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INTERFACIAL TENSION IN POLYMER BLENDS

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ABSTRACT

Theoretical models of the interfacial tension coefficient in polymer blends, ν_{12}, were evaluated. A new working relation was derived that makes it possible to compute ν_{12} from the chemical structure of two polymers. The calculations involve determination of the dispersive, polar and hydrogen-bonding parts of the solubility parameter from the tabulated group and bond contributions. The computed values of ν_{12} for 46 blends were found to follow the experimental ones with a reasonable scatter of ± 36%.

Next, the experimental methods of ν_{12}-measurements were critically examined. Although many have been developed for low viscosity Newtonian fluids, most are irrelevant to industrial polymeric systems. For the present studies two were selected. Values of ν_{12} were measured using the so-called "capillary breakup method," and a newly developed method based on the retraction rate of deformed drop.

INTRODUCTION

There is a strong desire to predict the variations of morphology in polymer blends during the compounding and processing stages. This in principle can be done knowing on the one hand the deforming stresses and their duration, and on the other the recovery forces given by the interfacial tension coefficient, ν_{12}, between the two polymers. Thus, during the recent years, there has been renewed interest in the theoretical and experimental description of ν_{12}.

Theoretical models are not sufficiently advanced to predict the interfacial tension coefficient, ν_{12}. Furthermore, most commercial polymers are modified by the manufacturer and formulated with diverse low molecular weight additives, e.g., stabilizers, lubricants, metal ion scavengers, etc. The modifying resins and especially the low molecular weight additives may have a strong influence on ν_{12}. The additives of one polymer may chemically react

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either with the other resin or its additives, changing their behavior. Clearly, these effects cannot be taken into account by even the most sophisticated theory. Although a great number of experimental methods are available for the interfacial tension measurements of low viscosity Newtonian fluids, most of these techniques are not relevant to common industrial polymers. Thus, a general method of ν_{12} measurements, suitable for any pair of commercial polymers, must be developed.

This study is divided into two parts — 1. evaluation of ν_{12}-theories, and 2. measurements of ν_{12}. In the first part an effort was made to examine available theories for the calculation of ν_{12}. In the second, the experimental values of ν_{12} were obtained using two methods: the so-called "capillary breakup method," and the new, deformed drop retraction method, DDRM. In this report the three sources of information on ν_{12} are compared.

THEORETICAL EVALUATION OF ν_{12}

Several theoretical approaches have been proposed for the description of the surface and interface phenomena[1-9]. The lattice theories by Helfand,[1] Roe,[2] Noolandi[3] and their collaborators are based on the study of conformation and molecular environment. The derived relations are written in terms of the binary thermodynamic interaction, χ_{12}, and the lattice parameters. The theories do agree that the interfacial tension coefficient is a function of χ_{12}, but the predicted functional dependencies are different: $\nu_{12} \sim \chi_{12}^{n}$, with exponent n = *1/2 to 3/2*, depending on the assumptions.

These and the more recent theories can be considered as guides for the expected dependencies, but they cannot be used directly to calculate either the interfacial tension coefficient or the interphase thickness.[4]

Since there is a significant disagreement between the theoretical relationships derived for the interfacial tension coefficient, several attempts were made to calculate its approximate values from other physical quantities. Two methods have been considered, the first using the surface tension coefficients, ν_i, as an intermediate physical quantity, and the second the solubility parameters, δ.

Calculation of ν_{12} from the surface tension coefficients

Among the different approaches used to calculate the surface tension coefficient, ν_i, the most useful seems to be the parachor method.[5-7] This parameter was defined by Sugden[7] as:

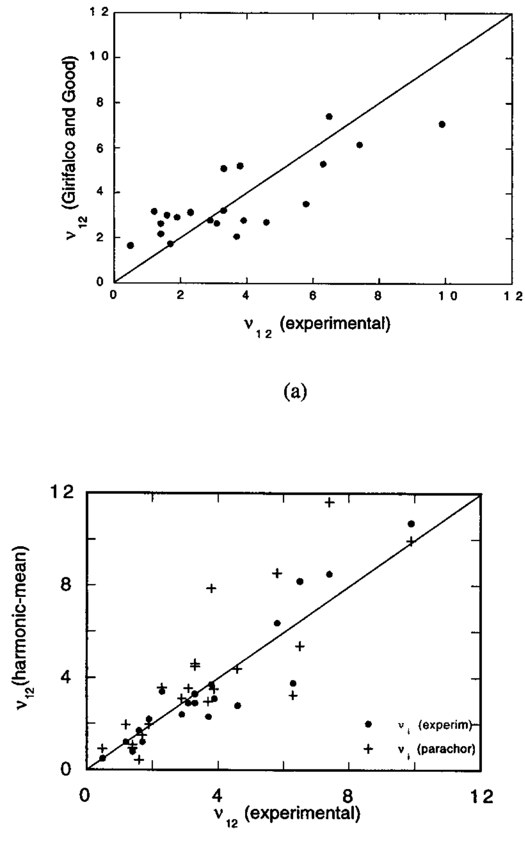
$$\mathbf{P}_i \equiv \mathbf{M}_i \nu_i^{1/4} / \Delta\rho_i \tag{1}$$

where M_i is the molecular weight of a liquid i, and $\Delta\rho_i$ is the liquid-minus-vapor density difference. The value of P_i can be calculated for any chemical compound from the contributions of the structural elements. Once the surface tensions are known, the second step for calculating the interfacial tension coefficient, ν_{12}, requires a relationship between ν_i and ν_{12}. Two basic relations have been used, that of Girifalco and Good, and an empirical one based on the so-called harmonic-mean.[6]

Girifalco and Good[8] proposed the following empirical dependence:

$$v_{12} = v_1 + v_2 - 2\varphi(v_1 v_2)^{1/2} \tag{2}$$

where φ is a semi-empirical interaction parameter.



(a)

(b)

Figure 1: Comparison between calculated and measured values of the interfacial tension coefficient. Fig. 1(a) calculated according to Girifalco & Good Eq. 2 from experimental values of surface tensions, Fig. 1(b) calculated according to the harmonic-mean Eq. 3 from experimental (●) and calculated values (+) of surface tensions incorporating the dispersive and polar contributions[4].

The concept of fractional polarity assumes that the intermolecular forces originate from the polar and dispersive interactions. Based on it, the so-called harmonic-mean equation was proposed in the form:

$$v_{12} = (v_{1d} - v_{2d})^2 / (v_{1d} + v_{2d}) + (v_{1p} - v_{2p})^2 / (v_{1p} + v_{2p}) \tag{3}$$

In Eq 3, superscript's *d* and *p* refer to dispersive and polar components of the surface tension coefficients. These are calculated assuming that there is a proportionality between them and squares of the solubility parameter. Fig.1(a) and (b) shows the result of the calculation of the interfacial tension coefficients calculated from Girifalco and Good equation and the harmonic mean. For the selected pairs of polymers,[6] the latter seems to provide a better correlation with the measured values of v_{12}.

Calculation of v_{12} from the solubility parameters

The cohesive properties of a material are related to the solubility parameter, δ_i, that originates from different types of interactions: dispersive or atomic, molecular of the type polar and hydrogen bonding, induced dipoles, metallic, etc. The first three types are most important, thus respectively:

$$\delta_i^2 = \delta_{id}^2 + \delta_{ip}^2 + \delta_{ih}^2 \tag{4}$$

The values of the δ_i-components can be calculated for any chemical substance from the tabulated group and bond contributions. Once δ_i is known for both polymers in the blend, the Huggins-Flory binary thermodynamic interaction parameter, χ_{12}, can be calculated from:

$$\chi_{12} = (V / RT)[\delta_1 - \delta_2]^2 \tag{5}$$

From Eqs 4 and 5, and predictions of the lattice theories of the interfacial tension coefficient, the authors obtained[4]:

$$\begin{aligned} v_{12} &= kRT\chi^n = k_1'(\rho RT)^{n-1}\left\{(\delta_{1,d} - \delta_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2\right\}^n \\ \text{or:}\quad v_{12} &= k_1(T)\left\{(\delta_{1,d} - \delta_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,h} - \delta_{2,h})^2\right\}^n \end{aligned} \tag{6}$$

To evaluate validity of Eq 6, the experimental data of v_{12} are plotted in Fig. 2 as a function of the computed values of the bracketed sum for 46 polymer blends. The straight line represents the least-squares fit. It is noteworthy that the exponent $n = 0.402$ is near the value of 0.5 predicted by Helfand *et al.* [1].

