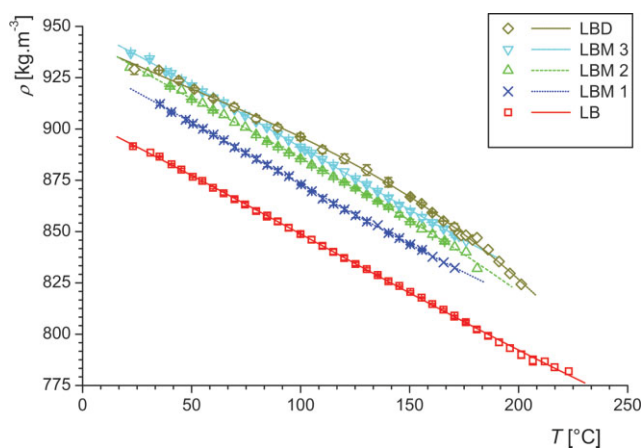
Figure 1 Dilatometrically measured densities of polybutadienes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

coefficients of linear equation for their temperature dependences are listed in Table II.

The dynamic component of surface tension of functionalized PBDs was quite high, e.g., at 150°C it was approximately 2–3 mN/m. At temperatures about 150°C and more, further changes of surface tension occur, apparently caused by chemical changes. Similar behavior for other polymers is commented, e.g., by Funke et al.[26] We tried to take the static surface tension before those changes as results, but the quality of the results seems to be unfavorably affected by overlapping of both processes. The reproducibility of surface tensions of functionalized PBDs as well as interfacial tensions PBD-PDMS above 170°C is poor.

Interfacial tensions between PDMS and PBDs show very small temperature dependences, at the low limits of the ranges found in literature[49] for other systems, or even growing interfacial tension with temperature. Nevertheless, such behavior is
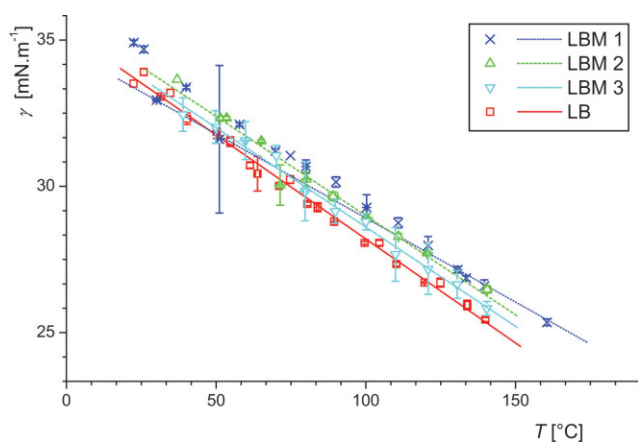
Figure 2 Measured surface tensions of polybutadienes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
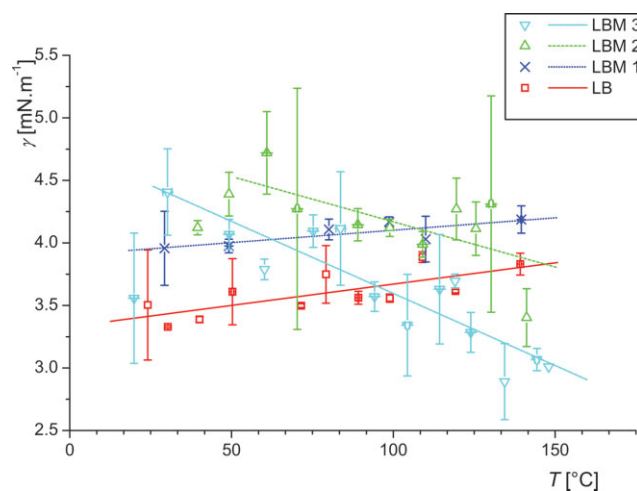
Figure 3 Measured PBD-PDMS interfacial tensions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

consistent with lattice theory with χ increasing with temperature in eqs. (13) and (14), but different from dependence measured on similar unsubstituted PBD by another authors,[59] when similar interfacial tensions were measured at about 60°C.

