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Original Contributions

Elastic steric stabilization of polyethylene-asphalt emulsions by using low molecular weight polybutadiene and devulcanized rubber tire

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Abstract: Emulsions containing 3% polyethylene were stabilized against coalescence in an asphalt medium by low molecular weight virgin polybutadiene and recycled styrene-butadiene stabilizers. The recycled styrene-butadiene steric stabilizer precursor was obtained as a thermo-mechanical devulcanized ground rubber tire in asphalt. The low molecular weight butadiene and styrene-butadiene rubbers were in situ reacted with sulfur in order to increase the compatibility of the stabilizer with the asphalt phase.

Because of the high molar volume of the asphalt phase and the similarity in contact energy between stabilizer and matrix phase, it is assumed that the stabilization is caused by entropic effects only. The fundamental aspects of elastic stabilization of polyethylene-asphalt emulsions are discussed. The total interaction free energy profile between the polyethylene particles shows that the efficiency of the steric stabilizer formation reaction can be improved significantly.

The use of devulcanized rubber tire as a replacement for the virgin polybutadiene precursor in the in situ stabilization process can significantly reduce the cost of the technology.

Key words: Polyethylene – asphalt – elastic steric stabilization – styrene-butadiene – ground rubber tire – devulcanize

1. Introduction

Unstabilized polymer emulsions in asphalt suffer from rapid coalescence followed by gravity induced flocculation and creaming [1]. If left at a temperature of 150°C, the polymer can form a thick congealed layer within half an hour after mixing which will eventually result in serious processing difficulties and a loss of properties in the pavement. The tendency for these systems to phase separate so rapidly has been a major obstacle for their acceptance in large scale paving operations.

A recent paper by Liang and Hesp [2] describes the design and synthesis of effective steric stabilizers to prevent phase separation in polyethylene-asphalt systems of commercial interest. They have shown that it is extremely difficult to find an asphalt soluble polymer. This is mainly because of the low entropy of mixing caused by the high molecular weight and rigid structural nature of the asphaltene resinous fraction as it is dissolved in the asphalt's oily phase. Moreover, most available synthetic polymers have positive enthalpies of mixing due to a finite difference in their solubility parameter as compared to that of the asphalt. It was found that only low molecular weight butadiene polymers, after being reacted with sulfur in the asphalt phase, could form effective steric stabilizers.

In this paper an analysis of the elastic contribution to the steric stabilization mechanism according to the theories developed by Evans et al. [3] is given. By considering the interaction free energy between two polyethylene particles under conditions of varying surface coverage and stabilizer molecular weight, a better understanding of the factors which are of importance in these systems is obtained. The question of how the technology can be made more attractive will also be addressed. Devulcanized rubber tire may serve as an economic alternative to the virgin liquid polybutadiene precursor which was used in previous systems.

2. Theoretical considerations

Before considering the stability of in situ stabilized polyethylene-asphalt systems, it is useful to discuss the attractive van der Waals forces and repulsive stabilizing forces between polyolefin droplets in an asphalt medium. These attractive forces need to be shielded by a thick enough steric layer if the emulsions are to be stabilized against coalescence.

Attractive forces in polyolefin-asphalt emulsions

For two equally sized spheres, it was Hamaker who first derived the following relationship for the attractive potential, $\Delta G_S^{\mathrm{att.}}$, originating from the London–van der Waals dispersion forces [4]:

$$\Delta G_S^{\mathrm{att.}} = -\frac{A_{11}}{6}\left[\frac{2}{s^2-4}+\frac{2}{s^2}+\ln\frac{s^2-4}{s^2}\right], \quad (1)$$

where

$s = R/a$

R = the distance between the particle centers

a = the particle radius

A_{11} = the Hamaker constant for the particles.

For small interparticle distances compared to the particle diameters, this relationship reduces to [5]

$$\Delta G_S^{\mathrm{att.}} = -A_{11}\frac{a}{12h}, \quad (2)$$

where

h = the surface to surface distance between the particles.

