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Reduction of the Interfacial Tension between Poly(dimethylsiloxane) and Poly(ethylene oxide) by Block Copolymers: Effects of Molecular Architecture and Chemical Composition

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ABSTRACT: Interfacial tensions σ were measured by means of the sessile drop method for mixtures of poly(ethylene oxide) [PEO, $M_w = 41$ kg/mol] with five samples of poly(dimethylsiloxane)s [PDMS, M_w ranging from 4 to 177 kg/mol] in the temperature interval 70−130 °C. Within experimental error σ does not depend on T and the influences of molar mass can be well described by a linear dependence on $M_n^{-2/3}$. The ability of block copolymers to reduce σ when added in small amounts was studied for two families of these substances. With type **I** all blocks are made of either DMS or EO and the members differ in the molecular architecture only (diblocks, triblocks, and "bottle-brushes"). Type **II** comprises diblock copolymers, and the members differ in the chemical composition of the blocks which consist of EO, styrene, or methyl methacrylate. The reduction of σ upon an increase in x_{add}, the base mole fraction of the additive in the PEO phase, is substantial for all additives under consideration; it can be well described by an equation of Tang−Huang containing two characteristic parameters: σ_s, the saturation interfacial tension approached in the limit of large x_{add}, and x_{char}, the additive concentration required to achieve 1/*e* of the maximum reduction. In the case of type **I** block copolymers, ν, the total number of DMS segments, turns out to be more decisive for their efficiency than their architecture, in contrast to the theoretical expectation. A lower limit of $\sigma_s \cong 1$ mN/m is reached for $\nu > 30$. At least the present representatives of type **II** additives are less efficient than those of type **I**; an increase in the number of segments does not change σ_s in a noteworthy way, whereas there exist indications that it reduces x_{char}.

Introduction

Instead of developing new polymers to meet the demand for advanced materials with desired properties, existing plastics are nowadays often mixed; the blending of commercial products is normally much cheaper than the synthesis of a new class of polymers. In the course of such blending attempts the incompatibility of most polymers and the need for their "compatibilization" plays an important role. One is therefore particularly interested in efficient additives which reduce the interfacial tension, i.e. make a fine dispersion of the phases easier, and improve the adhesion at the phase boundaries.

Block copolymers are the most promising "compatibilizers" encountered so far. For this reason several authors have already studied such additives with respect to the influences of concentration,[1] chain length,[2,3] chemical nature of the monomers,[4,5] molecular architecture,[6,7] and orientation.[8] The present, essentially experimental study deals with two aspects: first, with the effects of the molecular architecture of the block copolymers containing the same monomeric units as the homopolymer pair, and, second, with the effects resulting in the case of diblock copolymers from different kinds of monomeric units.

Experimental Section

Materials. The characteristic data[9−15] of the samples are given in Table 1. The subscripts in the abbreviations for the block copolymers indicate their degree of polymerization. In addition to diblock and triblock copolymers of dimethylsiloxane (DMS) plus ethylene oxide (EO), we also studied diblock copolymers of EO plus styrene (S) and that of S plus methyl methacrylate (MMA). Furthermore two bottle-brush-like copolymers of DMS (backbone) and EO (side chains at one of the end of the backbone on consecutive units) were also investigated.

Table 1. Characterization of Homopolymers and Copolymer Additives: PDMS, Poly(dimethylsiloxane); PEO, Poly(ethylene oxide); S, Styrene; MMA, Methyl Methacrylate

sample	M_n	M_w	produced by	range of wt % added to PEO
PDMS 177w	103	177	Wacker[9]	
PDMS 73w	47	72.5	Wacker[9]	
PDMS 40w	23.6	39.4	Wacker[9]	
PDMS 24w	12.5	23.7	Wacker[9]	
PDMS 4w	2.6	3.8	Wacker[9]	
PEO 41w	32	41	Hoechst[10]	
Copolymers Consisting of DMS and EO Blocks				
$DMS_8{-}EO_{27}$		1.8	ABCR[11]	0.5−38.0
$DMS_{21}(MS(-EO_{15}))_5{-}DMS$		5.0	Goldschmidt[12]	0.3−3.7
$DMS_{14}(MS(-EO_{15}))_5{-}DMS$		4.4	Goldschmidt[12]	0.2−21.5
$DMS_{15}{-}EO_{77}{-}DMS_{15}$		5.6	Dr. Maassen[13]	0.7−1.9
Diblock Copolymers of the X-*block*-Y Type				
$EO_{68}{-}S_9$		4.0	Goldschmidt[12]	0.5−71.1
$EO_{22}{-}S_{28}$		4.0	Goldschmidt[12]	0.1−70.4
$S_{75}{-}MMA_{110}$		17	Dr. Auschra[14]	0.8−18.8
$S_{238}{-}MMA_{290}$		54	Dr. Auschra[14]	0.1−14.6