PVT data and reduction parameters

Determination of reduction parameters

Reduction parameters were calculated from PVT data using the methods listed in Table III. Initial reduction parameter estimates (called ansatz values in Ref. 7) for this regression were made by numerical solution of equations [(7) of Ref. 2] – [(25a) of Ref. 4] with known p, V, T, α.

The calculated reduction parameters are presented in Figures 4 (p^*), 5 (V^*), and 6 (T^*). Calculations using Dee's equation with δ as a fourth adjusted parameter led always to $\delta = 0.9532$ or close to this value and to the reduction parameters identical or differing at the third significant digit. Differences between the results of all three procedures using the Sanchez equation of state occurred at 3rd or 4th digit. When using PVT data from respective temperature and pressure intervals, the calculations did not converge in all of them to the result. PVT data from the low pressure ranges provided reduction parameters of pressure much higher than overall data or data from other ranges. The best fit of experimental PVT data of these materials was provided by the original Prigogine equations of state and by its modification by Dee.

Surface tension estimates

Figure 7 presents values of $\tilde{\kappa}$ parameter for eq. (5) as adjustable parameters to get experimental surface

TABLE III
Methods Used to Determine Reduction Parameters from PVT Data

Method Shortly	Equation of state	Parameters Adjusted	Input	Further information
Flory	Flory (1)	p^*, V^*, T^*		
Prigogine	Prigogine (2)	p^*, V^*, T^*	$\delta = 2^{-1/6}$	
Dee	Prigogine modified by Dee (2)	p^*, V^*, T^*	$\delta = 0.9532$	
Dee 4	Prigogine modified by Dee (2)	p^*, V^*, T^*, δ		Alternating steps of P^*, V^*, T^* fit with step of δ fit
Sanchez	Sanchez (3)	p^*, V^*, T^*	r	r determined by dividing M by segment size
Sanchez B	Sanchez (3)	p^*, V^*, T^*		r expressed using formula [eq. (39) of Ref. 4]
Sanchez ∞	Sanchez (3)	p^*, V^*, T^*	$1/r = 0$	

tension data from reduction parameters for respective equations of state. They are near to the value of $\tilde{\kappa} = 0.5$ suggested by Poser and Sanchez[16] for the cell models in Dee's modifications and the Sanchez-Lacombe model, when the chain length in Sanchez model was chosen as a number of nonhydrogen atoms in molecule and c/r was chosen as 0.111. Estimates from parachor (determined from Quayle data as reported by van Krevelen[23]) and density gives results not too far from experimental values. Estimates based on DICM using eqs. (7)–(10) appeared to be best fitable using formula (10) by Funke et al.[26] with W near to 0.8.

The effective thickness of surface layer was calculated nearly the same (0.7 – 0.8 nm) for all equations of state.

Interfacial tension, models of interphase, and estimates of Flory-Huggins interaction parameters

Expressing Flory-Huggins interaction parameters

The measured interfacial tensions and density data were used to calculate Flory-Huggins interaction pa-