The relative success of the group contribution method raises the possibility of further improvement of this approach using the newly developed computational method of the molecular dynamics. Two approaches can be suggested. The first, an indirect one, would involve systematic computation of the group contributions to the solubility parameters, δ_{id}, δ_{ip}, and δ_{ih}, from which the interfacial tension coefficient and other physical quantities can be computed. The second, a direct one, would involve computation of the surface and interface interaction coefficients. The latter approach was recently described by Yao and Kamei.[10]

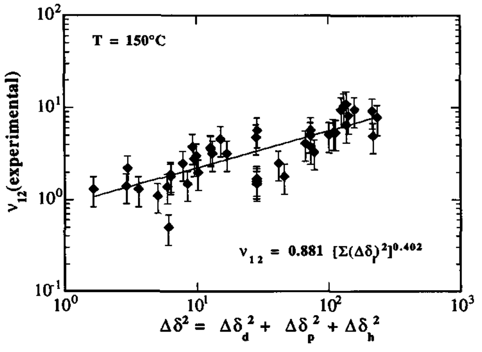


Figure 2: Interfacial tension coefficient at 150°C for 46 polymer blends plotted vs. the solubility parameter contributions.

MEASUREMENTS OF v_{12}

The available methods

For the low viscosity Newtonian fluids several methods of v_{12}-measurements have been developed.[11] However, the high viscosity of industrial polymer melts makes most of these techniques irrelevant. The remaining ones, useful for determination of v_{12} in high molecular weight polymeric blends, can be divided into two categories: equilibrium and dynamic methods.[12]

Pendant, sessile, and spinning drop methods are well-known equilibrium techniques. However, they are rarely applicable for the measurements of v_{12} of common, high viscosity industrial polymer blends. A long time is usually required to reach the equilibrium what may lead to thermal degradation and uncertain validity of the measurement. As a solution, most authors have been using a low molecular weight model system. This approach, however, defeats the main purpose of the data generation — to characterize the resins of interest, with all the modifiers and additives they bring into the blend.

In dynamic methods, the determination of the interfacial tension coefficient is based on the time evolution of the shape of a fluid particle, from a non-equilibrium to an equilibrium state. The evolution is basically driven by the interfacial tension and depends on the initial shape of the particle.

The capillary breakup method, based on Tomotika's theory, is the best known. It seems that Chappelear[13] was the first to apply this technique to measure the interfacial tension coefficient of polymer blends. Further refinements of the method can be found in Ref. 14. The method is relatively simple and requires no use of highly specialized equipment, providing that the zero-shear viscosity of the investigated polymers at the processing temperature is known.

The deformed drop retraction method,[15] DDRM, has been recently proposed and makes it possible to determine ν_{12} from the time evolution of deformed ellipsoidal fluid particle toward its spherical equilibrium form. Assuming an ellipsoidal shape for a drop of initial radius R_0 deformed under simple shear, the following relation was found:

$$D = D_0 \exp\left\{ -t \left[\frac{40(\lambda+1)}{(2\lambda+3)(19\lambda+16)} \frac{\nu_{12}(t_c)}{\eta_m R_0} \right] \right\} = D_0 \exp\{-t/\tau\} \qquad (7)$$

with $D \equiv (L - B)/(L + B)$ (where L and B represent the long and short diameter of the prolate ellipsoid, respectively), λ is the viscosity ratio, η_m the matrix viscosity, $\nu_{12}(t_c)$ the interfacial tension at the polymer-polymer contact time t_c, and D_0 is the initial value of D at $t = 0$.

In principle, this relation is valid only for Newtonian systems. However, the method can be used to characterize viscoelastic materials provided that: 1. The retraction rate is sufficiently slow to ensure that the material behave as Newtonian, and 2. The elastic relaxation of the materials after deformation is faster than the ellipsoidal droplet retraction, that is, a clear separation of the two mechanisms can be achieved. The experimental results reported in this study were obtained using this latter technique and the capillary breakup method.