The densities, ρ, of the pure polymers are taken from the literature.[16] For small concentrations of the added copolymer, it was assumed that the density of the homopolymers can be used for the evaluation of interfacial measurements; i.e., the ρ values of the additives were not required. In the case of the EO−S block copolymers where the range of the additive concentration under investigation was much larger (up to 50−70 wt %) than usual and the pure block copolymer was also

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taken as a drop, this information is indispensable. Here ρ_{EO-S}, the density of the copolymer, was calculated (assuming additivity of volumes and masses of the monomeric units) according to:

$$\frac{1}{\rho_{EO-S}} = \frac{w_{EO}}{\rho_{PEO}} + \frac{w_S}{\rho_{PS}} \tag{1}$$

where w_{EO} and w_S are the weight fractions of ethylene oxide and of styrene in the block copolymer. The density of the drop (PEO plus block copolymer) was evaluated with a formula in analogy with eq 1.

Methods. The interfacial tensions were measured using a sessile drop apparatus; pictures of the drops are recorded by means of a CCD video camera. The image of the droplet and the temperature measured in the matrix phase are fed into a computer which determines the dimensions of the droplet (height, h; maximum radius, r) and calculates the interfacial tension σ according to the equation of Porter,[17] which holds true as long as $h/r < 0.5$[18]:

$$\sigma = \Delta\rho g h^2\,(0.5 - 0.3047h/r + 1.219h^3/r^3) \tag{2}$$

$\Delta\rho$ is the density difference between the two coexisting phases and g is the gravitational constant.

The block copolymers were exclusively added to PEO 41w, the denser compound forming the drop, since they are almost insoluble in the matrix phase consisting of PDMS. The additive concentrations are therefore given in terms of the weight fractions w^*_{add}, where the asterisk serves as a reminder that this is not the composition of the entire two-phase system.

In order to achieve reproducible results in the interfacial measurements, the mixture of the droplet phase had to be prepared in slightly different manners for the different additives. (i) With DMS_8-EO_{27} and with the "bottle brush" polymers, the components were simply weighed together. In the latter case a sample was also prepared by freeze drying, using benzene as the solvent; but all data were identical within experimental error. (ii) For the copolymers of EO and S stirring turned out to be essential to guarantee a reasonably homogeneous distribution of the additive in the PEO phase. Another possible route to this state was found by dissolving the material in chloroform and precipitating it with methanol. The results of interfacial tension measurements with drops prepared in the above manners do not differ. (iii) Finally, with the copolymers of S and MMA the precipitation (in diethyl ether) from a common solvent (chloroform) turned out to be the only feasible route to produce homogeneity. Droplets of the required size—approximately 0.3 g with the "bottle brush" polymers and the triblock copolymer and 0.7 g with the diblock copolymers—were in all cases prepared under vacuum from these mixtures by melting weighted amounts of the PEO/copolymer mixture within an appropriate mold shaped from an aluminum foil.

All interfacial tension measurements were carried out in the temperature interval from 70 to 130 °C. The equilibration times (at 70 °C) after introducing the droplet into the matrix phase remained below 6 h (the value for σ being independent of time after this period). The measuring procedure consisted of at least one series upon heating and one upon cooling. In agreement with earlier observations concerning polymer solutions,[19] local equilibria are rapidly achieved (typically within 30 min) after changing the temperature. The typical experimental errors of the interfacial tensions resulting with the sessile drop apparatus are estimated to be ca. 10%

Results

Influences of Temperature and Molar Mass of PDMS. The interfacial tension measured for the binary system PDMS 177w/PEO 41w at 100 °C is 10.5 mN m^{-1}. This agrees well with the values obtained by Wagner[16] (10.6 mN m^{-1}) and Roe[20] (10.2 mN m^{-1}) for the same temperature. With the homopolymer blend and with almost all ternary systems, temperature influences turned out to be small as shown in Figure 1 for some representative examples. In view of this fact the subsequent discussion concerning the efficiency of different additives is performed on the basis of σ data for 100 °C taken from the linear regression of the T-dependence.