rameters according to the models mentioned in "Theory of interfacial region" section. The χ parameter was expressed by the measured interfacial tension using an interpolation polynomial obtained by calculations for many values of χ. The profile calculation was made using both an approximating hyperbolic function (11) and by solution of simultaneous equations describing the profile, by the method of successive approximations[31] with following calculation parameters: lattice face-centered cubic ($m = 1/3$), 100 layers. For the calculation, the ratio of the number-average molecular weight and molecular weight of a chosen segment was taken as the number of segments in the chain (r). The calculations were performed for three segment definitions: segments corresponding to the monomer unit (structure unit A, B, MA, or ME, see "Materials"section), to one atom of the polymer main chain, and to any nonhydrogen atom. For the two-component systems (i.e., for interfacial profile calculations), the geometrical mean of volumes corresponding to segments of each component was taken in accordance with Helfand and Tagami[27] or Kamal et al.[60] The choice of
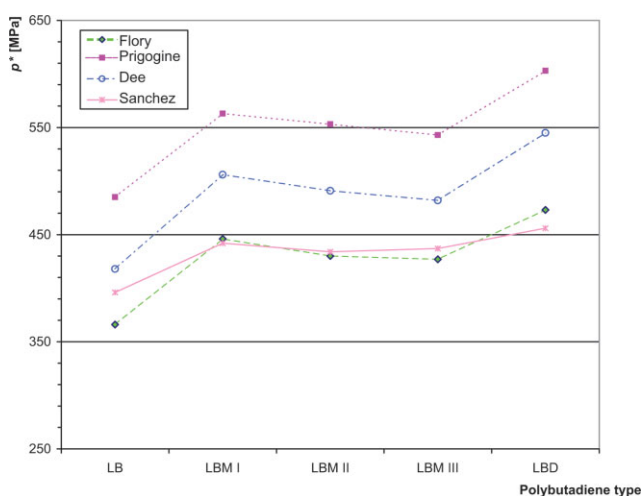
Figure 4 Reduction parameter of pressure p^* of measured PBD using different equations of state determined from PVT data for 350 K and whole pressure range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
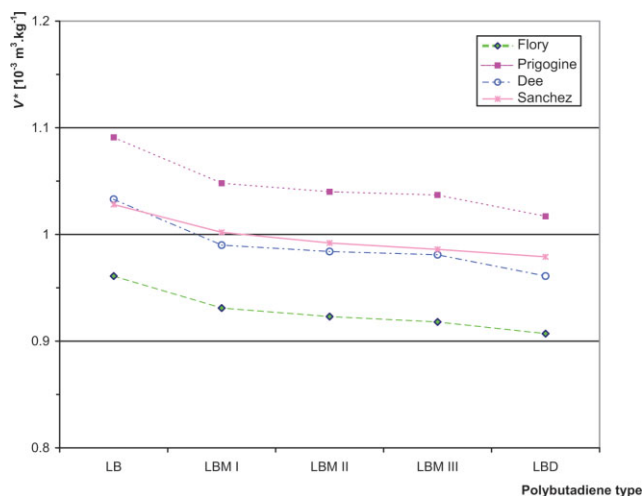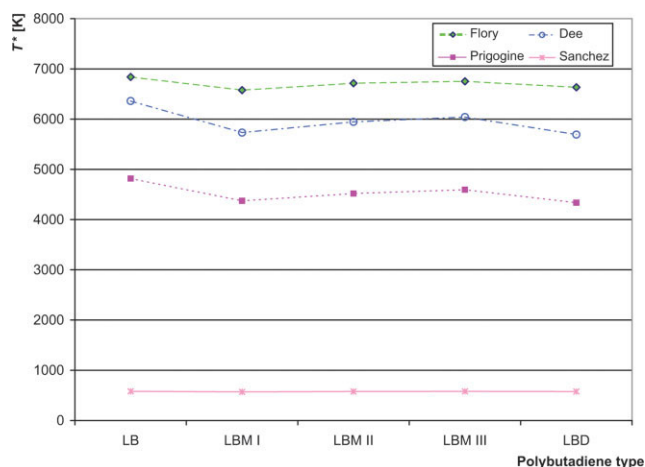
Figure 5 Reduction parameters of volume V^* of measured PBD using different equations of state determined from PVT data for 350 K and whole pressure range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
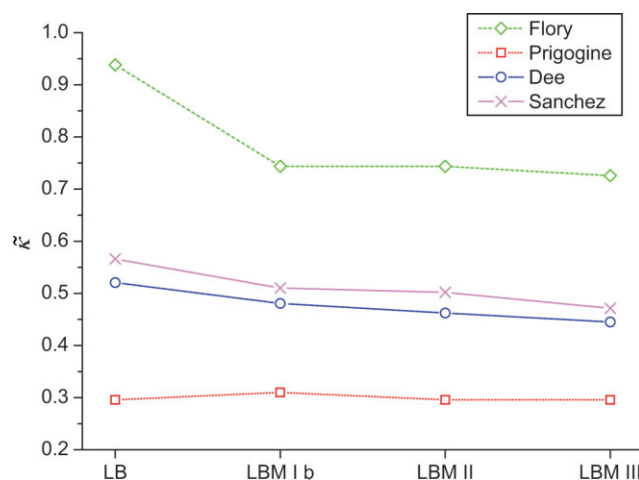
Figure 6 Reduction parameters of temperature T^* of measured PBD using different equations of state determined from PVT data for 350 K and whole pressure range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 Parameters $\tilde{\kappa}$ in eq. (5) providing the surface tensions corresponding to the experimental values for different equations of state. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the segment number as the number of monomer units in the molecule brings the problem of units of both components being of different size.

