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Surface tension and interfacial tension of polyolefins and polyolefin blends

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This paper focuses on the calculation of the interfacial tension of two systems: low-density polyethylene with isotactic polypropylene and high-density polyethylene with syndiotactic polypropylene. For this, three methods to measure the interfacial tension are compared: the use of Palierne's model, and Gramespacher and Meissner's model, both based on additional elasticity or long relaxation times brought by shape recovery of dispersed phase, and ab-initio calculation which requires the knowledge of the surface tension of the neat polymer measured at the same temperature. For that, a database collected from the literature is built in the first section of this paper, whether for the studied systems or for other systems of various olefinic homopolymers or copolymers with polypropylene. The results show the effectiveness of the Gramespacher and Meissner's model to calculate the interfacial tension of the studied systems for which the results were in agreement with ab-initio calculation and Palierne's model. Extension of the ab-initio calculation to olefinic copolymers was proposed.

1. Introduction

Polyolefins are the largest commodity thermoplastics in terms of production and consumption because of their numerous advantages such as ease of processing, relatively low cost, good mechanical properties, chemical resistance and good recyclability. Despite a wide variety of existing olefinic homopolymers or copolymers, the range of properties and the application domain can still be improved by blending and a considerable number of scientific papers have focused on this scope.^[1] Because synergistic properties are mostly obtained in heterogeneous mixtures, the control of the morphology of immiscible polymer blends and of its evolution during processing is very important. It is commonly admitted that a stable morphology and good adhesion usually provide interesting functional properties. Among important parameters, the knowledge of the interfacial tension between the components in the melt state is of major importance since it dictates the evolution of the morphology of immiscible polymer blends. Indeed, the interfacial tension is directly connected to the capillary number that describes the deformation and breakup of dispersed droplets or filaments of one polymer in the other.^[2] For example, the deformation of the dispersed droplets in a shear flow is governed by the balance between the interfacial forces, tending to maintain their spherical shape, and the viscous stress, that acts to deform it, thus increasing the interfacial area. The value of interfacial tension has also an effect on the equilibrium between coalescence and dispersion mechanisms. In the case of dispersed phase morphology, a finer morphology with a smaller equilibrium radius, is obtained by a higher shear, a lower interfacial tension between the phases and a lower volume fraction of the minor component.^[3] For co-continuous morphologies, in addition to its effect on phase dimensions, the interfacial tension also influences the continuity window and the percolation threshold at which the system changes from isolated dispersed droplets to at least one continuous domain.^[4]

The interfacial tension is also a key parameter that relates the physico-chemical properties to molecular and phase interactions. A poor interaction between the two phases and weak interfacial adhesion impacts the macroscopic properties of the blends. For polyolefins as PE and PP, the interfacial tension in the melt state is low as they are similar in their chemical structure. Even though, the control of the interfacial adhesion through the polymer structure, and therefore by a proper choice of the catalyst system, has been proposed as a possible alternative to the use of compatibilizers.^[5,6] The measurement of the interfacial tension has been presented as a tool to assess the effectiveness of the catalyst system showing a slight decrease of the interfacial tension with polyolefins polymerized with metallocene catalysts.^[7] The interfacial tension between polymer pairs has been widely studied in the 70's with reviews and data sets.^[8-10] Data are generally measured directly or indirectly by one of the five methods described in the comparison by Demarquette et al. :^[11] pendant drop, Neumann triangle, breaking thread, imbedded fiber retraction or rheological methods using the Palierne's model or Gramespacher-Meissner analysis both based on additional elasticity or long relaxation times brought by shape recovery of dispersed phase.^[12,13] These latter long relaxation times also affect the elongational viscosity which, when amplified by the consideration of multilayer structures, could be used to determine the interfacial tension.^[14] In the specific case of polyolefins blends, especially polypropylene and polyethylene or copolymers of α -olefins with ethylene, some data exist for isotactic (iPP) and syndiotactic polypropylene (sPP) mixed with high density polyethylene (HDPE), low density polyethylene (LDPE) and random copolymers of ethylene with α -olefins such as propene (EP), 1-butene (EB), 1-pentene (EPent), 1-hexene (EH) and 1-octene (EO). For iPP, the limits of miscibility with α -olefins copolymers are well established.^[1] Apart from polymers having low molecular weight,^[15] for which the range of composition for miscibility is larger, random copolymers of ethylene and propene are miscible when the content of ethylene is lower than 11 wt-%.^[16] On

the basis of many works of the same group, Yamagushi proposed that all copolymers whose α -olefin (1-butene, 1-hexene or 1-octene) content is above 50 mol-% may be miscible with amorphous iPP chains in the molten state.^[17] This was verified for 1-hexene with copolymers showing miscibility with ethylene content until 25 wt-%.^[18] But another group found that copolymers with 1-butene are only fully miscible when the content of ethylene is lower than 12 wt-%.^[19] Out of these composition ranges, at the boundary of the phase diagram, the polymers are immiscible, and in the melt state, a non-zero interfacial tension can be measured. **Table 1** summarizes the data of interfacial tension found in the literature for iPP and sPP with various ethylene polymers or copolymers with α -olefin monomers often obtained from measurements on blends. In the same table, the method of measurement at the given temperature is indicated. Some authors do not give the uncertainty range of the measures. When they are available, the molecular structures of the studied polymers are given. Unfortunately, in some cases, the comonomer contents were not given in the reference though they might be inferred from the density of the copolymers assuming a linear variation of the density with the weight fraction of comonomer for composition between 10 and 30 wt-%,^[20] independently of the comonomer nature, since the density is mainly driven by the crystallinity of ethylene sequences.

For iPP/HDPE, the average interfacial tension is 1.6 ± 0.2 mN/m at 220 °C.^[11] Another paper of the same group reports two values: 1.7 ± 0.3 mN/m for iPP/HDPE 90/10 blends and 2.6 ± 0.3 mN/m for the composition 80/20 of the same blend but the later concentration is very high and coalescence might be suspected.^[21] Recently, Samuel et al. have shown differences in the interfacial tension between HDPE and iPP related to the type of catalyst used for the polymerization of HDPE.^[7] The values reported for metallocene HDPE blended in metallocene iPP (0.9 to 1.2 mN/m) were significantly lower than that of Ziegler Natta type HDPE blended in metallocene iPP (1.6 to 1.9 mN/m). The difference was observed on measurements by the Gramespacher and Meissner's method but more accurate data were

obtained by the pendant drop method (0.5 ± 0.1 mN/m). For iPP / LDPE, the value of 2.1 mN/m at 190 °C was reported by Yamaguchi et al. but this is high in comparison to other data for any other ethylene-based polymer.^[22]

Table 1: Interfacial tension between various PP and PE homopolymers or copolymers, wt-% of comonomer is indicated or estimated from density (between parenthesis). *Method: P: Palierne, SB: sessile bubble, GM:Gramespacher-Meissner, IFR: imbedded fiber retraction.