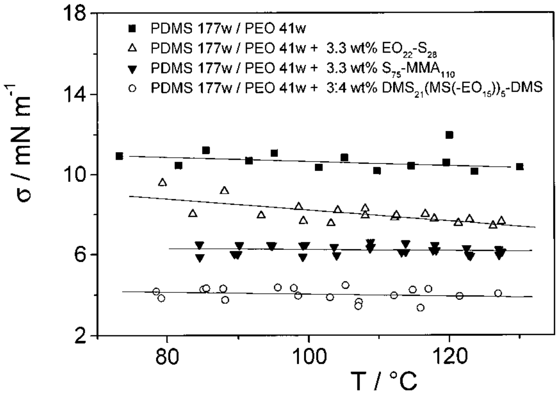

Figure 1. Temperature dependence of the interfacial tension σ for the systems indicated in this graph (concerning the abbreviations, see Table 1).

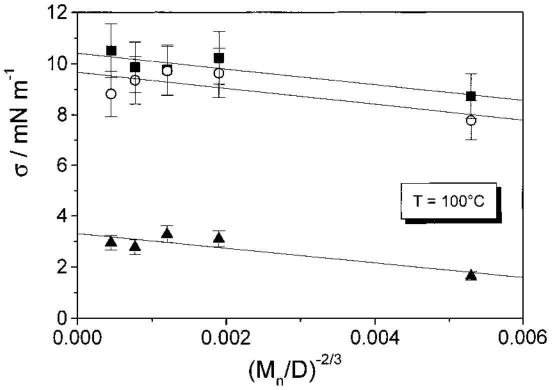

Figure 2. Interfacial tensions at 100 °C for blends consisting of PDMS (samples of different molar mass) and PEO 41w as a function of $M_n^{-2/3}$. The corresponding dependencies are also shown for the two ternary systems indicated in the graph and an additive concentration of 0.14 wt % in the droplet phase.

The dependence of the interfacial tension on the molar mass M of the polymers is often formulated[21]—by analogy with the situation in the case of surface tensions—as being proportional to $M_w^{-2/3}$. With the present measurements the molecular weight of PEO was kept constant and the molar mass of PDMS was varied between 4 and 177 kg/mol. The σ values for 100 °C are shown in Figure 2 as a function of $M_n^{-2/3}$. This graph demonstrates the applicability of the relation to the present system and shows that the molecular weight influences of the homopolymer PDMS are within experimental error identical for the binary system and for the ternary systems containing small amounts of the additive. Naturally this does not prove the dependence of σ on the $-^2/_3$ power of the molar mass.

Variable Molecular Architecture of the Additives (DMS−EO Block Copolymers). Diblock, triblock, and "bottle brush" like copolymers were studied. The results of these measurements as a function of the concentration of the different additives are shown in Figure 3 for 100 °C in terms of w^*_{add}, the weight fraction of the block copolymer *in the droplet*.

The graph in Figure 3 (some high concentration data for the diblock copolymer are not shown) demonstrates the following sequence in the efficiency of the additives

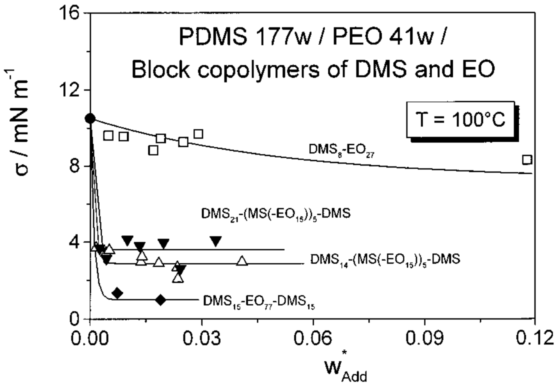

Figure 3. Interfacial tension at 100 °C for the systems containing DMS-EO additives of different architecture as a function of w^*_{add}, the weight fraction of the additive in the droplet.