The numerical segment density and polymer chain segment length are parameters in the model analogous to diffusion equation; the dimensions, the number of segments in chain, and the lattice type are parameters of the lattice theory. They were expressed from density, number-average molar mass, and molar mass of the chosen segment.

The value of q parameter in the profile-approximating function (11) was determined by solution of one of the equations describing the profile [eq. (9) in Ref. 32] where all φ_i were expressed using eq. (11). The equation for a layer adjacent to the central layer was chosen since both sides of the equation would be identically equal to zero for the central layer.

The equilibrium composition of both phases had to be calculated as an intermediate result of composition profile solution. For this operation, the range limits of possible solutions and an initial estimate were expressed analytically from an approximate formula for high molecular weight. The simultane-

ous equations were solved in this interval using the Newton-Raphson method with controlled damping and definition domain observation.

## Comparison of models and influence of segment choices

Comparison was made for nonfunctionalized PBD (LB) and 350 K with the input (measured) value of interfacial tension 3.6 mN/m. The influence of segment choice on input parameters of the calculation is shown in Table IV.

Comparison is shown in Figure 8, calculations using the profile approximation with hyperbolic function (11) and successive approximations method give quite similar results considered to be true results according to model of Roe for all systems and segment choices. An approximate formula for infinite chain length (13) provides the Flory-Huggins interaction parameters lower by ca. 10%. The Flory-Huggins interaction parameters found using Helfand's formulae lie between 0.3 and 0.75 of the value obtained by Roe's successive approximations method, depending on the chosen segment size.

TABLE IV
Influence of Segment Choice on Parameters Used in the Calculation in PBD/PDMS System

Segment choice	Monomer unit	Main chain atom	Nonhydrogen atom
Number of PDMS segments	1851	3703	7405
Number of PBD segments	45	180	180
Critical χ	0.0148	0.00414	0.0037
Segment volume (nm^3)	0.1175	0.0415	0.029
Volume fraction of PBD in PDMS phase	10^{-6}	10^{-9}	10^{-7}
Volume fraction of PDMS in PBD phase	10^{-204}	10^{-161}	10^{-240}
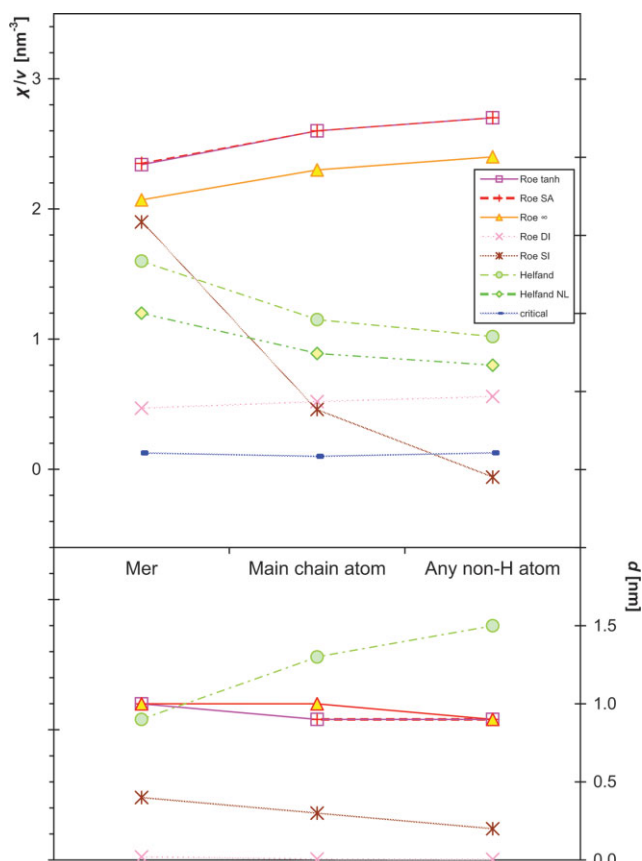
Figure 8 PBD (LB)-PDMS interaction densities and effective thicknesses of interphase calculated from measured interfacial tension and density data using several procedures for different segment choices. Roe tan h = Roe's model with profile approximation using tanh function; Roe SA = Roe's method of successive approximations; Roe ∞ = Roe's approximation for infinite chain length; Roe DI = Roe's formula for diffuse interface; Roe SI = Roe's formula for sharp interface; Helfand = Helfand's model neglecting nonlocal energy; Helfand NL = Helfand's model without neglecting nonlocal energy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Experimental data do not allow preferring either Roe's or Helfand's model.