Polypropylene	Polyethylene polymer or copolymer	T [K]	γ_{12} [mN/m]	Method*	Data PP	Data PE (or copolymer)	Ref
iPP	HDPE	493	1.6 ± 0.2	P	$M_w=76000$ $M_w/M_n=4.5$	$M_w=44000$ $M_w/M_n=3.2$	[11]
	HDPE	493	1.7 ± 0.3	GM	$M_w=340000$ $M_w/M_n=4.5$	$M_w=140000$ $M_w/M_n=3.2$	[21]
	HDPE	473	1.6-1.9	GM	$M_w=157000$ $M_w/M_n=3.0$	$M_w=65000$ $M_w/M_n=5.0$	[7]
	HDPE	473	0.9-1.2 0.4-0.6	GM PD	$M_w=157000$ $M_w/M_n=3.0$	$M_w=53000$ $M_w/M_n=2.8$	[7]
	LDPE	463	2.1	P	$M_w=570000$ $M_w/M_n=13.3$	$M_w=180000$ $M_w/M_n=5.1$ LCB= 4/1000C	[22]
	EP (26.3)	473	0.5	P	$M_w=304000$ $M_w/M_n=8.2$		[23]
	EP (24, estimated)	473	1.1 ± 0.1	IFR		d=0.870	[24]
	EB (24, estimated)	473	0.9 ± 0.1	IFR		d=0.870	[24]
	EB (19.4)	483	0.6	P		$M_w=114000$ $M_w/M_n=2$ d=0.880	[25]
	EB (12, estimated)	463	1.0	P	$M_w=570000$ $M_w/M_n=13.3$	$M_w=100000$ $M_w/M_n=3.3$	[22]
	EB (10, estimated)	503	1.7	GM		d=0.902 to 0.864	[26]
	EB (20, estimated)		2.0				
	EB (30, estimated)		1.5				
	EPent (24, estimated)	473	0.0 ± 0.1	IFR		d=0.870	[24]
	EO (9)	473	1.5 ± 0.2	IFR		d=0.910 to 0.870	[27]
	EO (12)		1.0 ± 0.2				
	EO (14)		0.9 ± 0.2				
	EO (18)		0.7 ± 0.1				
	EO (24)		0.6 ± 0.1				
	EO (25.5)	483	0.6	P		$M_w=98600$ $M_w/M_n=2.1$ d=0.882	[25]
EO (10)	503	1.2	GM		d=0.902 to 0.882	[26]	
EO (20)		1.5					
EO (15)	473	2.3	P	Contains 2.5 wt-% of ethylene		[27]	
EO (23)		1.4					
EO (27)		1.2					
EO (36)		0.7					
sPP	EH (80)	463	0.3	P	$M_w=150000$ $M_w/M_n=1.4$		[17]

The effect of comonomer type was evaluated by a direct measurement of the interfacial tension between polypropylene and polyolefin elastomer. For copolymers with propene, the range of value of interfacial tension with iPP is between 0.5 mN/m and 1.1 mN/m at similar temperature (190-200°C) and compositions (24-27 wt-%) though this can be only estimated from the density in the paper.^[23,24] For copolymers with 1-butene, the same authors give values

of 0.9 mN/m but the composition is not clearly indicated in the paper (presumably 24 wt-% of butene according to density). Other reported values range from 0.6 mN/m (19.4 wt-% butene) and 1 mN/m (12 wt-% butene).^[22,25] Very high values were also reported by Tranninger et al. but the compositions are not well described (presumably from 10 to 30 wt-% butene).^[26] The PP samples were containing a small amount of ethylene copolymer (2.5 wt-%) which might interfere. The temperature of the study was also very high (230°C) and problems of stability of the polymers might be suspected. A single result with pentene was found in the literature,^[24] but the value of interfacial tension is reported to be zero at 200 °C, using the retraction method. The composition is not given in the paper and therefore the reliability of the results is questionable. The largest set of data was found for octene copolymers. Values by the previous authors are given at 200 °C for well described polymers. The results show that when the octene content increases from 9 to 24 wt-%, the interfacial tension decreases from 1.5 ± 0.2 mN/m down to 0.6 ± 0.1 mN/m. The authors propose the general equation (1) from the variation of the interfacial tension with the octene content in relation with the molecular weight between branch points of the chain:

$$\gamma_{12} = \gamma_{\infty} - \frac{k}{\Phi^{-z}} \quad (1)$$

Where γ_{∞} is the interfacial tension at infinite molecular weight ($\gamma_{\infty} = 2.9 \pm 0.4$ mN/m)

k and z are fitted parameters $k = 4.6 \pm 0.2$ and $z = 0.45 \pm 0.17$

Φ is the volume fraction of octene.

Making the assumption that the volume fraction of the octene is proportional to the molecular weight between the branch points, Equation 1 shows that when the octene content increases,

the number of chain ends increases and the molecular weight between the chain ends decreases. It must be noted that, the extrapolation to pure ethylene leads to a high value of interfacial tension between iPP and PE. The values at 24 wt-% of octene are in agreement with that found in at nearly the same composition and 190°C.^[25] Higher values are also reported.^[26] For sPP, there are very few values available in the literature. Only one result with EH copolymer with 80 wt-% of hexene is given with the value of 0.3 mN/m at 190 °C.^[17] Generally, copolymers of ethylene and α -olefins, such as ethylene-octene copolymers, are used as compatibilizers. Therefore, the measurement of the interfacial tension is a tool to assess the effectiveness of the used compatibilizer.

Although a sizable number of papers on polyolefins blends are available, only a few of them presents and compares the different results of surface and interfacial tension measurements found in the literature. This is the primary source of motivation behind this paper. Therefore, in this work, we first aim to complete the interfacial tension data for polyethylene and polypropylene blends, especially for iPP/LDPE and sPP/HDPE blends, using the Palierne's model, Gramespacher and Meissner's model and using ab-initio calculation. Secondly, these results are compared with data from the literature.