Materials

The polymers used in this work are listed in Table 1. Polystyrene (PS), ethylene-ethyl acrylate-maleic anhydride copolymer (EEA-MA), polymethylmethacrylate (PMMA), and two poly-ε-caprolactams, (PA-6) were dried under vacuum at 70°C for 72 hours before using. To verify the effects of small molecules on ν_{12} a typical additive for industrial polymer formulation, an antioxidant and metal deactivator, 1,2-bis(3,5-di-tert-butyl-4-hydroxy hydrocinnamoyl) hydrazine (*Irganox*™ MD 1024, Ciba-Geigy), was added to LDPE/PS and LDPE/PA-6 blends.

Rheological characterization

Both methods of ν_{12} measurements, the capillary breakup and the ellipsoidal drop retraction, involve low deformation rates, thus the only rheological parameter required for calculation of ν_{12} is the zero-shear viscosity, η_0 (see Table 1).

TABLE 1: ZERO-SHEAR RATE VISCOSITY OF MATERIALS

Material	η_0 (Pa·s) at (°C)	Supplier (Grade)
Polydimethylsiloxane (PDMS 31)	53 (25)	Aldrich Chemicals
Polydimethylsiloxane (PDMS 120)	2500 (25)	Aldrich Chemicals
Polyethylene glycol (PEG 400)	5 (25)	Fisher
Polybutadiene (PBD)	21 (25)	Stanchem (Indopol H100)
Polystyrene (PS 555)	5210 (200)	Novacor (555)
Polystyrene (PS 580)	66 (25)	Polysciences
Polystyrene (PS 103)	5770 (230)	Novacor (103-300)
Polystyrene (PS 220)	5210 (220) 1210 (230)	Novacor (PS 220)
High Density Polyethylene (HDPE)	$1\mathrm{x}10^5$ (200) $6\mathrm{x}10^4$ (230)	Novacor (HDPE 455)
Low density polyethylene (PE 300)	16900 (220) 6700 (250) 4200 (260) 2800 (280)	Dow Chemical (LDPE 300)
Low Density Polyethylene (LDPE 1001)	690 (230) 1280 (200)	Esso (Escorene 1001)
Ethylene-propylene copolymer (EP)	12000 (220) 8200 (240) 3960 (260)	Exxon (EP 047 S)
Polyamide 6 (PA-6 Z211)	1560 (230)	DuPont (Zytel 211 NC 10)
Polyamide 6 (PA-6 C316)	450 (220) 300 (240) 150 (250) 60 (280)	Rhone-Poulenc (PA-6 C316)
Polyvinylidenefluoride (PVDF)	21000 (220) 14400 (240) 7800 (260) 5400 (280)	Atochem (Foraflon FO 4000)
Poly(methyl methacrylate) (PMMA)	21000 (200) 2320 (230)	Rohm & Haas (V920-100)
Ethylene-ethyl acrylate-maleic anhydride terpolymer (EEA-MA)	-	Atochem (Lotader HX8690)

1) Results from the capillary breakup measurements

Optical micrographs of a typical capillary breakup experiment (PA-6 Z211 fiber, imbedded in PS 103 at T = 230°C) are presented in Fig. 3. The measured interfacial tension coefficient values are reported in Table 2. The two PE/PA-6 systems show different values: $v_{12} = 8.9$ and 11.3 mN/m for LDPE/PA-6 Z211 and PE 300/PA-6 C316, respectively. These results demonstrate that industrial polymers are not pure laboratory-grade products, with well-known composition and sharp molecular weight distribution. The materials contain nonnegligible amounts of stabilizers, antioxidants, lubricants, etc., each having its own interfacial activity. Similarly, differences in molecular weight distribution can lead to significant modification of v_{12} — low molecular weight oligomers tend to migrate to the interface, lowering the surface energy. Hence, it is not surprising that blends of PE and PA-6 supplied by different producers have different interfacial tension characteristics.