The larger segment leaded naturally to higher absolute value of Flory-Huggins interaction parameters representing interaction energy per segment pair. An interaction density,[29] χ value divided by segment volume, is more suitable to compare the results obtained for different segment choices. The interaction density slightly increases with decreasing segments for most Roe's procedures, whereas interaction densities obtained using Helfand's formulae slightly decrease, approaching one another and deviating from the results by Roe's methods. For the largest chosen segment size, the χ parameters obtained using various formulae are closest to each other.

Influence of modifications on material properties of polybutadienes

Influence of modifications on density, surface, and interfacial tensions

Density. As shown in Figure 1, the density increases with functionalization of PBDs, according to the assumption of volume contraction due to attractive forces of functional groups. The density increase due to terminal OH groups is about 1%, due to maleic acids on one chain end about 2%, whereas due to them on second end about 1%, and due to side maleic anhydride groups only 0.5%. Prepolymer Krasol LBD[TM] has the density at the higher end of this range, but its temperature dependence is not linear, becoming more rapid at higher temperatures. At ca. 170°C, a rapid density decrease together with marked viscosity increase occurs for maleinized samples. The probable cause is the formation of intermolecular anhydride (it can have higher density, but the released water lowers the measured density).

Surface tension. The surface tension was unexpectedly highest for PBD maleinized at one end of chain and decreased with further maleinization.

Interfacial tension. The interfacial tension between PBDs and PDMS generally grows with hydroxylation and maleinization at lower temperatures. Although interfacial tension usually decreases with growing temperature for general systems, it grew for nonfunctionalized PBD and for PBD maleinized at one end of chain and decreased for PBDs with both chain ends maleinized.

### Relations between properties of polybutadienes

A simple correlation analysis of all known material characteristics of PBDs as well as of measured and calculated parameters was made. Because of only six samples (four, where all characteristics were measured) with an incidental increase in the maleinization degree with molecular weight, any conclusion can be interpreted only as tentative.

The molecular weight shows strong correlation with the density and with volume reduction parameter. Correlation coefficients between molecular weight and Flory-Huggins interaction parameters about 0.5 might be due to the content of carboxyl or other groups with a compatibilization effect than to molecular weight; the influence of chain length on surface tension might be involved in the entropic term in both the used models. The reduction parameter of pressure seems to increase, and reduction parameter of temperature to decrease with the presence of OH or isocyanate groups rather than with other characteristics.
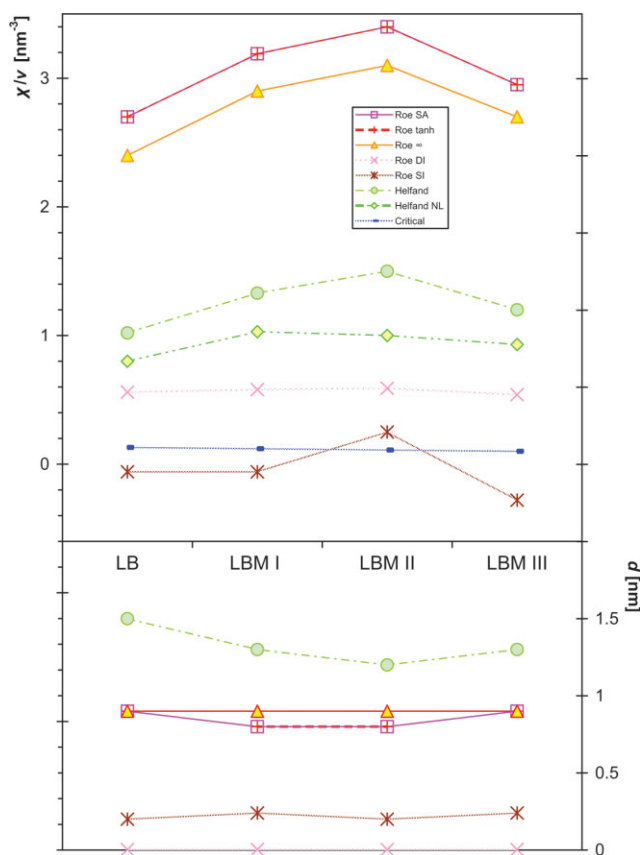
Figure 9 PBD-PDMS interaction densities and effective thicknesses of interphase calculated from measured interfacial tension and density data using several procedures for different polybutadienes. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