2. Experimental Section and Methods

2.1. Materials and blends

Polyethylenes and polypropylenes of various structures obtained by different polymerization processes were supplied by the Total company (Feluy, Belgium). Details on the molecular weight distribution and synthesis are presented in **Table 2**. The LDPE was stabilized with a mixture of 50/50 wt-% of Irganox 1010 (Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)) and Irgafos 168 (Tris(2,4-di-tert-butylphenyl) phosphite) prior to any processing.

Table 2: Structural properties of the polymers (rad: radicalar, m: metallocene, ZN: Ziegler Natta).

Polymer	Synthesis	M _n [g/mol]	M _w [g/mol]	M _z [g/mol]	M _w /M _n
LDPE	rad	16300	147000	688000	9.0
HDPE(m)	m	24000	65800	123000	2.7
sPP(m)	m	40100	190000	549000	4.7
iPP(ZN)	ZN	35000	211000	1040000	6.0

Two sets of binary blends of PE with PP, LDPE/iPP(ZN) and HDPE(m)/sPP(m), were prepared at four compositions (90/10, 80/20, 20/80, 20/80 wt-%). The mixing was carried out in a co-rotating twin-screw extruder (Eurolab, Thermo Scientific) with screw diameter of 16 mm and L/D ratio of 40 using constant extrusion conditions at 190°C. The flow rate was 3.2 kg/h and the screw rotation was 200 rpm. The materials were shaped in bands using a flat die (50 mm in width and thickness of 1.5 mm). The bands were cast and cooled on a drawing belt with a speed adapted to the output rate at the die exit in order to avoid any stretching.

2.2. Rheological measurements

The dynamic mechanical properties in the melt were measured using a rotating strain-controlled rheometer (ARES, TA Waters) with parallel plane geometry (diameter: 25 mm, gap: 1.5 mm). Before introduction in the rheometer, samples were precut from the extruded bands in discs with a diameter of 25 mm and a thickness of 1.5 mm to preserve the morphology. In order to avoid thermal oxidation, all rheological tests were performed under nitrogen atmosphere at 190 °C equal to the processing temperature. Dynamic frequency sweep tests were carried out from 100 to 0.01 rad/s in the linear domain. The measurements were repeated three times on fresh samples and variation of the moduli was found to be within the range of $\pm 2.5\%$. The stability of the polymers and blends was checked and the content of stabilizer for LDPE was adapted for the duration of the test.

2.3. Interfacial tension measurements

The interfacial tension of the blends was measured from rheological data and morphology examination by the Palierne's model and by the Gramespacher and Meissner's model. ^[12,13]

The Palierne's model predicts the linear viscoelastic behavior in the melt of blends with a dispersed phase morphology. For this type of morphology, the elasticity at low frequency is partly due to the variation of the interfacial area under shear deformation. Therefore, the model allows the calculation of the dynamic modulus of a blend having a dispersed phase morphology (G_{blend}^*) from the dispersed phase radius R , the volume fraction of the dispersed phase Φ , the interfacial tension σ , the dynamic modulus of the dispersed phase (G_1^*) and that of the matrix (G_2^*). The complex shear modulus of the blend is calculated using Equation 2:

$$G_{blend}^i = G_2^i \frac{1 + 3 \sum_i \Phi_i H_i^i}{1 - 2 \sum_i \Phi_i H_i^i} \quad (2)$$

Where H_i^* is calculated by Equation 3:

$$H_i^i = \frac{4 \frac{Y_{12}}{R_i} [2G_2^i + 5G_1^i] + [G_1^i - G_2^i] [16G_2^i + 19G_1^i]}{40 \frac{Y_{12}}{R_i} [G_2^i + G_1^i] + [2G_1^i + 3G_2^i] [16G_2^i + 19G_1^i]} \quad (3)$$

Using a minimization method, this allows the calculation of the interfacial tension from the size of the dispersed phase if the rheological properties of the phases and of their blend is known at a given composition. Distribution of radii can also be described by the number average radius R_n and volume average radius R_v calculated by Equations 4 and 5:

$$R_n = \frac{\sum_i R_i}{n} \quad (4)$$

and:

$$R_v = \frac{\sum_i (R_i \Phi_i)}{\sum_i \Phi_i} = \frac{\sum_i R_i^4}{\sum_i R_i^3} \quad (5)$$

Palierne suggested the use of the volume average radius R_v of the dispersed phase in Equation 2 and 3 when the ratio R_v / R_n is lower than 2. Otherwise, if the ratio $R_v / R_n > 2$, it is necessary to consider the particle size distribution.

The Gramespacher and Meissner's model was alternatively used to calculate the interfacial tension between LDPE and iPP (Zn) or HDPE (m) and sPP (m). This model calculates the modulus of the blend as a combination of viscoelastic contributions corresponding to three relaxation times since in addition to the contribution of the matrix and of the dispersed phase, an additional relaxation is related to the interface. The interfacial tension can be calculated from the relaxation time of the interface $\tau_{\text{interface}}$ given by Equation 6:

$$\tau_{\text{interface}} = \frac{\eta_m R_v (19p+16)(2p+3)}{\gamma_{12} 40(p+1)} \left(1 + \Phi \frac{5(19p+16)}{4(p+1)(2p+3)} \right) \quad (6)$$

where $p = \eta_d / \eta_m$ is the viscosity ratio,

η_m is the matrix viscosity,

η_d is the dispersed phase viscosity,

Φ is the volume fraction of the dispersed phase,

γ_{12} is the interfacial tension.

The imaginary part of the complex viscosity η'' gives a good picture of the relaxation time spectrum, therefore it can be conveniently used to isolate the contribution of each relaxation mechanism. For the blend, η''_{blend} was written as a sum of three terms (Equation 7) describing the contribution of polyethylene (η''_{PE}), that of polypropylene (η''_{PP}) and that of the interface ($\eta''_{\text{interface}}$). The contributions were described by Cole-Cole equations following Equation 8:

$$\eta''_{\text{blend}} = \alpha \eta''_{\text{PE}} + \beta \eta''_{\text{PP}} + \gamma \eta''_{\text{interface}} \quad (7)$$

and:

$$\eta''_k = \frac{\eta_{0k} (\omega\tau_k)^{1-h_k} \sin\left(1-h_k\right) \frac{\pi}{2}}{1 + (\omega\tau_k)^{2(1-h_k)} + 2 (\omega\tau_k)^{1-h_k} \cos\left(1-h_k\right) \frac{\pi}{2}} \quad (8)$$

Where k stands for PE, PP or interface,

η_{0k} is the zero-shear viscosity,

τ_k is an average relaxation time,

h_k describes the width of the distribution of relaxation times.

