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## ***Influence of Surfactants on Interaction Forces Between Polyethylene Surfaces in a Hydrocarbon Solvent***

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*The polyolefins, mainly polyethylene and polypropylene particles, are used as an active filler material in polymer-polymer blends and are being used for the modification of asphalts to provide for high-load, low-maintenance road construction. The stability of prepared blends depends on the interaction forces between polyolefin filler and the matrix and/or between two polyolefin filler surfaces in the polymeric matrix. Various additives, especially surfactants, can be used to modify these interactions and improve the stability of polymer blends.*

*In current research, direct force measurements between polyethylene (PE) surfaces in *n*-tetradecane, a nonaqueous solvent imitating the polymer matrix, were performed in the presence of lauric acid and dodecylamine using the AFM colloidal probe technique. Additionally, the zeta potential of polyethylene particles in the presence of surfactants in *n*-tetradecane was measured. The interaction forces between the polyethylene surfaces can be described as a combination of electrical double layer repulsion and steric repulsion between polymer chains extending into the *n*-tetradecane solvent. The addition of surfactant to the *n*-tetradecane was found to increase the repulsive force between the PE surfaces. The strongest repulsion was observed for dodecylamine. Additionally, the temperature effect on the interactions in *n*-tetradecane was studied. It was found that steric repulsion between the PE surfaces increases with an increase in temperature.*

### **INTRODUCTION**

Preparation and stability of nonaqueous dispersions are of great technological importance. Many important products such as inks, paints, lubrication oils, pharmaceutical

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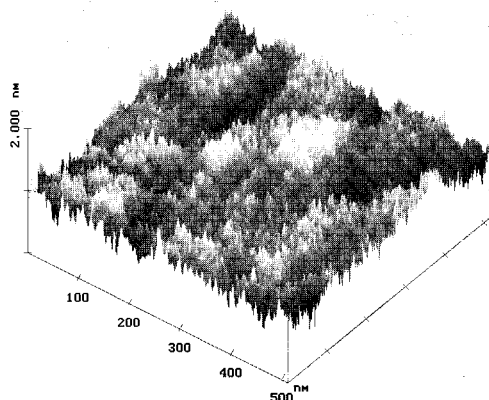
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formulations and cosmetics are examples where the stability of the nonaqueous dispersion is crucial for their application. Nonaqueous suspensions of mineral particles are also used in manufacturing of advanced ceramic materials (Bergstrom, 1996). Other systems where the stability of a dispersion in nonaqueous medium is critical for successful application include polymer-filler composites. Mineral particles are used as an active filler in polymer blends (Ahsan and Taylor, 1998; Guerrica-Echevarria, Eguiazabal, and Nazabal, 1999; Pastorini and Nunes, 1999) for mechanical strength and flame-retardant properties. Polymer particles are also used as active fillers in polymer blends, and polyethylene (PE) is most extensively used as a dispersed filler phase in polymer matrices (Arnal and Muller, 1999; Huneault et al., 2001; Lerdwijitjarud, Sirivat, and Larson, 2002). Polyolefin particles, especially PE, are also extensively used for modification of asphalts considered for high-load, low-maintenance road construction (Liang and Hesp, 1993; Giavarini et al., 1996). Addition of dispersed polyolefins to the asphalt blends helps to retard the low-temperature thermal stress cracking as well as rutting of the pavement at elevated temperatures. Other benefits include greater fatigue resistance, reduced temperature susceptibility, increased tire traction and greater adhesion to the aggregate. Polyolefin polymers such as PE do not contain double bonds and therefore have good thermal and ageing resistance. Different methods of stabilization of such dispersions are employed including modification of the filler surface, addition of surfactants, and/or steric stabilization by extending polymer chains (Morrison, Hedmark, and Hesp, 1994; Zeiler, Kellermann, and Munstedt, 2000). However, the major obstacles to widespread application of polyolefins for asphalt modification is still the low stability of the PE dispersion in asphalt at elevated temperature, which results in coalescence of polyolefin droplets and separation of polymer phase from the asphalt blend (Hesp and Woodhams, 1991).