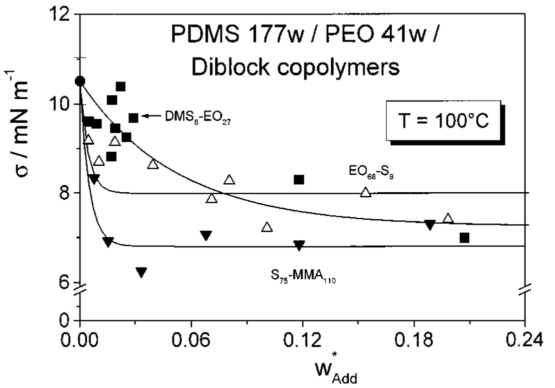

Figure 4. Interfacial tension at 100 °C for the systems containing diblock copolymers of different chemical nature as a function of w^*_{add}, the weight fraction of the additive in the droplet.

with respect to the maximum reduction of σ: triblock > "bottle brush" like > diblock copolymers.

Variable Chemical Nature of the Additives (Diblock Copolymers). The results for three of the five additives of the present type under investigation are shown in Figure 4, where some data for high copolymer concentrations are again omitted. From a comparison of these results with the findings presented in Figure 3 (also containing the data for DMS$_8$−EO$_{27}$) it is obvious that the diblock copolymers are substantially less efficient than the multiblock products under investigation.

Discussion

Influences of Additive Concentration. In order to facilitate the discussion on a molecular basis, the following considerations are performed in terms of x_{add}, the base mol fraction of the additives *in the droplet phase* defined as

$$x_{add} = \frac{N_{add}P_{add}}{N_{PEO}P_{PEO} + N_{add}P_{add}} \qquad (3)$$

where the N_i signifies the number of molecules of a degree of polymerization P_i (in the case of the copolymer, it is the total number of mers).

The measured dependencies $\sigma(x_{add})$ can be well represented within experimental error by two relations, that of Tang−Huang[22] and an equation formulated in analogy to the adsorption isotherm of Langmuir.[23] The former reads

$$\sigma = (\sigma_0 - \sigma_S)e^{-x_{add}/x_{char}} + \sigma_S \qquad (4)$$

where σ_0 is the interfacial tension of the binary system, σ_s is the saturation value of the interfacial tension, approached for high values of x_{add}, and x_{char} is the additive concentration that is required to achieve 1/*e* of ($\sigma_o - \sigma_s$), the maximum reduction.

The Langmuir analogue relation reads

$$\sigma = \sigma_0 - \frac{k_1 x_{add}}{1 + k_2 x_{add}} \qquad (5)$$

where k_1 and k_2 are fit parameters from which the quantities analogous to σ_s and x_{char} can be easily calculated from k_1 and k_2. Figure 5 shows two examples for the representation of the measured dependencies according to the above equations. It also contains the data points at high additive concentrations not shown so far.

Since it turned out that the evaluation according to eq 5 requires a relatively large number of data points at very low additive concentrations (which we could not obtain in all cases so far), the subsequent discussion is exclusively performed on the basis of eq 4 (Tang−Huang). The corresponding graphs are shown in Figures 6 and 7 where the different scale of the ordinate should be noted.

The characteristic parameters of eq 4 are collected in Table 2 for all additives. A comparison of the effects of the copolymers irrespective of the molecular architecture and chemical composition does not disclose a general interrelation of σ_s and x_{char}. In other words the efficiency of the different copolymers in terms of the maximum reduction of the interfacial tension ($\sigma_o - \sigma_s$) and in terms of the amount of additive required to realize a certain percentage of this effect (proportional to x_{char}) are independent of each other. Additives exist which are highly efficient with respect to x_{char}, but not so with respect to σ_s, like with S$_{238}$−MMA$_{290}$ and others, like DMS$_{32}$−EO$_{37}$−DMS$_{32}$, which are highly effective in both regards.

In view of the above statements the further discussion is performed separately for the additives consisting exclusively of the monomeric units of the homopolymers and for the diblock copolymers of different chemistry.

Effects of the Molecular Architecture. In principle the interpretation of the findings with the DMS−EO additives should be easier since the effects are expected to be primarily due to the geometrical arrangements of the monomeric units in the copolymer and its molar mass. A clear-cut discussion is nevertheless rather difficult for two reasons. (i) The experimental material is limited due to the unavailability of additive samples for which more than one of three parameters (molar mass, chemical composition, and molecular architecture) is kept constant and (ii) to theoretical problems in the translation of the differences in the molecular architecture (constant chemical composition) into the corresponding changes in the Flory−Huggins interaction parameter.