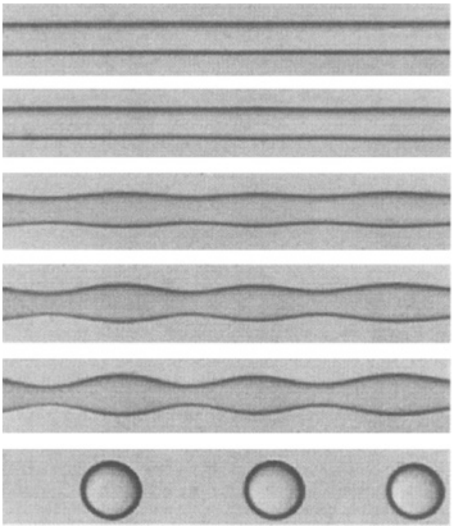


***Figure 3:** Optical micrographs of a PA-6 Z211 fiber imbedded in PS 103 matrix at 230°C. The initial diameter of the fiber was 46 μm. The photographs were taken (from the top) after: t = 0, 10, 19, 23, 25, and 29 min.*

Table 3 summarizes the average interfacial tension coefficients measured for each system, and compares the results with the literature data. Again, it is not surprising to find differences between the ν_{12} values determined in this work and those published for similar systems. In particular, the differences observed for PS/PA-6 blends at 230°C are large (the measured value was ν_{12} = 6.3 mN/m, to compare with ν_{12} = 20 mN/m[14]). However, the measured value is not far off that reported for PS/PA-66 at T = 266 to 283°C, viz. ν_{12} = 5.2-5.9 mN/m.[13]

It is known that addition of a copolymer with an appropriate chemical structure (a compatibilizer) can considerably lower the interfacial energy of immiscible polymer pair. Such a decrease is usually required for the generation of suitable blends' morphology. To examine effects of a compatibilizer on ν_{12} in the PA-6/EP blends, the following method was used. First, specimens of PA-6 C316 were soaked in a toluene solution of EEA-MA. After drying, the PA-6 fibers were imbedded in EP and v_{12} was measured. As evident from the data in Table 2, upon addition of EEA-MA the value of v_{12} at T = 220°C decreased from 10.3 to 2.8 mN/m.

TABLE 2: THE INTERFACIAL TENSION COEFFICIENT DETERMINED USING THE CAPILLARY BREAKUP METHOD.

Matrix	Fiber	T (°C)	v_{12} (mN/m)	Matrix	Fiber	T (°C)	v_{12} (mN/m)
PS 103	PA-6 Z211	230	6.3	EP	PVDF	220	3.4
LDPE 1001	PA-6 Z211	230	8.9			260	2.5
PE 300	PA-6 C316	220	11.7	EP	PA-6 C316	220	10.3
		250	10.9			240	9.4
		280	9.2	EP	PA-6 C316+ Lotader	220	2.8
PS 220	LDPE 1001	200	6.4	LDPE 1001 +Irganox	PS 220	200	6.4
		230	5.4	LDPE 1001 +Irganox	PA-6 Z211	230	14.4
PS 220	PMMA	200	1.8				
PMMA	LDPE 1001	200	5.9	PMMA	PA-6 Z211	230	6.9

TABLE 3: COMPARISON OF THE DETERMINED v_{12} VALUES WITH THE LITERATURE DATA.[13,14,16-22]

Matrix	Fiber	T(°C)	v_{12} (mN/m) measured	v_{12} (mN/m) literature
PS 103	PA-6 Z211	230	6.3	20, 5.2-5.9†
LDPE 1001	PA-6 Z211	230	8.9	13.5, 12.5
PE 300	PA-6 C316	250	10.9	10.7
PS 220	LDPE 1001	200	6.4	3.5, 4.2, 4.4, 4.7,4.8, 5.2
PS 220	PMMA	200	1.8	0.8, 1.2,1.26, 2.09.2.75
PMMA	LDPE 1001	200	5.9	8.6, 8.72, 8.8, 10

† PA-66 in PS at 266-283°C

The presence of additives incorporated into industrial polymers may have different effects on the interfacial energy. For example, low molecular weight ingredients, usually migrate to the interface, lowering v_{12}. They may also possess a structure prone to chemical reaction with the other blend's components, that may significantly modify v_{12}. To illustrate these effects, 0.5 wt% of a common antioxidant/metal deactivator (*Irganox*™ MD 1024) was added to LDPE before forming it into films for the capillary break-up experiments with either PS or PA. As shown in Table 2, the results for fibers of PS 220 do not indicate significant variation of v_{12}. However, the data for fibers of PA-6 Z211 show an increase from v_{12} = 8.9 to 14.4 mN/m. The effect could be due to a chemical reaction involving amine or amide groups of PA-6 and one of the many functional groups of the antioxidant/metal deactivator.