Due to the technological significance, the stability of nonaqueous dispersions has been studied in detail using bulk observations of coagulation and settling and electrophoretic measurements (Romo, 1963; McGown, Parfitt, and Willis, 1965; McGown and Parfitt, 1966, 1967). To complement these measurements it seems appropriate that surface forces be measured to gain a more fundamental understanding of the phenomena involved. Unfortunately, despite numerous contributions which report direct interaction force measurements in aqueous systems, nonaqueous systems have received much less attention in this field. Only several papers pertaining to the direct measurement of interaction force between solid surfaces in nonaqueous surfactant solutions have been published (Gee and Israelachvili, 1990; Chen, Xu, and Israelachvili, 1992; Bergstrom and Blomberg, 2000; Briscoe and Horn, 2002). In these studies generally the surface force apparatus (SFA) (Israelachvili, and Tabor, 1972) was used with mica surfaces. Recent advances in force measurements using atomic force microscopy (AFM) (Binnig, Quate, and Gerber, 1986) in conjunction with the colloidal probe technique (Ducker, Senden, and Pashley, 1991) have made possible the measurement of interaction forces between a spherical particle (colloidal probe) and almost any other surface. With the AFM colloidal probe technique surfaces composed of almost any material of interest can be studied.

In this paper, direct force measurements between a PE spherical particle and a PE surface were made in *n*-tetradecane (nonaqueous solvent imitating polymer matrix) using the AFM colloidal probe technique. The effect of surfactant type (lauric acid and dodecylamine) on the interaction force and the effect of temperature on the interactions have been determined. Additionally, the electrophoretic mobility/zeta potential of polyethylene particles in *n*-tetradecane surfactant solutions was measured. According to our knowledge this is the first paper where interfacial forces between polyolefin surfaces



**FIGURE 1** AFM image of flat PE surface (mean roughness 0.13 nm)

have been measured in hydrocarbon solutions of surfactants using AFM. The understanding of interaction forces existing between the polymeric particles in nonaqueous medium has not only significant fundamental implications but also may help in further modification of these forces in order to improve stability of the polymer-filler blends.

## EXPERIMENTAL

### Materials

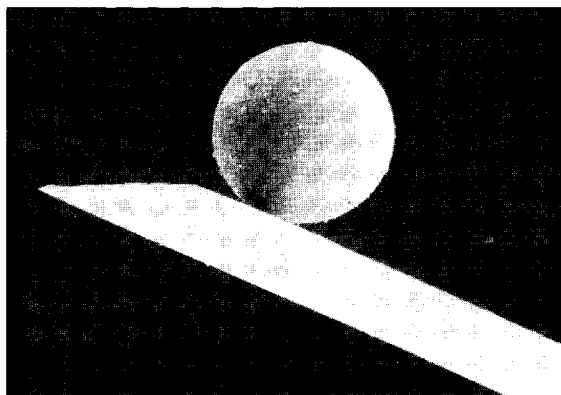
The polyethylene (PE) powder used was a low-density PE (Scientific Polymer Product, Inc.) with a molecular weight  $MW = 1800$  and a melting point  $mp = 117^{\circ}\text{C}$ . Reagent grade n-tetradecane (Sigma), dodecylamine (DDA) (Aldrich) and lauric acid (Aldrich) were used during the experiments.

### Methods

**Preparation of Flat PE Surface.** The PE surface was prepared by melting powdered material in a vacuum and pouring on a freshly cleaved mica surface. After cooling the PE disc was separated from the mica substrate under water. The PE surface obtained in this way had a very smooth surface as was determined by contact mode atomic force microscopy imaging, see Figure 1. The roughness measured from AFM images was determined to be 0.13 nm.

**Colloidal Probe Preparation.** Spherical polyethylene (PE) particles were obtained using a procedure, which involves suspending a powder of polymeric thermoplastic materials, such as PE, in glycerol, heating the suspension above the melting point of the polymer, and then solidification of the dispersed polymeric droplets at a reduced temperature. After appropriate filtration and drying, this procedure was found not to change the surface properties of PE particles, which retained a high degree of hydrophobicity. These particles had a relatively smooth surface and were particularly useful for investigating interaction forces using the AFM colloidal probe technique (Nalaskowski et al., 1999).

The prepared spherical particles were glued to the AFM cantilever with a small amount of epoxy resin using a procedure described elsewhere (Ducker, Senden, and



**FIGURE 2** SEM image of 18  $\mu\text{m}$  spherical PE particle glued to the end of AFM cantilever

Pashley, 1991). Tipless rectangular silicon cantilevers (Digital Instruments, Inc.) were used. The cantilever was placed under the CCD camera fitted with long distance lens giving a 500 $\times$  magnification. A small amount of epoxy resin was transferred on the tip of the cantilever using a 20  $\mu\text{m}$  diameter tungsten wire attached to a micromanipulator. Subsequently, a selected sphere was picked up using a new tungsten wire and carefully placed on the cantilever using the micromanipulator. It has been established that there is no contamination of spherical particles with epoxy resin during gluing. Using this procedure, particles in diameter from 1  $\mu\text{m}$  to 200  $\mu\text{m}$  can be precisely glued to the AFM cantilever. Cantilevers were used for measurements after at least 24 hours of drying. An example of the cantilever with attached PE spherical particle is shown in Figure 2.