The above relationship is only valid for two spheres interacting in a vacuum. To account for a dispersion medium of material 2, which attenuates the interaction, an effective Hamaker constant A^* is typically used [5]

$$A^* = A_{11} + A_{22} - A_{12} \sim (A_{11}^{1/2} - A_{22}^{1/2})^2. \quad (3)$$

Using literature values for the Hamaker constant of a polyethylene and estimating a reasonable value for the Hamaker constant of asphalt, an approximate van der Waals interaction potential for systems of interest to this work can be calculated [6, 7]. The interparticle distance for which this interaction potential equals $3/2\,kT$ (the average kinetic energy for the particles) then yields a reasonable estimate for the minimum steric layer thickness.

In Table 1, a number of Hamaker constants are given for polymer colloids calculated from both the approximate Hamaker and more accurate Lifshitz theory. The Lifshitz theory, which includes zero-order Keesom and Debye interactions [8] and resonance frequencies in other than the ultraviolet region (the infrared and microwave frequencies [9]), gives Hamaker constants typically higher than those calculated from the original Hamaker approximation.

For the four polymers in this table, the Lifshitz–van der Waals values are approximately twice as high as the composite Hamaker constant (in water).

Asphalt has a refractive index between 1.60 and 1.64 [12] and a dielectric constant between 2.62 and 2.78 [13, 14] which are very close to the values reported for polystyrene [15]. If it is assumed that asphalt has a Hamaker constant approximately the same as that of polystyrene ($A_{22} = 7.09\ 10^{-20}$ J), then a reasonable estimate for the effective Hamaker constant for a polyethylene-asphalt system is $4.3\ 10^{-22}$ J. If the more accurate Lifshitz–van der Waals value for this system is estimated as twice the composite Hamaker constant (it is likely less since the polyolefin is highly swollen by asphalt components), then it is possible to calculate some approximate interparticle attraction curves as shown in Fig. 1.

If the surface coverage of the steric stabilizer is high and its anchoring is strong, then these curves will give a reasonable estimation for the minimum steric layer thickness necessary to obtain a stable system. Thus for two particles of 5 μm, interacting in an asphalt medium, a steric layer thickness of approximately 20 nm on each particle should prevent flocculation. The particles will have

Table 1. Hamaker constants for various polymers in water [4, 10]

Polymer	A_{11}, 10^{-20} J	A_{121}*), 10^{-20} J	A_{121}†), 10^{-20} J
Polyethylene [11]	6.03	0.23	–
Polystyrene	7.09	0.41	0.95
Polyvinyl chloride	10.09	0.75	1.30
Polymethyl methacrylate	8.56	0.55	1.05
Polyisoprene	5.99	0.27	0.74

*) Simple Hamaker constant calculated from A_{11} (for water; $A_{22} = 3.7\ 10^{-20}$ J)
†) Value from Lifshitz-van der Waals calculations

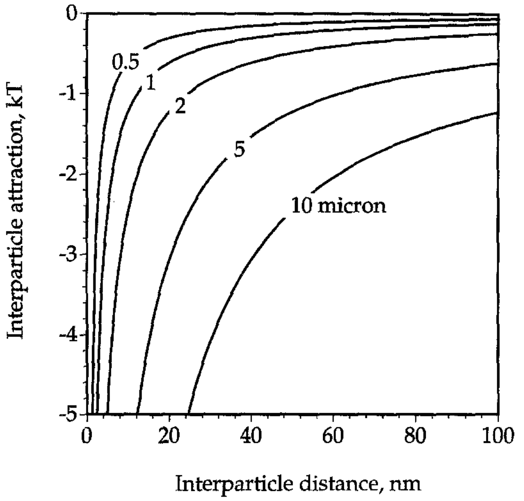

Fig. 1. Van der Waals attractive energy curves for pairs of polyethylene particles of various diameters in asphalt. ($A^* = 8.6\ 10^{-22}$ J and $T = 150\,°\mathrm{C}$)

enough thermal energy to escape from the secondary minimum, assuming that the steric layer is impenetrable.

Since the asphalt has a high molecular volume, it may be expected that a soluble polymer will take on dimensions close to its unperturbed mean-square end-to-end distance, i.e. [16]

$$\alpha^5 - \alpha^3 \propto \left(\frac{1}{2} - \chi_1\right)\frac{V_s^2}{V_1} \approx 0\,, \qquad (4)$$

where

α = the chain expansion parameter

χ_1 = the Flory–Huggins solvent-polymer interaction parameter

V_s = the molar volume of a chain segment

V_1 = the molar volume of the continuous asphalt phase.