The measurements were also performed using high viscosity polymers. Specimens were prepared from HDPE, having $\eta_0(200°C)$ = 100 kPa·s and $\eta_0(230°C)$ = 60 kPa·s. Although the capillary breakup method should theoretically deal with such materials, all attempts to measure ν_{12} between HDPE and either PA-6 Z211, PS 103, or PS 220 failed — the distortions on the fibers were irregular and asymmetric. Furthermore, the determined values of q led to erroneous magnitude of ν_{12}. It seems that the fiber break-up method is limited to systems with the matrix viscosity below the 30-40 kPa·s.

It is important to mention the artifacts engendered by the fiber's stress relaxation observed during these studies. The fibers melt-spun from materials with high T_g exhibit high level of residual stresses that must be relaxed before attempting the interfacial tension measurements. If the fiber is not completely relaxed, the increases of the fiber diameter caused by fiber retraction mechanism superimpose on the break-up mechanism, modifying the kinetic of the process. The measurements performed using non-relaxed fibers can lead to values very much different from the true ν_{12}. For example, the measurements conducted on non-relaxed PA-6 Z211 fibers imbedded in PS 103 gave ν_{12} = 35 and 39 mN/m, to be compared to the average value of 6.3 mN/m obtained for the relaxed specimens.

2) Results from deformed drop retraction method, DDRM

Model specimens from the low viscosity liquids were prepared by first placing a 1 mm thick film of the more viscous component on a glass slide, placing on top of the film a fine fiber of the less viscous component (created by gently touching the surface of the film with a spatula previously wetted with the second liquid), preparing a second film of the more viscous material on another glass slide and placing it over the first film with the fiber. The fiber disintegration by the capillary instability resulted in formation of droplets with diameter $d = 50\text{-}200$ μm. In some cases, the breakup process was slow enough to determine the interfacial tension coefficient by the fiber disintegration method as well.

The specimens from the high viscosity industrial polymers were prepared by placing particles of the first polymer between two 1 mm thick films of the second polymer. The imbedded specimens were placed between two microscope glass slides, then on a hot-stage under a microscope. Heating at a temperature sufficient for melting both polymers provided good imbedding of the particles, that subsequently were able to relax their irregular form into spheres. The manual displacement of the guided upper glass slide induced shearing of the matrix, distorting the initial spherical drop by about 15% into a prolate ellipsoid.

After the deformation, evolution of the ellipsoidal drop shape was measured as a function of time. The experiments reported here involved viscoelastic liquids with relaxation time smaller than 1 s (exception was HDPE, which had a relaxation time in the 5-10 s range). In each case, care was taken to let the materials relax the elastic energy before beginning the measurements.

A typical retraction of deformed drop at T = 20-25°C is illustrated in Fig. 4. Here, a PS 580 droplet was immersed in PDMS 120. The retraction was nearly complete after 600 s. As expected, the extrema of the major ellipsoid's axis, L, were out of focus due to tilting of the prolate drop by the angle ϕ. The central part of the drop was placed in focus to follow the variations of B.