**Interaction Force Measurement.** A Nanoscope IIIa atomic force microscope (Digital Instruments, Inc.) equipped with a fluid cell was used for the measurements of interaction force between PE sphere and PE flat surface in pure n-tetradecane and in  $1 \times 10^{-3}$  M n-tetradecane solutions of lauric acid and DDA. During the AFM surface force measurement the laser beam is focused on the back of the cantilever to detect the cantilever's deflection as it interacts with the surface beneath it. The reflected light is directed onto a split photodiode detector, which produces a voltage signal proportional to the cantilever deflection. If the spring constant is known, the deflection of the spring can be converted to force using the Hooke's law. Using such a setup the force acting on the cantilever can be determined with sensitivity greater than 0.1 nN. The sample beneath the cantilever is moved using a piezoelectric transducer. In the force measurements, motion in the x and y directions is disabled and the piezoelectric tube is used to move the surface in the z direction and the cantilever deflection is continuously measured. The surface is first moved toward the cantilever until the particle contacts the surface and then is retracted from the cantilever until the particle snaps off from the surface. The interaction force is obtained from measuring the deflection of the cantilever during the approach. For measurements at different temperatures, the AFM setup was placed in a modified solid-state cooling-heating chamber (ECHOtherm, Torrey Pines Scientific) which allows for operating AFM while in the chamber. The temperature was monitored and maintained by the internal controller. The spring constant of the cantilever was given by the manufacturer to be 0.12 N/m, a value which has been confirmed using the Cleveland method (Cleveland et al., 1993). After measurement, the particle diameter was measured using scanning electron microscopy (SEM). At least 10 consecutive

**TABLE 1** Electrophoretic mobility and zeta potential of PE particles in n-tetradecane in the absence and presence of surfactants

System	Electrophoretic Mobility	
	$\left(\frac{\mu\text{m} \cdot \text{cm}}{\text{s} \cdot \text{V}}\right)$	Zeta Potential (mV)
PE/n-tetradecane	$2.14 \times 10^{-3}$	2.5
PE/ $1 \times 10^{-3}$ M lauric acid solution in n-tetradecane	$-4.01 \times 10^{-3}$	-4.78
PE/ $1 \times 10^{-3}$ M DDA solution in n-tetradecane	$1.04 \times 10^{-2}$	12.4

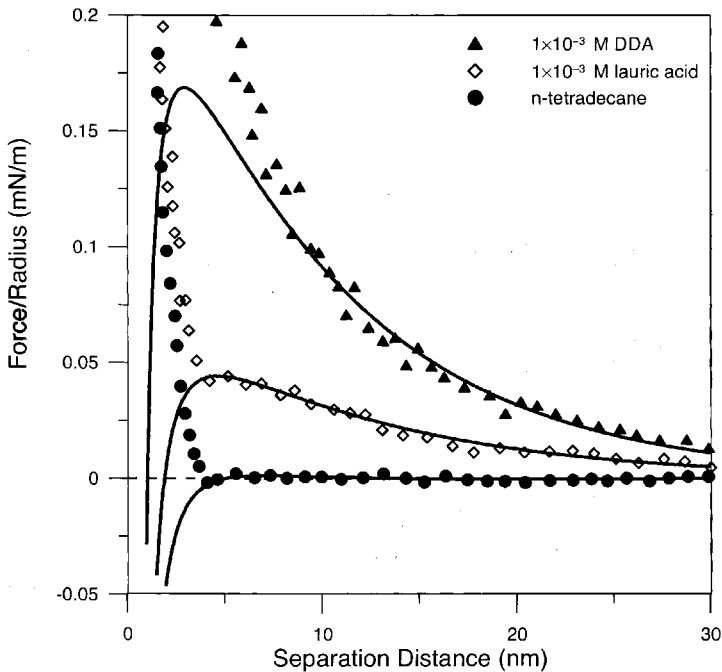
measurements were taken, values of the cantilever's deflection converted to force, normalized with respect to the PE sphere radius, and averaged.

**Electrophoretic Mobility Measurements.** Electrophoretic mobility of the spherical PE colloidal probe particles was measured using the Brookhaven ZetaPALS apparatus. This instrument employs phase analysis light scattering (PALS) method which has been found suitable for the measurement of low electrophoretic mobilities in nonaqueous media (McNeil-Watson, Tscharnuter, and Miller, 1998). After 15 minutes of equilibration of PE particles in the n-tetradecane solution, six consecutive measurements were taken at room temperature and an applied electric field of 357.14 V/cm. The measurements were averaged and the zeta potential was calculated using Smoluchowski equation with bulk properties of the pure n-tetradecane as the medium.