Table 2. Unperturbed end-to-end distances for polystyrene, polydimethylsiloxane and polybutadiene [17]

Polymer	Molecular weight, g·mol^{-1}	$\langle r_0^2\rangle^{1/2}$, nm
Polystyrene	25,000	10.6
	50,000	15.0
	250,000	33.5
Polydimethylsiloxane	25,000	9.7
	50,000	13.7
	250,000	30.6
Polybutadiene	12,000	10.2
	25,000	15.0
	50,000	21.2
	250,000	47.5

Table 2 gives a list of the unperturbed mean-square end-to-end distance for three different polymers of various molecular weights. These values indicate that steric stabilization for polyethylene particles with diameters of several microns *is* possible in the asphalt system. The only requirement is that a segment of the stabilizer must be soluble in, or compatible with, the asphalt phase. Further, the rough estimate of the van der Waals attractive energy between the particles is most likely too high. In the asphalt emulsion, the polyethylene is highly swollen, therefore the Hamaker constant may be less than the estimated value of $A^* = 8.6\ 10^{-22}$ J.

Repulsive forces in stabilized polyolefin-asphalt emulsions

The basic forces which are operative in sterically stabilized colloidal systems are often divided into those with an enthalpic origin and those with an entropic or volume restriction origin. The interparticle distance in relation to the steric layer thickness, the particle size, the concentration of steric stabilizer and the interaction between the stabilizer and the continuous phase will determine whether the enthalpic or the entropic force will dominate the repulsion between the particles. In conventional sterically stabilized colloidal systems it is usually the enthalpic contribution which accounts for the total repulsion.

A relationship which gives the enthalpic or mixing contribution to the interaction energy as a function of the interparticle distance was first given by Fischer [18]. For interparticle distances of less than two times the steric layer thickness, Fischer derived the following formula for the interaction free energy due to enthalpic or mixing effects:

$$\frac{\Delta G_S^{\text{mix.}}}{kT} = \frac{4\pi}{3V_1}\phi_2^2\left(\frac{1}{2}-\chi_1\right)\left(L-\frac{h}{2}\right)^2 \times\left(3a+2L+\frac{h}{2}\right), \qquad (5)$$

where

V_1 = the molar volume of the continuous phase
ϕ_2 = the polymer volume fraction in the steric layer
χ_1 = the Flory–Huggins polymer-solvent interaction parameter
L = the steric layer thickness
h = the surface-to-surface interparticle distance
a = the particle diameter.

This relationship shows that the mixing free energy contribution is inversely proportional to the molar volume of the continuous phase and directly proportional to the $(1/2-\chi_1)$ term. In the systems which are the focus of this paper, the average molar volume of the asphalt phase is *at least* an order of magnitude higher than the typical solvents which are used in conventional colloidal systems, e.g. toluene, benzene. Moreover, the Flory–Huggins parameter could at best reach zero after sufficient grafting of asphalt onto the polybutadiene, but will more likely be near or above 0.5. This means that the stabilizer has poor solubility in the asphalt phase. It is therefore obvious that the enthalpic effect will not be contributing significantly to the steric stabilization of the polyethylene particles. In polyethylene-asphalt emulsions we are dealing with a system similar to a polymer blend which is stabilized by a block or graft copolymer. The only difference between the two systems is that in the asphalt system, phase separation proceeds significantly faster than in polymer blends because of the much lower viscosity of the continuous phase.

The entropic or elastic contribution to the steric stabilization mechanism has been considered in detail by Dolan and Edwards [19] and subsequently by Evans et al. [3]. The latter paper describes the use of Flory's elasticity theory to develop relationships which give the elastic free energy of repulsion as a function of interparticle distance for a constant segment density model, a denting model and a Gaussian segment density distribution function model for the adsorbed polymer. For two spherical particles covered with Gaussian tails, the following relationship for the elastic free energy of interaction, $\Delta G_S^{\text{el.}}$, is obtained [3]:

$$\Delta G_S^{\text{el.}} = 2L\nu\pi akT\left(\frac{2}{3}-\frac{\delta_0}{2}-\frac{\delta_0^3}{6}+\delta_0\ln\delta_0\right), \qquad (6)$$

where

ν = the total number of chains per unit area
a = the particle diameter
$\delta_0 = h/L$
h = the surface-to-surface distance between the particles
L = the steric layer thickness.