α , β and δ are adjustable parameters,

2.4. Scanning electron microscopy (SEM)

SEM observations were carried out using a FEI NovananoSEM 200 instrument equipped with an electron backscatter diffraction detector. The applied accelerating voltage was 10 kV.

Ruthenium tetroxide RuO_4 was used as staining agent to enhance the contrast of the phases by increasing the electron density. The staining solution was prepared by reacting hydrated ruthenium chloride (0.2 g $\text{RuCl} \cdot x\text{H}_2\text{O}$, Aldrich) with sodium hypochlorite (10 ml 5% active Cl, Aldrich). Samples were trimmed with a glass knife under nitrogen atmosphere at -125°C using an ultra-microtome to avoid deformation of the structures and to obtain small analysis surface. Samples were stained in the vapor phase during 24 h for HDPE/sPP blends and during 3 to 4 h for LDPE/iPP blends and then washed with distilled water. Longer staining can be explained by a lower amount of double bonds in sPP due to a better thermal stability during processing in comparison to iPP.^[28] After 48h of drying, the stained samples were cut at room temperature using a diamond knife. Before observation, a sputter coater was used to treat the obtained smooth surface with a thin layer of conductive carbon. For SEM observation, using the backscattered electron diffraction detector, the stained phase appeared bright and the less stained phase appeared dark. The average diameter of the dispersed phase

was then calculated using the ImageJ software. About 300 particles were analyzed to calculate the average radii.

2.5. Ab-initio calculation of interfacial tension from surface tension of polyolefins

The interfacial tension between polymers can be calculated from the values of the surface tensions using Equation 9 for non-polar polymers combined with the variation of surface tension with temperature, which is generally considered to be linear.^[29] The variation with melting or crystallization is not considered because the data of surface tension at high or low temperature are extrapolated from each other starting from experimental data in the solid or molten state.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \frac{\gamma_1 \gamma_2}{\gamma_1 + \gamma_2} \quad (9)$$

where γ_1 is the surface tension of polymer 1 and γ_2 is the surface tension of polymer 2 and γ_{12} is the interfacial tension. This method requires the knowledge of the surface tension of the neat polymers measured at the same temperature. Equation 10 was used to calculate the surface tension at the relevant temperature.^[30]

$$\gamma(T) = \gamma(T_0) + \frac{d\gamma}{dT} (T - T_0) \quad (10)$$

where $\gamma(T)$ is the surface tension of the polymer at the temperature T , $\gamma(T_0)$ is the surface tension of the polymer at the temperature T_0 , $d\gamma/dT$ is the coefficient of variation of surface

tension with temperature. **Table 3** summarizes data of surface tension of the melt available in the literature with some molecular characteristics when they are available in the article.

Table 3: Surface tension of various PP and PE homopolymers or copolymers, wt-% of comonomer is indicated or estimated from density (between parenthesis). *Method: PD: pendant drop, SB: sessile bubble, WP: Wilhelmy plate, E: Extrapolated from Alcanes C₅-C₁₈.

Polymer or copolymer	γ [mN/m], T in K	Temperature range [K]	Method*	Data polymer	Ref	
HDPE	36.8 - 0.056 (T - 293)	273-473	EX	High molecular weight	[8-10, 31]	
LDPE	36.0 - 0.064 (T - 293)	393-453	PD		[32]	
PB	26.3 - 0.044 (T - 293)	443- 473	WP	M _w =68000, M _w /M _n =3.8	[33]	
EH (10)	29.7 - 0.043 (T - 293)	443-473	PD		[34]	
EB	25.9 - 0.044 (T - 293)	443-493	PD		[33]	
EB (90)	29.1 - 0.057 (T - 293)	403-483	PD		[33]	
EB (82)	33.6 - 0.076 (T - 293)	403-473	PD		[33]	
EB (48)	30.8 - 0.060 (T - 293)	423-463	PD		[33]	
EB (24)	32.6 - 0.054 (T - 293)	423-483	PD		[33]	
EB (10)	32.5 - 0.045 (T - 293)	443-503	PD		[33]	
EP (44)	32.6 - 0.062 (T - 293)	293-473			M _w =37000	[35]
EP (46)	31.9 - 0.059 (T - 293)	293-473			M _w =33000	[35]
EP (54)	30.8 - 0.061 (T - 293)	293-473			M _w =15000	[35]
EP (60)	29.8 - 0.058 (T - 293)	293-473			M _w =63000	[35]
EP (70)	29.5 - 0.058 (T - 293)	293-473			M _w =58000	[35]
iPP	29.4 - 0.056 (T - 293)	453-483	PD		M _w =318000, M _w /M _n =4.9	[10, 31, 34, 36]
sPP	30.0 - 0.058 (T - 293)	463-553	SB	M _w =150000, M _w /M _n =3	[33]	

3. Results and discussion

3.1. Calculation of the interfacial tension by the Palierne's model

Direct measurement of the interfacial tension between molten polyethylene and polypropylene is possible only using rheological methods. Indeed, interfacial tension measurements by observation of emulsions at high temperature are made difficult by the small difference of the refraction index between the two molten polymers and the small size of the phases.^[11] Therefore, the interfacial tension between LDPE/iPP and HDPE/sPP was calculated using the Palierne's model. **Figure 1** and **Figure 2** show the storage modulus of the neat polymers and of their blends. The SEM pictures of the extruded blends are presented in **Figure 3** and **Figure 4**.