## RESULTS AND DISCUSSION

Generally speaking, a suspension of particles in nonpolar medium can be stabilized by electrical double layer repulsion (Overbeek, 1966) or by entropic repulsion of the interacting polymer chains (Luckham and Manimaaran, 1997), especially in the studied case where PE can swell in the hydrocarbon liquid and where additional charging of the PE surface can occur due to the presence of surfactants. Both mechanisms may coexist and to differentiate between them may be quite difficult.

In many cases it is assumed that electrical double layer interactions in nonpolar liquids are of little significance. This assumption is usually explained by the fact that ions have extremely low solubility in nonpolar liquids. However, potential at the interface can still develop in a nonpolar solvent due to the differences in electronic properties of the two phases (Morrison, 1993). In addition the role of water dissolved in the nonpolar solvent cannot be neglected. For example the n-tetradecane used in this study was not dried before use and can be assumed to contain water originating from the laboratory atmosphere. It is expected that the level of dissolved water could amount to as much as 40 ppm which corresponds to a molar concentration of  $2.2 \times 10^{-3}$  M. Such an amount of water cannot be ignored and may allow for accommodation of ions and formation of the electrical double layer. Additionally, water molecules can be introduced to the tetradecane with surfactant. It has been generally accepted that the presence of even traces of water allow for increased dissociation of molecules and charging of particles in nonpolar media as has been shown by electrophoretic measurements (McGown, Parfitt, and Willis, 1965). Indeed the electrophoretic mobility and zeta potential of particles in nonpolar liquids has been successfully measured as reported in the literature (McNeil-Watson, Tscharnuter, and Miller, 1998; Kosmulski, 1999). The electrophoretic mobility and zeta potential of PE particles in n-tetradecane is given in Table 1. The addition of surfactants changes the measured zeta potential significantly (Kitahara et al., 1977), which is visible also in our system, especially in the presence of



**FIGURE 3** Interaction force between PE surfaces in n-tetradecane and in  $1 \times 10^{-3}$  M solution of DDA and lauric acid in n-tetradecane. Every fifth experimental point is shown for clarity. Continuous lines indicate constant charge DLVO fit. Hamaker constant calculated using combining relations is  $A = 1.65 \times 10^{-21}$  J.

DDA. It has to be noted that the error of measurements reported in Table 1 is quite significant and was found to be in range of  $\pm 2$  mV. Nevertheless the observed change in the value of zeta potential in the presence of surfactants is evident.

Interaction force curves measured between PE surfaces in n-tetradecane in the absence and the presence of surfactants are shown in Figure 3. Although the appropriateness of the use of the Derjaguin/Landau/Verwey/Overbeek (DLVO) theory for describing the behavior of particles in nonaqueous liquids is still discussed in the literature, many authors agree that DLVO theory can be applied to such systems quite successfully (Romo, 1963; McGown, Parfitt, and Willis, 1965; Briscoe and Horn, 2002). The experimental data from the force measurements have been fitted with the constant charge model for electrical double layer repulsion combined with van der Waals attraction, where force normalized with respect to particle radius is a function of separation distance as given by Equation 1:

$$\frac{F(D)}{R} = -\frac{A}{6D^2} + \frac{4\pi\sigma^2}{\epsilon\epsilon_0\kappa} e^{-\kappa D} \quad (\text{EQ 1})$$

where  $A$  = Hamaker constant,  $\sigma$  = surface charge,  $\epsilon$  = dielectric constant of medium (tetradecane) and  $\kappa$  = Debye constant (reverse Debye length).

It has been shown that such a simple model can be successfully used for describing interaction forces in nonpolar liquids especially when a significant amount of water is

**TABLE 2** Parameters for fitted constant charge electrical double layer interactions between PE surfaces in n-tetradecane in the absence and presence of surfactants

System	Debye Length $\kappa^{-1}$ (nm)	Surface Charge ( $\mu\text{C}/\text{m}^2$ )
PE/n-tetradecane	907.5	0.0017
PE/ $1 \times 10^{-3}$ M lauric acid solution in n-tetradecane	10.5	0.109
PE/ $1 \times 10^{-3}$ M DDA solution in n-tetradecane	9.36	0.204