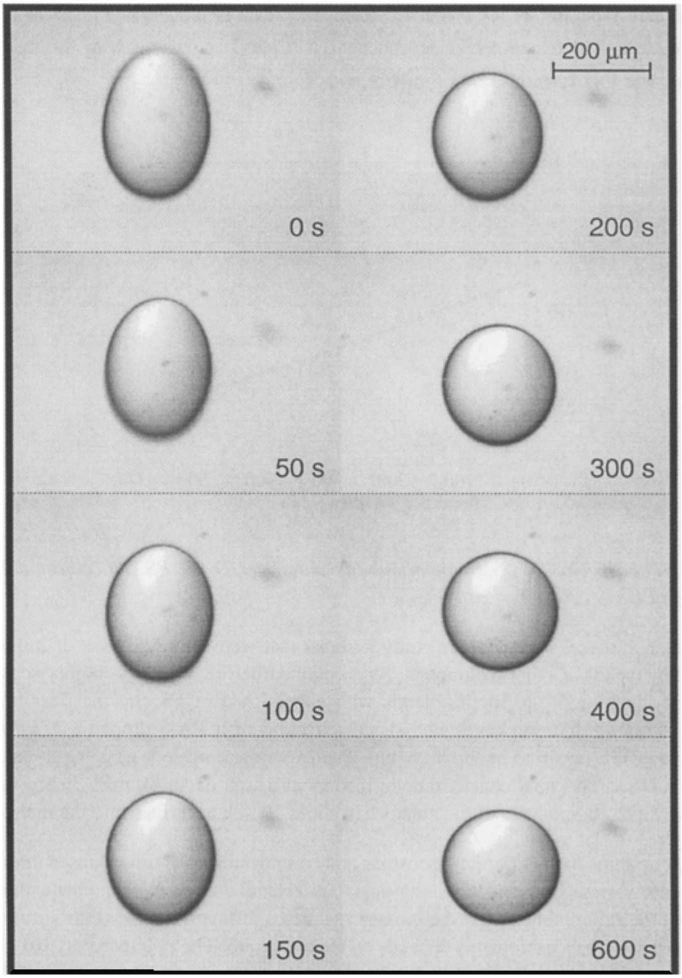


Figure 4: *Retraction of a PS 580 ellipsoidal drop immersed in PDMS 120 matrix at T = 20-25°C. Time of measurement is reported on each micrograph.*

The deformability parameter, D, calculated from these data is plotted in Fig. 5 in a semi-logarithmic scale. The experimental dependence is in good agreement with the theoretical predictions. For this system $v_{12} = 1.5$ mN/m, was found.

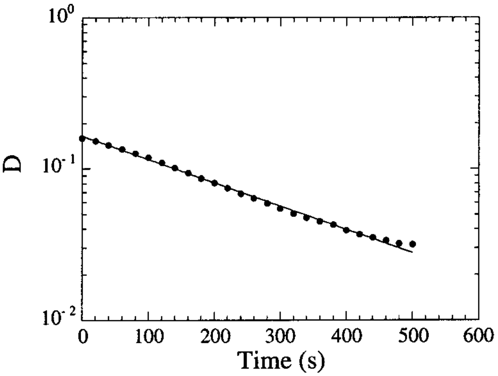


Figure 5: *Time evolution of the deformability parameter D for PS 580 ellipsoidal drop immersed in PDMS 120 at T = 20-25°C.*

The new method makes it possible to study systems that were either difficult or impossible to evaluate by means of other techniques. As mentioned before, owing to high viscosity of HDPE, determination of v_{12} for its blends with either PA-6 or PS, by the fiber breakup method was impossible. However, the shape retraction of a PA-6 droplet ($R_0 \approx 100\mu$m) imbedded in HDPE occurred in about 20 min. The experiment made it possible to calculate: $v_{12} = 10.2$ mN/m. The total contact time in molten state was about 30 min, hence the low molecular weight components of the blends had about 30 min to diffuse into the interphase.

As different systems have different viscosities and compositions, the time elapsed during the measurements varies. Consequently, the degradation and diffusion phenomena that take place during the experiments affect the measurement to a different degree. Furthermore, the time required for the measurements depends on the technique. The polymer-polymer contact times in, e.g., filament breakup and droplet retraction experiments, are usually different. Thus, it is not surprising that values of $v_{12} = v_{12}(t_c)$ determined for the same polymeric pairs using various methods are different.

The values of v_{12} measured by the deformed drop retraction method, DDRM, are compared in Table 4 with those determined using the filament breakup method (the values reported in the literature are cited in Table 3). The values are different, but the variation is acceptable. The agreement is expected to be improved by comparing the experimental data collected after similar polymer-polymer contact times.