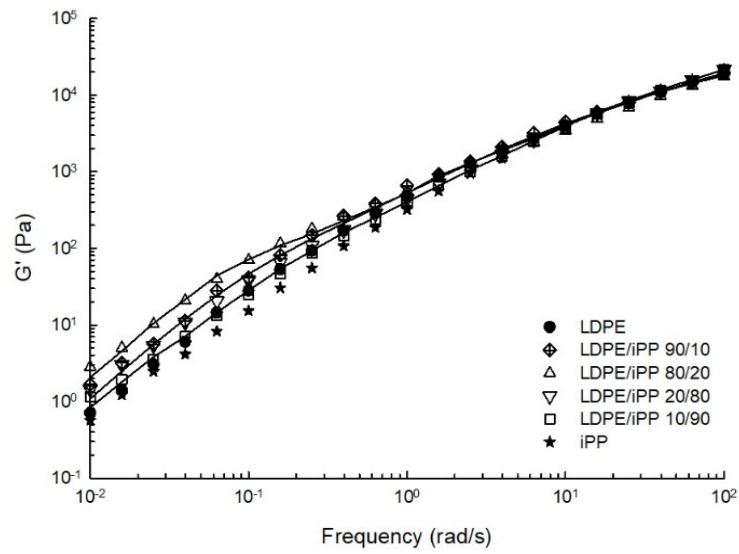


Figure 1: Variation of the storage modulus of LDPE, iPP and their blends as a function of frequency at 190°C, lines indicate the fit by the Palierne's model.

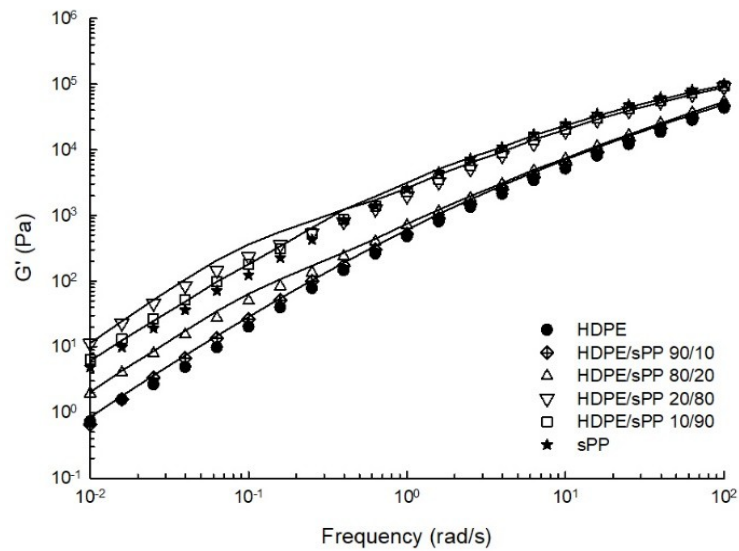


Figure 2: Variation of the storage modulus of HDPE, sPP and their blends as a function of frequency at 190°C, lines indicate the fit by the Palierne's model.

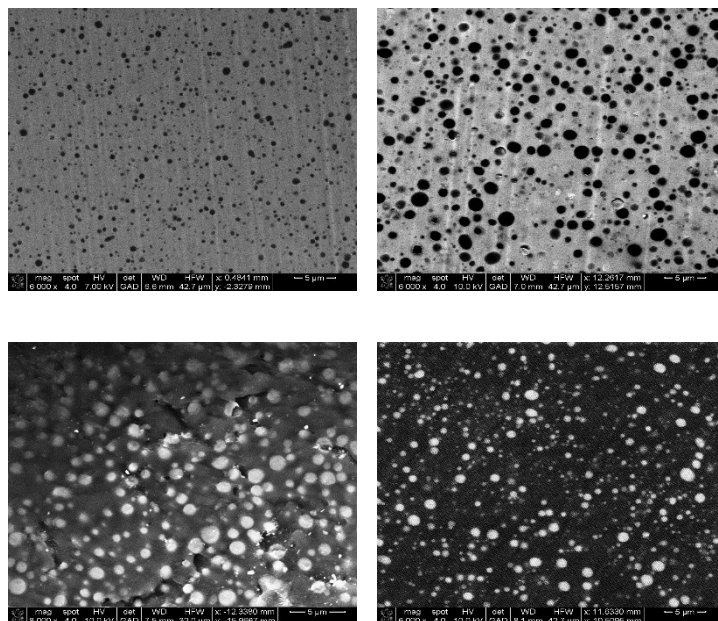


Figure 3: SEM pictures (x6000 or x8000) of LDPE/iPP blends (from top to bottom and left to right: 10, 20, 80, 90 wt-% iPP).

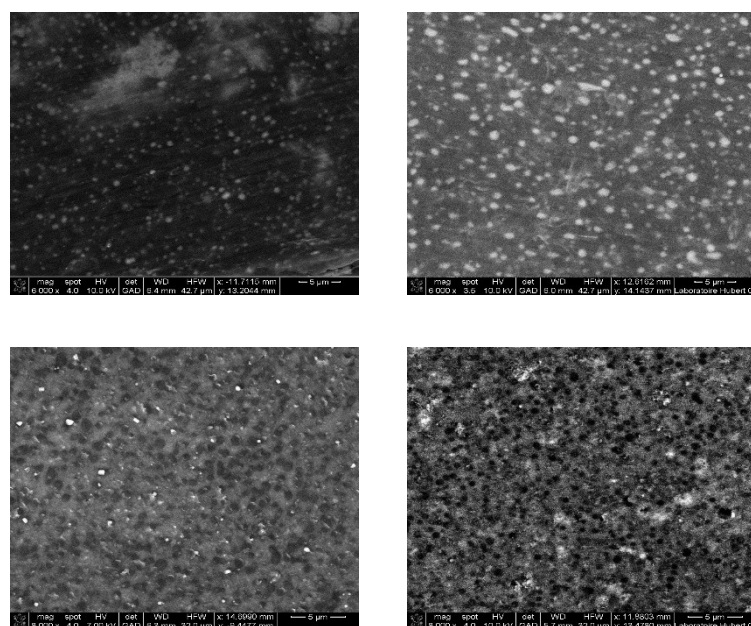


Figure 4: SEM pictures (x6000 or x8000) of HDPE/sPP blends (from top to bottom and left to right: 10, 20, 80, 90 wt-% sPP).

In the case of LDPE/iPP blends, LDPE is the stained phase and it appears as a bright matrix for 90/10 and 80/20 blends, or as bright droplets for 10/90 and 20/80 blends. In the case of

HDPE/sPP blends, the stained phase is the syndiotactic polypropylene. The HDPE is the dark phase. The volume average radius and the polydispersity of particle size (R_v / R_n) of the extruded blends are presented in **Table 4**. The ratios R_v / R_n were smaller than 2 for all the extruded blends. Therefore, Equations 2 and 3 can be used to describe the complex shear modulus and to determine the interfacial tension after fitting to the experimental values.