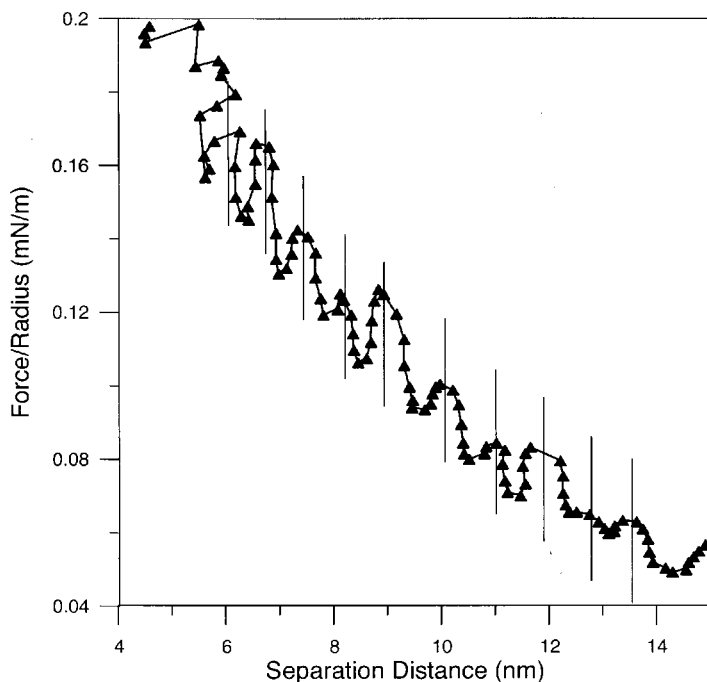
present. The Hamaker constant for van der Waals interaction between PE surfaces across n-tetradecane has been calculated from Hamaker constants for the crystalline hydrocarbon PE ( $A = 7.1 \times 10^{-20}$  J) and for n-tetradecane ( $A = 5.1 \times 10^{-20}$  J) in vacuum (Israelachvili, 1991), and was found from combining relations to be  $A = 1.65 \times 10^{-21}$  J. The parameters for the fitted DLVO curves (Debye length and surface charge) are given in Table 2.

In pure n-tetradecane the electrostatic repulsion is negligible as can be seen from experimental points. This is also reflected in the extremely small charge density value obtained from the theoretical fit. The thickness of the electrical double layer is extremely large, which is typical for a medium of low dielectric constant and with a very low concentration of ions in solution. At a separation distance around 5 nm van der Waals attraction is clearly visible and can be quite successfully fitted with the theoretical value for the Hamaker constant. The total interaction force between PE surfaces in n-tetradecane is consistent with the observed low stability of such systems, which are governed by the van der Waals forces. It has to be also noted that a long-range repulsive force related to interactions between extended polymer chains in solvent was not observed here, which can indicate that swelling of the PE under such conditions is not significant.

The addition of either surfactants (lauric acid or DDA) into the system dramatically changes the character of the interaction forces between PE surfaces. Strong repulsive components of the interaction force can be observed. The measured repulsive force is much stronger in the presence of DDA as is also demonstrated by the value of the surface charge that is almost two times greater than in the case of lauric acid. It has to be noted that the Debye length obtained from the theoretical fit is significantly smaller than for the pure hydrocarbon (see Table 2) that can indicate the presence of ions and water close to the interface. In the case of lauric acid the interaction force curve can be quite successfully fitted to the DLVO curve and even the small van der Waals component can be observed at separation distance close to 5 nm. However, in the presence of DDA the additional repulsive component of interaction force cannot be fitted to the DLVO curve at separations below 10 nm.

This additional repulsion can be explained by the presence of surfactant molecules, layers or micellar aggregates between the interacting PE surfaces. At distances below 14 nm in the presence of DDA significant oscillations in the force curve can be observed on a magnified part of the force curve as shown in Figure 4. The average value of the peak-to-peak distance for these interactions has been found to be  $0.8 \pm 0.07$  nm. Such oscillations can suggest presence of surfactant layers or reversed micelles between interacting surfaces (Gee and Israelachvili, 1990; Chen, Xu, and Israelachvili, 1992). It has to be noted, however, that the observed value is significantly smaller than the size of the expected DDA micelle.

Although the swelling of PE was not observed in pure tetradecane, it cannot be completely ruled out for surfactant solutions. In order to characterize possible steric repulsion between polymeric chains extending into the solvent, a scaling theory framework developed by de Gennes (de Gennes, 1987) can be used. According to this theory the repulsive force between two surfaces due to the interaction of protruding polymer chains can be given by Alexander-de Gennes equation (Equation 2):