Disregarding these uncertainties, a comparison of the characteristic parameters of Table 2 gives the impression that it is only *v*, the total number of the monomeric units of DMS contained in the additive, which governs its efficiency, irrespective of the molar mass of the EO blocks and the distribution of DMS on different blocks.

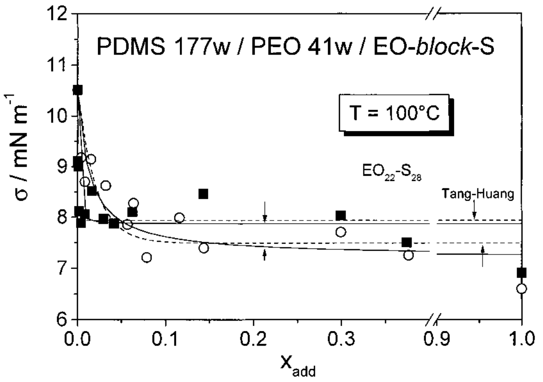

Figure 5. Interfacial tension at 100 °C for the ternary systems specified in the graph as a function of x_{add}, the base mole fraction of the additive in the droplet phase. The broken lines are drawn according to eq 4 (Tang−Huang) and the full ones according to eq 5 (Langmuir analog).

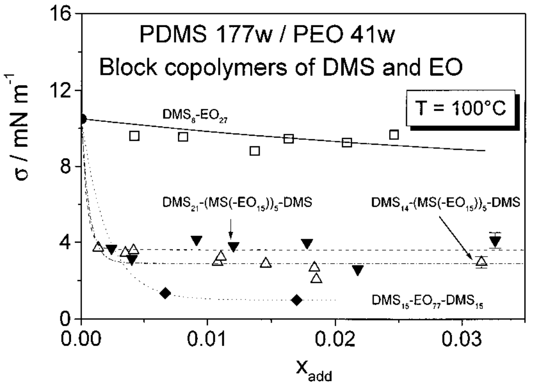

Figure 6. Interfacial tension at 100 °C for the ternary systems specified in the graph as a function of the base mol fraction of the additive in the droplet phase; the lines are fits to eq 4

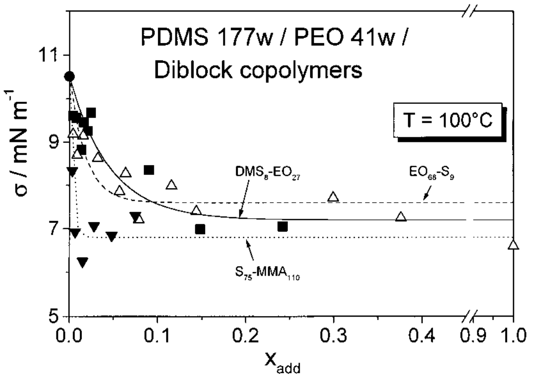

Figure 7. Interfacial tension at 100 °C for the ternary systems specified in the graph as a function of the base mole fraction of the additive in the droplet phase. The lines are fits to eq 4

The corresponding quantitative examination of the data shown in the Figures 8 and 9 corroborates this inference.

The lower boundary of σ_s reached as v exceeds approximately 30 is in good agreement with earlier observations[16] for triblock copolymers (DMS-*block*-EO-*block*-DMS) according to which each DMS block must contain 15 at least monomeric units for the effects to level off. Analogously to σ_s, the efficiency in terms x_{char} also approaches a lower limit upon an augmentation of v; in this case, however, the scale of the ordinate is logarithmic.

Table 2. σ_s**, Interfacial Tension at Saturation, and** x_{char}**, Characteristic Additive Concentration**

copolymer	σ_s (mN/m)	$10^3 x_{char}$
DMS_8-EO_{27}	7.2	50
$DMS_{21}(MS(-EO_{15}))_5-DMS$	3.6	0.4
$DMS_{14}(MS(-EO_{15}))_5-DMS$	2.9	1
$DMS_{15}-EO_{77}-DMS_{15}$	1.0	< 6
$DMS_4-EO_{37}-DMS_4$[16]	7.3	
$DMS_{16}-EO_{37}-DMS_{16}$[16]	1.2	
$DMS_{23}-EO_{37}-DMS_{23}$[16]	0.8	
$DMS_{32}-EO_{37}-DMS_{32}$[16]	0.8	0.3
$DMS_4-EO_{77}-DMS_4$[16]	8.6	
$DMS_{32}-EO_{77}-DMS_{32}$[16]	0.7	
$EO_{22}-S_{28}$	7.9	1
$EO_{68}-S_9$	7.6	20
$S_{75}-MMA_{110}$	6.8	3
$S_{238}-MMA_{290}$	7.7	0.1