Table 4: Number and volume average radius of the extruded blends

PP [wt-%]		10	20	80	90
LDPE/iPP	R_v [μm]	0.4 ± 0.1	0.6 ± 0.2	0.7 ± 0.2	0.5 ± 0.1
	R_v / R_n	1.12	1.35	1.50	1.20
HDPE/sPP	R_v [μm]	0.4 ± 0.1	0.7 ± 0.2	0.4 ± 0.1	0.4 ± 0.1
	R_v / R_n	1.22	1.39	1.21	1.30

Figure 1 shows that at low concentration of the dispersed phase in the 90/10 or 10/90 blends, the relaxation of the interface at low frequency is not clearly visible. This is the same for the LDPE/iPP 20/80 blend. Actually, the shoulder on the storage modulus associated to the relaxation of the interface is only well defined for the LDPE/iPP 80/20 blend. Therefore, this composition is the only one that can be used to calculate the interfacial tension with reasonable uncertainty. The interfacial tension between LDPE and iPP was found to be to 0.6 ± 0.1 mN/m. Figure 2 presents the variation of the storage modulus of the neat polymer of HDPE, sPP and their blends. Once again, the shoulder at low frequency is only visible for the 80/20 and 20/80 compositions. Therefore, they were used to calculate the interfacial tension which was found to be 1.1 ± 0.2 mN/m for HDPE/sPP 80/20 and 1.0 ± 0.2 mN/m for the opposite composition 20/80 of the same blend. The limits of Palierne's model are related to the concentration of the dispersed phase. On one hand, the intensity of the shoulder on the blend storage modulus at low frequency is too weak as for example in the diluted compositions 90/10 or 10/90. On the other hand, at high concentrations, 70/30 or 30/70, it was

found that the ratio R_v/R_n became higher than 2 because of probable coalescence. Therefore, only the compositions 80/20 and 20/80 can be considered and the result should be validated only when the obtained values of interfacial tension are the same for the two opposite compositions.

3.2. Calculation of the interfacial tension by the Gramespacher and Meissner's model

The Gramespacher and Meissner's model was used to validate the results obtained by the Palierne's model. For the same reasons that those exposed previously, the relaxation due to the interface cannot be identified for the compositions 90/10 or 10/90 of the extruded blends. Therefore, only the compositions 80/20 and 20/80 were considered. The average relaxation times of the matrix, dispersed phase and interface were calculated by fitting the experimental measurements of the imaginary part of the complex viscosity with Equations 7 and 8. Figures 5 and 6 show the evolution of the imaginary part of the viscosity as a function of frequency of the neat polymers and their blends 20/80 and 20/80.

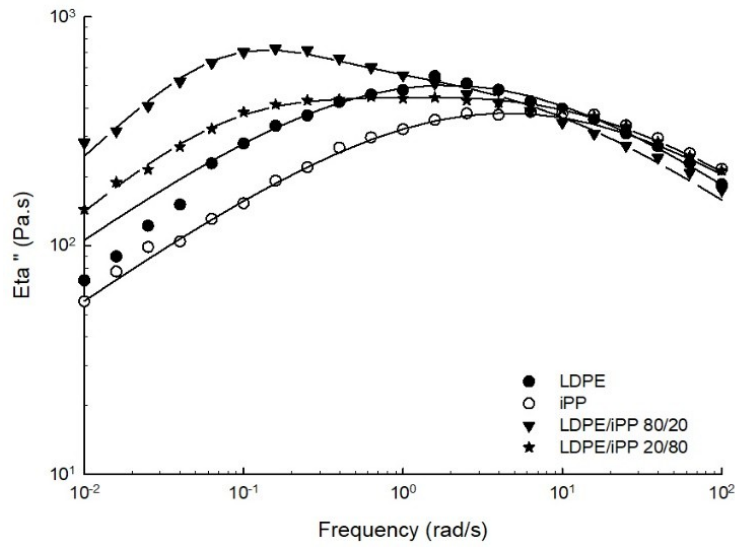


Figure 5: Variation of the imaginary part of the complex viscosity as a function of the frequency at 190 °C of the LDPE/iPP blends 20/80 and 20/80. Symbols: experimental measurements. Dashed lines: fit by Equations 7 and 8.

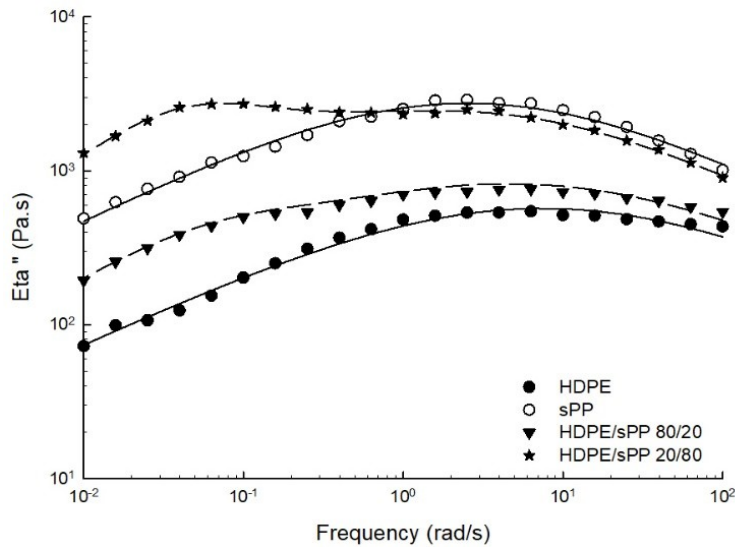


Figure 6: Variation of the imaginary part of the complex viscosity as a function of the frequency at 190 °C of the HDPE/sPP blends 20/80 and 20/80. Symbols: experimental measurements. Dashed lines: fit by Equations 7 and 8.