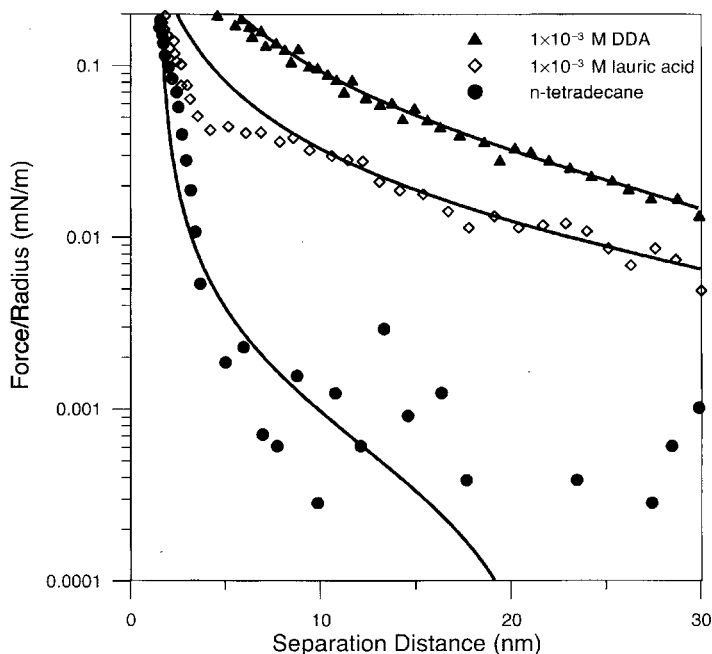
**FIGURE 4** Interaction force between PE surfaces in  $1 \times 10^{-3}$  M solution of DDA in *n*-tetradecane. Vertical lines indicate peaks of the oscillations of force curve. Average peak-to-peak distance is 0.8 nm.

$$\frac{F(D)}{R} = \frac{16\pi kTL}{35s^3} \left[ 7 \left( \frac{2L}{D+2\delta} \right) + 5 \left( \frac{D+2\delta}{2L} \right) - 12 \right] \quad (\text{EQ 2})$$

where  $L$  is the thickness of brush layer extending from the surface,  $s$  is the distance between the chain anchoring points and  $\delta$  is the thickness of the highly compressed polymer layer. This theoretical approach was developed originally for the grafted polymer chains at surfaces but was chosen here due to its simplicity and small number of parameters describing the state of the polymer layer.

The experimental values of interaction force between PE surfaces in pure tetradecane and with surfactants added, together with corresponding fits from the Alexander-de Gennes equation are shown in Figure 5. The Alexander-de Gennes equation was fitted to the experimental values of force at larger distances (larger than 5 nm) in order to see how well experimentally measured interactions correlate with values from the scaling theory. It can be shown that especially for the interactions in pure tetradecane and in the presence of lauric acid significant deviations from the theoretical fit are present. A much better fit was obtained for the interaction forces between PE surfaces in the DDA solution. The corresponding parameters of the Alexander-de Gennes equation are given in Table 3. The real significance of the values of  $L$  and  $s$  obtained for the pure nonpolar solvent and for the lauric acid solution may be, however, small in view of the poor fit to the theoretical equation. The steric component of repulsion with layer thickness  $L = 13.3$  nm and distance between





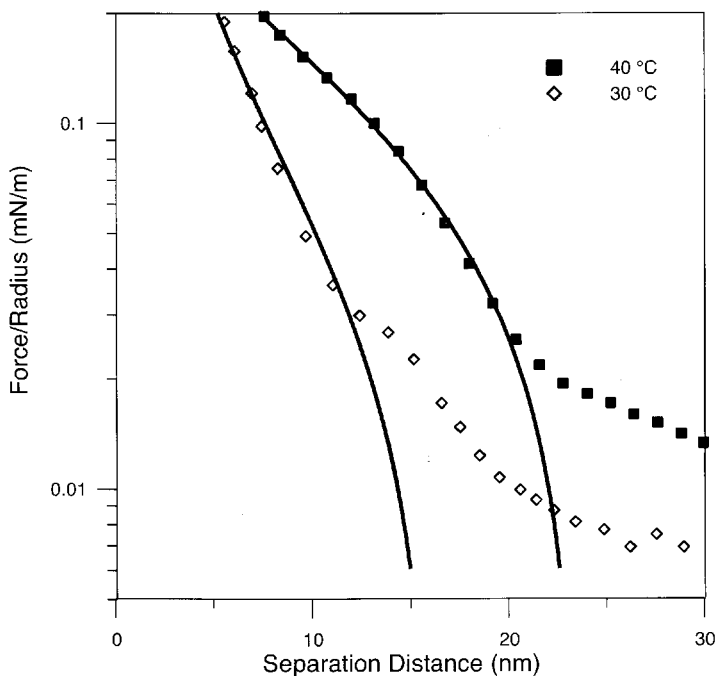
**FIGURE 5** Interaction force between PE surfaces in n-tetradecane and in  $1 \times 10^{-3}$  M solution of DDA and lauric acid in n-tetradecane. Every fifth experimental point is shown for clarity. Continuous lines indicate fit to the Alexander-de Gennes equation.