The correlation between reduction parameters of temperature and Flory-Huggins interaction parameters of PBD/PDMS system is significant: -0.5 for cell models and from -0.8 to -0.9 for the Sanchez-Lacombe equations. This is consistent with the connection of those parameters with cohesion and the interaction energy of material.
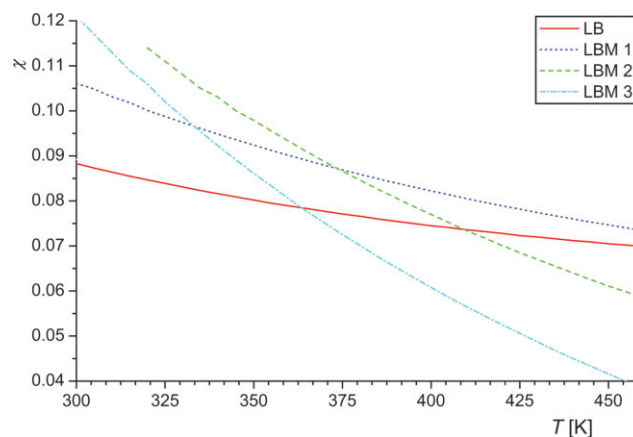
Figure 10 Temperature dependence of Flory-Huggins interaction parameters of PBD/PDMS systems evaluated from interfacial tension. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Rather than the interfacial tension between PBD and PDMS, the χ parameters calculated from them show a dependence on composition, as shown later.

Functional groups and Flory-Huggins interaction parameters

Flory-Huggins interaction parameters for a segment chosen as a part of macromolecule containing one nonhydrogen atom, calculated from interfacial tensions for systems PDMS/PBD at 350 K, and calculated thicknesses using different models and approximations are shown in Figure 9. The Flory-Huggins interaction parameters of PBD-PDMS systems determined using Roe's successive approximations method from experimental interfacial tension in temperature range 300–450 K are presented in Figure 10, showing χ decreasing with temperature, more markedly for more maleinized materials. It shows that maleination makes its temperature dependence steeper, whereas the hydroxylation

TABLE V
Components of Flory-Huggins Interaction Parameters for PBD/PDMS System

PBD	Average number of non-H atoms in groups					Flory-Huggins interaction parameter components			
	B	A	ME	MA	Molecule	χ	χ_H	χ_S	Formula
LB	180	0	0	0	180	0.08	0.049	0.031	$\chi_{LB} = \chi_B$
LBM 1b	186.4	4	11	0	201.4	0.092	0.084	0.008	$201.4\ \chi_{LBM1} = 186.4\ \chi_B + 11\ \chi_{ME} + 4\ \chi_A$
LBM II	190	0	22	0	212	0.098	0.158	-0.060	$212\ \chi_{LBM2} = 190\ \chi_B + 22\ \chi_{ME}$
LBM III	205.2	0	22	5.5	232.7	0.086	0.203	-0.117	$232.7\ \chi_{LBM3} = 205.2\ \chi_B + 22\ \chi_{ME} + 5.5\ \chi_{MA}$
Group									
B						0.08	0.05	0.031	
A						-0.09	1.18	-1.27	
ME						-0.35	2.36	-2.72	
MA						0.25	1.10	-0.85	

increases it without the change of temperature dependence. Since the dependence is different for differently functionalized PBDs, an evaluation of components of χ corresponding to entropy and residual enthalpy[5,59,60] was made. The expression form by Sanchez and Lacombe[5] was used for this.