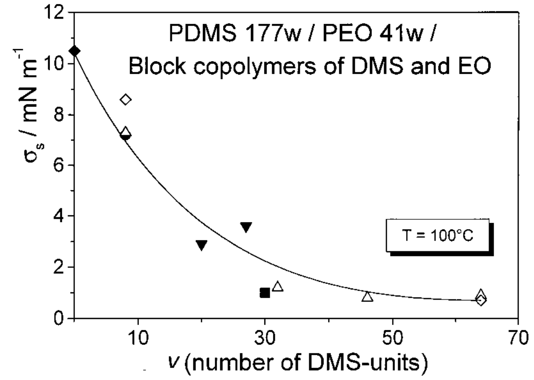

Figure 8. σ_s, the interfacial tension in the limit of large amounts of additive, as a function of v, the number of DMS units in the DMS-*block*-EO copolymers of different molar mass and molecular architecture. The line is just a guide for the eye.

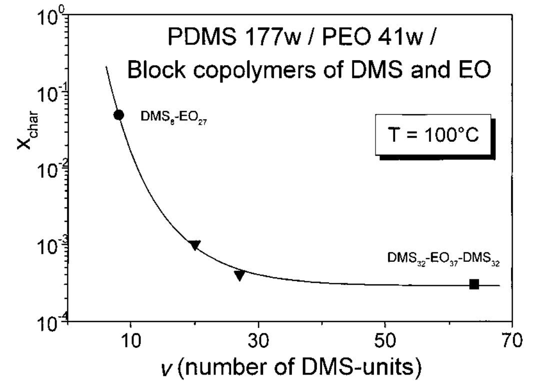

Figure 9. x_{char}, the characteristic base mol fraction of the additive, as a function of v, the number of DMS units in the DMS-*block*-EO copolymers of different molar mass and molecular architecture. The line is just a guide for the eye.

For the valuation of the present findings it must be kept in mind that the variation of the EO content of the different additives and of their molar masses is limited and that the above statement concerning their efficiency needs not be general for larger intervals of these variables. In any case the present results are at variance with some theoretical considerations according to which diblock copolymers should be generally more efficient than the corresponding triblock materials[24−27] and comblike copolymers, at a fixed molar mass, more efficient than linear multiblock copolymers.[28]

Effects of the Chemical Nature. The two diblock copolymers of ethylene oxide and styrene under investigation have the same molar mass and differ only in chemical composition. Keeping experimental uncertainties and the fact that σ_s is a derived quantity in mind, the lower limit of the interfacial tension does not differ; x_{char}, on the other hand, gives results considerably lower for the product with the higher content of styrene. It appears noteworthy that the effect is ca. 5 times larger than anticipated on the basis of the assumption that a certain concentration of S segments is required to reach saturation at the interface; this finding indicates that it is not only the content of mers in the additive that governs the value of x_{char} but also their assembly to different blocks.

With the two diblock copolymers of styrene and methyl methacrylate the ratio of the monomers is identical and the overall molar mass varies. A conclusive interpretation of these results is difficult due to the lack of a sufficiently large number of data points at high dilution. The values of σ_s do again not differ within experimental accuracy. The x_{char} value resulting from the primary data turns out to be considerably less for the higher molecular weight additive; this effect—which still requires confirmation—could be due to the above-mentioned effect of connectivity, i.e. distribution of mers onto blocks of different lengths.

The interpretation of the findings with the diblock copolymers in terms of the Flory—Huggins interaction parameters between the different monomeric species would be interesting. Calculations have therefore been performed starting from the solubility parameter theory. These results did, however, turn out to be inconclusive and could not account for the experimental observations. For that reason we have applied an approach reported in the literature for homopolymers to the present copolymers.