The fitted parameters using Equations 7 and 8 are summarized in **Table 5** for the LDPE/iPP blends and **Table 6** for HDPE/sPP blends. The values of coefficients α , β , and δ are not given because they are not useful for the determination of the interfacial tension. The relaxation time related to the interfacial tension $\tau_{\text{interface}}$, calculated by Cole-Cole's model, is used in Equation 6 to calculate the interfacial tension between PE and PP. As in the Palierne's model, the Gramespacher and Meissner's model requires the analysis of the morphologies of the blends. Therefore, the values of the volume average radii presented in Table 3 were used to calculate the interfacial tension.

Table 5: Parameters of Equations 7 and 8 for the LDPE/iPP blends (190°C).

Composition	η_0 [Pa.s]	τ_{PE} [s]	h_{PE}	τ_{PP} [s]	h_{PP}	$\tau_{\text{interface}}$ [s]	$h_{\text{interface}}$	γ_{12} [mN/m]
LDPE	2360	0.45	0.43	-	-	-	-	-
LDPE/iPP 80/20	-	0.13	0.51	0.22	0.50	9.23	0.65	0.7 ± 0.1
LDPE/iPP 20/80	-	0.13	0.51	0.22	0.50	11.59	0.20	0.6 ± 0.1
iPP	1830	-	-	0.22	0.50	-	-	-

Table 6: Results of relaxation times calculated by the Cole-Cole model for HDPE/sPP blends (190°C).

	η_0 [Pa.s]	τ_{PE} [s]	h_{PE}	τ_{PP} (s)	h_{PP}	$\tau_{\text{interface}}$ [s]	$h_{\text{interface}}$	γ_{12} [mN/m]
HDPE	2830	0.13	0.51	-	-	-	-	-
HDPE/sPP 80/20		0.13	0.51	0.39	0.47	121	0.20	1.0 ± 0.2
HDPE/sPP 20/80		0.13	0.51	0.39	0.47	18.20	0.14	0.9 ± 0.2
sPP	12580	-	-	0.39	0.47	-	-	-

Table 7 summarizes the values of the interfacial tensions for the LDPE/iPP and HDPE/sPP pairs at 190°C. Results are consistent for compositions 80/20 and 20/80. The interfacial tension between LDPE and iPP varies from 0.6 to 0.7 mN/m at 190°C. The interfacial tension between HDPE and sPP varies from 0.9 to 1 mN/m at the same temperature. The value values obtained by both methods are consistent provided that the composition is suitably chosen.

Table 7: Interfacial tension measurements for the LDPE/iPP and HDPE/sPP pairs (190°C).

Blend		γ_{12} [mN/m]	
		Palierne	Gramespacher and Meissner
HDPE/sPP	80/20	1.1 ± 0.2	1.0 ± 0.2
	20/80	1.0 ± 0.2	0.9 ± 0.2
LDPE/iPP	80/20	Non mesurable	0.7 ± 0.1
	20/80	0.6 ± 0.1	0.6 ± 0.1

3.3. Calculation ab-initio of the interfacial tension for HDPE/sPP and LDPE/iPP.

The calculation ab-initio of the interfacial tension at 190 °C was carried out. Variations of surface tension from Table 3 were used. At first, the surface tensions of the neat polymers were calculated at the same temperature of 190 °C and then Equation 9 was applied. Results and data used for the calculation are given in **Table 8**. Uncertainties were estimated from those on the values for the neat components. The obtained results of the interfacial tension using ab-initio calculation are in agreement with those obtained by Gramespacher and Palierne models.

The surface tension can be compared with the recent data from.^[7] In this article, the results of interfacial tension are lower for all polymers, even when recalculated at 190°C. At 190°C, the value is 22.1 ± 0.5 mN/m for metallocene HDPE, 18.8 ± 0.5 mN/m for Ziegler Natta iPP and 22.4 ± 0.5 mN/m for free radical LDPE. Data for sPP were not available. With these values, the calculated interfacial tension for the LDPE/iPP pair is 0.3 mN/m but with large uncertainty.

Table 8: Surface tension of PE and PP calculated at 190 °C (463 K) and interfacial tension between polymer pairs.

Polymer	Temperature variation of surface tension (T in K) from Table 3	γ [mN/m]	γ_{12} [mN/m]
LDPE	$\gamma = 36.0 - 0.064 (T - 293)$	25.1	0.7 ± 0.2
iPP	$\gamma = 29.4 - 0.058 (T - 293)$	19.5	
HDPE	$\gamma = 36.8 - 0.056 (T - 293)$	27.3	1.1 ± 0.2
sPP	$\gamma = 30.0 - 0.058 (T - 293)$	20.1	

3.4. Extension to other olefinic polymer pairs

In this part, the ab-initio calculation was used in combination with the surface tension of Table 3 to make a comparison with the experimental values of the literature for the interfacial tension of iPP with various olefinic homopolymers and copolymers as listed in Table 1.

Therefore, calculation was carried out at the temperature of Table 1 using the data of surface tension and of its variation with temperature in Table 3. In particular, starting from the surface tension at 20 °C of polyethethylene (36.8 mN/m), polypropylene (29.4 mN/m), polybutene (26.3 mN/m), it was assumed that the variation of surface tension with the monomer molar mass of other polyenes (polyhexene, polypentene, polyoctene) follows an empirical power-law in the form of Equation 11 (Figure 7):

$$\gamma = \gamma_{PE} \cdot \left(\frac{m_0}{m_{0PE}} \right)^b \quad (11)$$

with $\gamma_{PE} = 36.8 \text{ mN/m}$, $m_{0PE} = 28 \text{ g/mol}$ and $b = -1/2$.

leading to $\gamma = 23.6 \text{ mN/m}$ for polypentene, 21.7 mN/m for polyhexene and 18.8 mN/m for polyoctene.

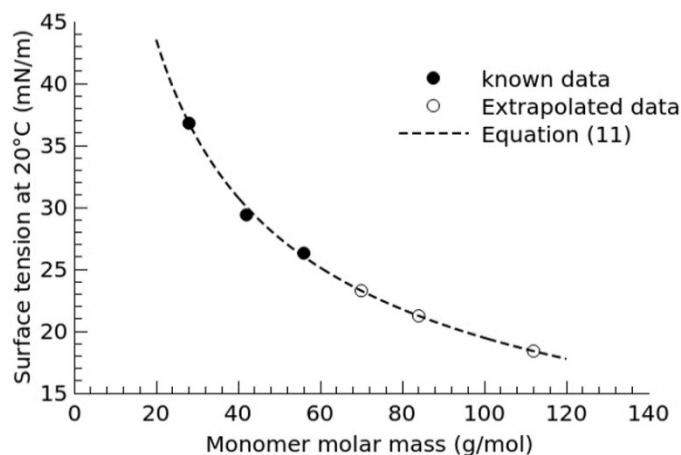


Figure 7: Surface tension at 20 °C of olefinic homopolymers.