Since polymers are consisting of several types of segments, differing in their numbers, a series of χ_{ij} parameters should be used for the precise system description. It can be taken into account that χ is an average or effective Flory-Huggins interaction parameter. An attempt was made to isolate contributions of groups that are common or different in measured PBDs. If the heat of mixing for homopolymer pair is[6]

$$\frac{\Delta U}{kT} = \frac{r_1 N_1 r_2 N_2}{r_1 N_1 + r_2 N_2} \chi_{12} \qquad (16)$$

If polymer 1 is supposed to be a homopolymer and polymer 2 is a copolymer, and with neglecting of interactions between segments of the same polymer, eq. (16) will be

$$\frac{\Delta U}{kT} = \frac{r_1 N_1 N_2}{r_1 N_1 + \sum_i (r_{2i}) N_2} \sum_i (r_{2i}\,\chi_{12i}), \qquad (17)$$

where χ_{12i} is the interaction parameter between a segment of the first polymer and the ith type of segment of the second polymer and r_{2i} is the number of such segments in the molecule, the χ evaluated from experiment would be expressed using partial contributions of distinguishable units

$$\chi_{12} \sum_i (r_{2i}) = \sum_i (r_{2i}\chi_{12i}). \qquad (18)$$

Values of χ as well as its entropic and enthalpic components and their contributions ascribed to respective units are presented in Table V. Comparison suggests that (at 350 K) contribution of hydroxy groups (units labeled A in this text) to the χ between PBDs and PDMS is slightly positive and contribution of maleic or fumaric acid linked to the polymer chain through ester bond (ME units) is markedly positive, prevalently due to enthalpic contribution, whereas that of pending maleic anhydride (MA) is markedly negative because of its entropic contribution.

CONCLUSIONS

For several liquid PBDs, PVT data, surface tensions, and interfacial tensions between them and PDMS were measured. The best fit of experimental PVT data of liquids PBDs was provided by the Prigogine equations of state, both the original and modified by Dee. The best prediction of surface tension using the Cahn and Hilliard procedure was obtained using Dee's modification of the Prigogine equation and the Sanchez-Lacombe equations of state. The equation by Funke et al.[26] appeared best applicable using the DICM.

For the description of interface between measured polymers, Helfand's formulae lead to lower values of Flory-Huggins interaction parameters and higher calculated effective thickness of interphase than results of Roe's procedures; nevertheless, no supporting information is available to decide, which of them is more appropriate. The Flory-Huggins parameters obtained using different methods are in the best mutual agreement for the choice of larger segment.

All investigated modifications of PBDs increase the density. The maleic ester end groups increase both surface tension and interfacial tension and bring a positive contribution to Flory-Huggins interaction parameter (again owing to its enthalpic component), whereas the pending maleic anhydride groups have shown the opposite effect, a negative contribution to χ parameters concerns mainly its entropic component.

NOMENCLATURE

A	geometrical constant for an attractive component of the Lennard-Jones potential
a	area of one position in the lattice
a	Helmholtz energy per volume unit
b	the layer distance in the lattice
B	geometrical constant for a repulsive component of the Lennard-Jones potential
d	effective interface thickness
k	Boltzmann constant
l	relative number of adjacent segments in the same layer
m	relative number of adjacent segments in one neighboring layer
M_s	molar mass per repeating unit
n	number of segments or cells in system
N	number of molecules in system
N_A	Avogadro constant
P	parachor
q	parameter for approximation of concentration profile (slope of interface)
R	gas constant = 8.31441 J mol^{-1} K^{-1}
r_i	number of segments in chain of polymer i
T	temperature (K)
V	volume, molar volume
v	segment volume

W	adjustable parameter in modified Patterson equation
z	number of neighboring segments
α	temperature dilatation coefficient $= (1/V)(\partial V/\partial T)_p$
β	isothermal compressibility $-(1/V)(\partial V/\partial p)_T$
γ	surface or interfacial tension
δ	geometric factor in free volume expression
κ	constant of the Cahn–Hilliard equation
ρ	density
ρ_j	number density of segments of the component j
φ_j^K	volume fraction of jth component in phase or layer K.
χ	Flory-Huggins interaction parameter
χ_c	critical Flory-Huggins interaction parameter

Indices

$\circ$	quantity value in pure, standard or reference state
∞	extrapolated value for infinite chain length
i,j	related to component i or j
K	related to the phase or layer K
$*$	reduction parameter

Varia

$\sim$	(over the symbol) reduced quantity

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