Noolandi[29] has formulated the conditions under which a homopolymer C reduces the interfacial tension in a binary system A/B as

$$\sigma_{AB} > \sigma_{AC} + \sigma_{BC} \tag{6}$$

We use this criterion analogously, with the modification that the homopolymer C is in our case a diblock copolymer of the type X-*block*-Y, where X and Y can be identical with or different from the homopolymers under consideration. In applying the above inequality it is assumed that the additive arranges itself at the interface in such a manner that it exposes one of its block to the homopolymer A and the other to homopolymer B (Janus-like behavior). The relation corresponding to the above expression thus reads for the present systems

$$\sigma_{PDMS/PEO} > \sigma_{PDMS/X} + \sigma_{Y/PEO} \text{ or } \sigma_{PDMS/PEO} > \sigma_{PDMS/Y} + \sigma_{X/PEO} \tag{7}$$

where the maximum reduction of the Gibbs energy (lower value on the right hand side of the inequalities) decides which of the two possible arrangements formulated above is actually realized.

$\sigma_{PDMS/PEO}$ is known from the present measurements (10.1 mN m^{-1} at 140 °C) and $\sigma_{PDMS/PS}$ can be taken from the literature[30] to be 6.1 mN m^{-1} at the same temperature. The unknown interfacial tensions of the binary subsystems PEO/PS, PDMS/PMMA, and PEO/PMMA were calculated according to the harmonic mean relation proposed by Wu[31]

$$\sigma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^{d}\gamma_2^{d}}{\gamma_1^{d} + \gamma_2^{d}} - \frac{4\gamma_1^{p}\gamma_2^{p}}{\gamma_1^{p} + \gamma_2^{p}} \tag{8}$$

using tabulated[31] values (140 °C) for γ_i^d, the contribution of dispersion forces to the surface tension of component i, and γ_i^p, that of the polar forces. The following values are obtained: $\sigma_{PEO/PS} = 1.3$ mN m^{-1}, $\sigma_{PDMS/PMMA} = 9.8$ mN m^{-1}, and $\sigma_{PEO/PMMA} = 0.1$ mN m^{-1}. In view of the small temperature dependencies of the interfacial tensions shown in Figure 1, these data were directly used to check the validity of the above inequalities. According to the present results the location of the blocks of the copolymers at the interface should be PDMS/S-*block*-EO/PEO and PDMS/S-*block*-MMA/PEO. In agreement with the experimental observation that the efficiency of the two types of block copolymers under consideration as measured by σ_s is very similar, the right hand side of eq 7 gives practically identical results, namely 6.1 and 6.2 mN/m, respectively.

Outlook

Although the experimental information on the efficiency of different kinds of block copolymers is still limited, the present results could fertilize a more realistic theoretical modeling of the typical features of such compatibilizers. The central characteristic parameters of block copolymers are (i) the chemical nature of the mers they contain, as compared to that of the homopolymer pair and their abundance in the molecule, (ii) the special arrangement of the monomeric units, i.e. number and lengths of the blocks plus functionality of the joints, and, last but not least (iii) the overall degree of polymerization of the additive. It is in the nature of this complexity that the parameters can often only be changed simultaneously so that the validity of the findings remains—as in the present case—limited. Some tentative statements can nevertheless be made if one keeps in mind that they need not necessarily be general.

With all systems under investigation, the reduction of σ upon an increase of the concentration of the additive can be well described by two parameters (σ_s, measuring the maximum attainable reduction of σ, and x_{char}, characterizing the amount of material that is required). The efficiency of additives in terms of σ_s is considerably larger for the block copolymers containing the monomeric units of the homopolymers than it is for the diblock copolymers, for which at least one of the blocks contains an additional kind of monomer. This finding calls for a more explicit theoretical discussion starting from the fact that the minimization of the Gibbs energy is based on only one interaction parameter in the former case, whereas at least three parameters are involved in the latter. An intuitively expected general interrelation between x_{char} and σ_s could not be observed. From the present findings one can also tentatively conclude that the diblock copolymers become more efficient in terms of x_{char} (less material is required to achieve a certain fraction of the maximum possible reduction of σ), at approximate constant values of σ_s, upon an augmentation of the length of the block interacting most favorably with one of the homopolymers. It appears obvious in this context that the spatial arrangement of the different blocks of the additives within the transition layer between the two bulk phases of the homopolymers plays a decisive role for the rationalization of the observation that the efficiencies, with respect to x_{add} and to σ_s, do not necessarily match. In any case there is still much more theoretical and experimental work required for a predictive understanding of the phenomena.

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