TABLE 4: COMPARISON OF ν_{12} MEASURED BY DDRM WITH THOSE OBTAINED BY CAPILLARY BREAKUP.

Matrix	Droplet	T (°C)	ν_{12} (mN/m)	
			Ellipsoid retraction	Filament breakup
PDMS 120	PS 580	20-25	1.5	1.6
PDMS 31	PS 580	20-25	1.3	-
PDMS 120	PBD	20-25	2.6	-
PDMS 120	PEG 400	20-25	7.7	-
PS 555	PMMA	200	1.0	1.8
PMMA	LDPE 1001	200	4.3	5.9
PS 555	LDPE 1001	200	5.2	6.4
LDPE 1001	PA-6	230	10.0	8.9
HDPE	PA-6	230	10.2	-

Time dependence of ν_{12}

Since ν_{12} is defined in terms of the equilibrium thermodynamics, the non-equilibrium values that are determined by the new method should be considered apparent. Only the values measured at long polymer-polymer contact times can be consider to represent the equilibrium value of ν_{12}. It is instructive to examine the variation of the apparent $\nu_{12} = \nu_{12}(t_c)$ with the polymer-polymer contact time, t_c. The dependence is illustrated in Fig. 6 for LDPE 1001/PS 555 at T = 200°C.

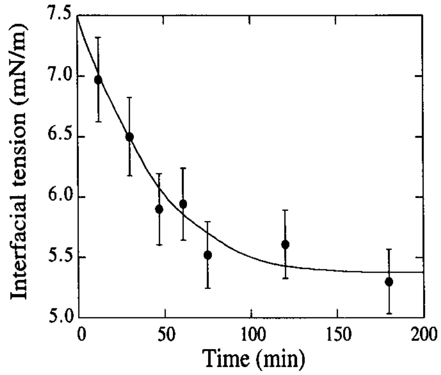


Figure 6: Evolution of the apparent interfacial tension coefficient in LDPE 1001/PS 555 system as a function of polymer-polymer contact time at 200°C. The vertical bars indicate ±10% error. The line is only a guide for the eye.

The data were collected repeating seven times the ellipsoid retraction measurement of the same specimen. The results show an initial rapid decrease of the apparent $\nu_{12}(t_c)$, then slower reduction of its value, and an equilibrium value, ν_{12} = 5.2 mN/m at the contact times larger than t_c = 75 min. Thus, for t_c varying from 12 to 180 min the apparent $\nu_{12}(t_c)$ decreased from 6.9 to 5.2 mN/m. This observation is in a qualitative agreement with the postulated migration of the low molecular weight species and impurities toward the interphase, the mechanism that would reduce the interfacial energy.

Note that at 200°C the filament breakup in LDPE/PS system occurred at t_c = 12 min. The average value of ν_{12} calculated from the data using the Rayleigh's instability equation was ν_{12} = 6.4 mN/m. This value is close to that of $\nu_{12}(t_c)$ = 6.9 mN/m obtained by DDRM for specimen exposed to 200°C for t_c = 12 min.

It is important to recognize that during compounding or processing of polymer blends there are high shearing and extensional stresses that cause continuous renewal of the interface. In such practical mixing conditions, it's difficult to say if this renewal accelerates the equilibration of the interfacial tension properties or at the opposite, if it creates a constant out-of-equilibrium state at the interphase.

CONCLUSIONS

1. This paper critically evaluated the theoretical models of the interfacial tension coefficient in polymer blends, ν_{12}.

2. A new working relation was derived that makes it possible to compute ν_{12} from the chemical structure of two polymers. The computed values for 46 blends were in a reasonable agreement with the experimental, literature values (error of ± 36%).

3. The experimental methods of ν_{12} measurement were critically examined.

4. The experimental values of ν_{12} for 12 polymer pairs were obtained using the capillary breakup method.

5. New method of ν_{12} measurements was developed. The deformed drop retraction method, DDRM, is based on the retraction of a deformed drop. Its two main advantages are: (i) simplicity and rapidity of measurements, and (ii) capability to determine the time evolution of ν_{12}.

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