**TABLE 3** Parameters for the theoretical fit of the Alexander-de Gennes equation for PE surfaces in n-tetradecane in the absence and presence of surfactants

System	Brush Layer Thickness L (nm)	Distance Between Anchoring Points s (nm)
PE/n-tetradecane	13.3	102.8
PE/ $1 \times 10^{-3}$ M lauric acid solution in n-tetradecane	41.5	82.9
PE/ $1 \times 10^{-3}$ M DDA solution in n-tetradecane	43.6	63.7

anchoring points  $s = 102.8$  nm cannot be ruled out, however, for the PE surfaces in the DDA solution.

Finally, the effect of temperature on the interaction forces between PE in nonpolar solvent has been studied. Interaction forces were measured in the lauric acid solution at  $30^\circ\text{C}$  and at  $40^\circ\text{C}$ . Experimental values have been fitted to the Alexander-de Gennes equation at a distance close to the contact of surfaces (below 20 nm) as can be seen in Figure 6. It can be observed that repulsive forces significantly increase with an increase of temperature. These results can be attributed to the more pronounced swelling of the polymer at the surface at higher temperatures and increased repulsion between polymer chains. The parameters for the theoretical equation as given in Table 4 show an increase in the brush layer thickness  $L$  and an increase in the compressed polymer layer thickness  $\delta$  at  $40^\circ\text{C}$  when compared to results at  $30^\circ\text{C}$ .



**FIGURE 6** Interaction force between PE surfaces in  $1 \times 10^{-3}$  M solution of lauric acid in n-tetradecane at 30°C and 40°C. Continuous lines indicate fit to the Alexander-de Gennes equation.

**TABLE 4** Parameters for the theoretical fit of the Alexander-de Gennes equation for PE surfaces in  $10^{-3}$  M lauric acid solution in n-tetradecane at different temperature

System	Brush Layer Thickness L (nm)	Distance Between Anchoring Points s (nm)	Compressed Polymer Layer Thickness $\delta$ (nm)
PE/ $1 \times 10^{-3}$ M lauric acid solution in n-tetradecane at 30°C	12.4	23.9	0
PE/ $1 \times 10^{-3}$ M lauric acid solution in n-tetradecane at 40°C	29.8	22.1	7.6

## CONCLUSIONS

The interaction forces between PE surfaces in pure n-tetradecane were found to be governed mostly by the attractive van der Waals component. After addition of surfactant into the n-tetradecane, a strong repulsive component appears, especially strong for the DDA solution. The mechanism of this repulsion can be attributed to the combined effect of electrical double layer repulsion due to the presence of traces of water in the system, steric repulsion related to the possible presence of the surfactant aggregates between the interacting surfaces, and possible steric repulsion between polymer chains extending into the solvent. Although strong swelling of PE was not evident from measurements of interactions between PE in pure tetradecane, the repulsive force increases with an increase in temperature which can suggest a slight swelling of PE surface in the n-tetradecane/lauric acid solution at elevated temperature. It can be

concluded that addition of DDA into the PE dispersion in nonpolar medium should stabilize PE dispersions and prevent coagulation/coalescence of PE droplets/particles.