For the various copolymers of ethylene, the surface tension was first calculated from the surface tension of homopolymers weighted by the molar composition (x_i) according to Equation 12:^[31,37]

$$\gamma = \gamma_1 x_1 + \gamma_2 x_2 \quad (12)$$

A similar Equation 13 was applied to the temperature variation of the surface tension:

$$\frac{d\gamma}{dT} = \frac{d\gamma_1}{dT} x_1 + \frac{d\gamma_2}{dT} x_2 \quad (13)$$

Results are given in **Table 9** at the temperature of 190 °C for comparison of the polymer pairs in addition to the values obtained in the present paper for LDPE/iPP and HDPE/sPP. For the homopolymers HDPE / iPP, this leads to a value of 1.3 mN/m at 190 °C close to values of the literature.^[21]

Table 9: Interfacial tension of various iPP and PE homopolymers or copolymers using γ_{iPP} (mN/m) = 29.4 - 0.056 (T - 293) and γ_{sPP} (mN/m) = 30.0 - 0.058 (T - 293). wt-% and mol-% of comonomer in PE copolymer are indicated between parentheses.

Polypropylene	Polyethylene polymer or copolymer	$\gamma_{PE \text{ or copolymer}}$ [mN/m]	T [K]	γ_{12} [mN/m]
iPP	HDPE	36.8 - 0.056 (T - 293)	463	1.3
	HDPE	36.8 - 0.056 (T - 293)	493	1.3
	LDPE	36.0 - 0.064 (T - 293)	463	0.7
	EP (88.5 / 92)	30.3 - 0.056 (T - 293)	493	0.0
	EP (84.4 / 89)	30.6 - 0.056 (T - 293)	493	0.0
	EP (78.5 / 84)	31.0 - 0.056 (T - 293)	493	0.1
	EP (24 / 17.4)	35.0 - 0.056 (T - 293)	473	0.9
	EB (24 / 13.6)	34.3 - 0.053 (T - 293)	473	0.7
	EB (19 / 11.2)	34.8 - 0.053 (T - 293)	483	0.9
	EB (12 / 6.4)	35.8 - 0.056 (T - 293)	463	1.0
	EPent (24 / 11.2)	33.4 - 0.053 (T - 293)	473	0.5
	EO (9 / 2.4)	35.3 - 0.055 (T - 293)	473	0.9
	EO (12 / 3.3)	34.9 - 0.054 (T - 293)	473	0.8
	EO (14 / 3.9)	34.6 - 0.054 (T - 293)	473	0.7
	EO (18 / 5.2)	34.0 - 0.054 (T - 293)	473	0.6
	EO (24 / 7.3)	33.1 - 0.053 (T - 293)	473	0.5
	EO (25.5 / 7.9)	32.3 - 0.053 (T - 293)	483	0.3
sPP	EH (80 / 57.1)	19.2 - 0.043 (T-293)	463	1.1

The good agreement with data from the literature of Table 1 is better viewed on **Figure 8**.

Data from Trenninger et al. at 230 °C were not included because the experimental values were found inconsistently high probably due to degradation effects as indicated before.^[26]

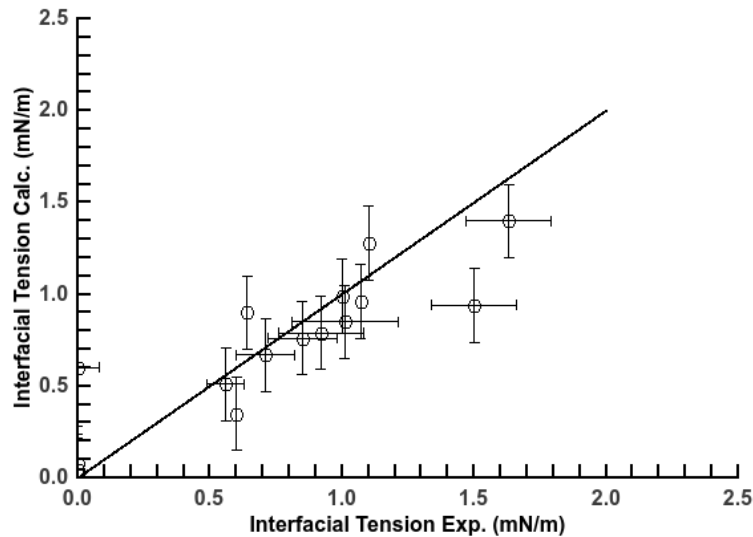


Figure 8: Calculated interfacial tension between iPP and olefinic homopolymers and copolymers compared to available experimental data (Table 1). Line indicates the ideal correlation.

4. Conclusion

Surface and interfacial properties of polymers have received a lot of interest for many decades because they are fundamental properties to define the interactions occurring between the components of polymer blends during mixing and in end-use properties. The interest has been particularly renewed in the polyolefin area by developments in the catalysis of polymerization for homopolymers and copolymers, offering a large variety of mixtures with or without compatibilizers.

This paper proposes new data of interfacial tension in the melt between LDPE and iPP on one hand and between HDPE and sPP on the other hand. The experiments were carried out on blends and interfacial determination was made by means of the Palierne's and Gramespacher and Meissner's analysis using rheological data and SEM observations. Results were in good

agreement with those obtained by calculation ab initio by the equation proposed by Wu with surface tension data issuing from the literature.^[31] The interfacial tensions were found to be 1.0 ± 0.2 mN/m for HDPE/sPP pair and 0.6 ± 0.1 mN/m for LDPE/iPP pair at 190°C. Ab-initio calculations were also extended to homopolymers and copolymers of ethylene with various α -olefins comonomers at different temperatures. Simple mixing rules depending on the composition of the copolymers can be applied to the surface tension and its temperature variation. Results were compared to data of the literature and both sets of values agree well. Therefore, these mixing rules prove to be robust for the calculation of the interfacial tension of various polymer pairs. Finally, a large set of values of interfacial tension for polyolefins can be compiled from various literature sources.

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