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## REFERENCES

- Ahsan, T. and Taylor, D.A. 1998. The influence of surface energetics of calcium carbonate minerals on mineral-polymer interaction in polyolefin composites. *J. Adhes.* 67:69.
- Arnal, M.L. and Muller, A.J. 1999. Fractionated crystallisation of polyethylene and ethylene/ $\alpha$ -olefin copolymers dispersed in immiscible polystyrene matrices. *Macromol. Chem. Phys.* 200:2559.
- Bergstrom, L. 1996. Rheological properties of concentrated, nonaqueous silicon nitride suspensions. *J. Am. Ceram. Soc.* 79:3033.
- Bergstrom, L. and Blomberg, E. 2000. Probing polymeric stabilization in nonaqueous media by direct measurements. *J. Am. Ceram. Soc.* 83:217.
- Binnig, G., Quate, C., and Gerber, C. 1986. Atomic force microscope. *Phys. Rev. Lett.* 56:930.
- Briscoe, W.H. and Horn, R.G. 2002. Direct measurement of surface forces due to charging of solids immersed in a nonpolar liquid. *Langmuir.* 18:3945.
- Chen, Y.L., Xu, Z., and Israelachvili, J. 1992. Structure and interactions of surfactant-covered surfaces in nonaqueous (oil-surfactant-water) media. *Langmuir.* 8:2966.
- Cleveland, J.P., Manne, S., Bocek, D., and Hansma, P.K. 1993. A nondestructive method for determining the spring constant of cantilevers for scanning force microscopy. *Rev. Sci. Instrum.* 64:403.
- de Gennes, P.G. 1987. Polymers at an interface; a simplified view. *Adv. Colloid Interface Sci.* 27:189.
- Ducker, W.A., Senden, T.J., and Pashley, R.M. 1991. Direct measurement of colloidal forces using an atomic force microscope. *Nature.* 353:239.
- Gee, M.L. and Israelachvili, J.N. 1990. Interactions of surfactant monolayers across hydrocarbon liquids. *J. Chem. Soc., Faraday Trans.* 86:4049.
- Giavarini, C., De Filippis, P., Santarelli, M.L., and Scarsella, M. 1996. Production of stable polypropylene-modified bitumens. *Fuel.* 75:681.
- Guerrica-Echevarria, G., Eguiazabal, J.I., and Nazabal, J. 1999. Morphology and physical properties of injection-molded, mineral-filled polyamide 6/poly(hydroxy ether of bisphenol a) blends. *J. Appl. Polym. Sci.* 73:1805.
- Hesp, S.A.M. and Woodhams, R.T. 1991. Asphalt-polyolefin emulsion breakdown. *Colloid Polym. Sci.* 269:825.
- Huneault, M.A., Mighri, F., Ko, G.H., and Watanabe, F. 2001. Dispersion in high viscosity ratio polyolefin blends. *Polym. Eng. Sci.* 41:672.
- Israelachvili, J.N. 1991. *Intermolecular and surface forces.* New York: Academic Press.
- Israelachvili, J.N. and Tabor, D. 1972. Measurement of van der waals dispersion forces in the range 1.5 to 130 nm. *Proc. Roy. Soc. London, Ser. A.* 331:19.
- Kitahara, A., Amano, M., Kawasaki, S., and Konno, K. 1977. The concentration effect of surfactants on zeta-potential in non-aqueous dispersions. *Colloid Polym. Sci.* 255:1118.

- Kosmulski, M. 1999. Zeta potentials in nonaqueous media. How to measure and control them. *Colloids Surf., A*. 159:277.
- Lerdwijitjarud, W., Sirivat, A., and Larson, R.G. 2002. Influence of elasticity on dispersed-phase droplet size in immiscible polymer blends in simple shearing flow. *Polym. Eng. Sci.* 42:798.
- Liang, Z. and Hesp, S.A.M. 1993. In situ steric stabilization of polyethylene emulsions in asphalt binders for hot-mix pavement applications. *Colloids Surf., A*. 81:239.
- Luckham, P.F. and Manimaaran, S. 1997. Investigating adsorbed polymer layer behavior using dynamic surface force apparatuses—a review. *Advances in Colloid and Interface Science*. 73:1.
- McGown, D.N.L. and Parfitt, G.D. 1966. Stability of nonaqueous dispersions. IV. Rate of coagulation of rutile in aerosol of + p-xylene solutions. *Discuss. Faraday Soc.* No. 42:225.
- McGown, D.N.L. and Parfitt, G.D. 1967. Stability of nonaqueous dispersions. V. Theoretical predictions for dispersions in hydrocarbon media. *Kolloid Z. Z. Polym.* 219:48.
- McGown, D.N.L., Parfitt, G.D., and Willis, E. 1965. Stability of nonaqueous dispersions. I. Relation between surface potential and stability in hydrocarbon media. *J. Colloid Sci.* 20:650.
- McNeil-Watson, F., Tscharnuter, W., and Miller, J. 1998. A new instrument for the measurement of very small electrophoretic mobilities using phase analysis light scattering (pals). *Colloids Surf., A*. 140:53.
- Morrison, G.R., Hedmark, H., and Hesp, S.A.M. 1994. Elastic steric stabilization of polyethylene-asphalt emulsions by using low molecular weight polybutadiene and devulcanized rubber tire. *Colloid Polym. Sci.* 272:375.
- Morrison, I.D. 1993. Electrical charges in nonaqueous media. *Colloids Surf., A*. 71:1.
- Nalaskowski, J., Drelich, J., Hupka, J., and Miller, J.D. 1999. Preparation of hydrophobic microspheres from low-temperature melting polymeric materials. *J. Adhes. Sci. Technol.* 13:1.
- Overbeek, J.T.G. 1966. Colloid stability in aqueous and nonaqueous media. *Discuss. Faraday Soc.* No. 42:7.
- Pastorini, M.T. and Nunes, R.C.R. 1999. Mica as a filler for abs/polycarbonate blends. *J. Appl. Polym. Sci.* 74:1361.
- Romo, L.A. 1963. Stability of nonaqueous dispersions. *J. Phys. Chem.* 67:386.
- Zeiler, T., Kellermann, S., and Munstedt, H. 2000. Different surface treatments to improve the adhesion of polypropylene. *J. Adhes. Sci. Technol.* 14:619.