With these equations we can estimate the total interaction free energy in elastically stabilized polyethylene-asphalt systems

$$\Delta G_S^{\text{tot.}} = \Delta G_S^{\text{att.}} + \Delta G_S^{\text{el.}}\,. \qquad (7)$$

It is also possible to get a better understanding of how the surface coverage (stabilizer concentration) and steric layer thickness (stabilizer molecular weight) influence the colloidal stability. Some systems will be considered in more detail in the results and discussion section.

3. Experimental

The experiments conducted on the polyethylene-asphalt emulsions are comprised of two

Table 3a. Properties of the materials used for the in situ stabilization of polyethylene-asphalt emulsions

Material	
Polyethylene (PE)	
Type	Linear low density
Molecular weight	$\bar{M}_n = 12{,}500\ \mathrm{g \cdot mol^{-1}}$ $\bar{M}_w = 40{,}000\ \mathrm{g \cdot mol^{-1}}$
Polybutadiene (LPBD)	
Composition	80 ± 5% trans and cis, 1,4 20 ± 5% 1, 2 vinyl
Molecular weight	12,000 $\mathrm{g \cdot mol^{-1}}$
Amine-terminated PBD (ATBN)	
Type	10% acrylonitrile-90% butadiene
Amine equivalent mol. wt.	1200 $\mathrm{g \cdot mol^{-1}}$
End group	1-(2-aminoethyl)piperidine
Anhydride modified PE (PE-g-MA)	
Melt flow	11–18
Density @ 25 °C	0.920 $\mathrm{g \cdot mol^{-1}}$
Anhydride content	0.07 $\mathrm{mol \cdot Kg^{-1}}$ (of resin)
Elemental sulfur	Anachemia Chemical Company analytical grade

parts. The first set of experiments was designed to obtain a better understanding of the efficiency for the in situ steric stabilizer formation reaction and to get an estimate of the maximum particle size which can be stabilized by the virgin polybutadiene stabilizer. The polybutadiene was reacted with an amine terminated butadiene and sulfur in the asphalt phase. It was subsequently added in various amounts to a 3 wt% polyethylene emulsion. For the stable systems the average and maximum particle sizes were determined.

In a second set of experiments it is shown that the virgin polybutadiene can be replaced with a devulcanized styrene-butadiene stabilizer. The use of this styrene-butadiene rubber can significantly reduce the cost of the technology.

Materials

The asphalts used in this study were a Canadian (Bow River) 290 penetration grade obtained from the Petro-Canada Refinery in Montreal, Quebec and a Venezuelan 85–100 penetration grade obtained from the Esso Petroleum Refinery also in Montreal, Quebec. These penetration grades, which are measured using a needle penetrating the asphalt under a specific load at a specific temperature, are typical of the most widely used asphalts in Canada [20].

The properties of the polymers which were used to produce the in situ stabilized emulsions with virgin polybutadiene are given in Table 3a.

The devulcanized styrene-butadiene was obtained as a 10% rubber tire concentrate in asphalt under the trade name Ecoflex from Bitumar Inc. of Montreal, Quebec. The thermo-mechanical integration process for the rubber tire particles produces a homogeneous system with the styrene-butadiene rubber dissolved in the asphalt phase. Gel permeation chromatographic (GPC) results for this asphalt are summarized in Fig. 2. The GPC curve shows only a minor shoulder on the main asphalt peak which is characteristic of the asphaltene and/or the styrene-butadiene fraction. Microscopic observations show a minor amount of insoluble carbon black. It is reported by the manufacturer that this rubber modified asphalt costs only 3 to 5% more than normal paving grade asphalt [21].

Procedures

The steric stabilizers were prepared as reported in a previous paper by Liang and Hesp [2]. The

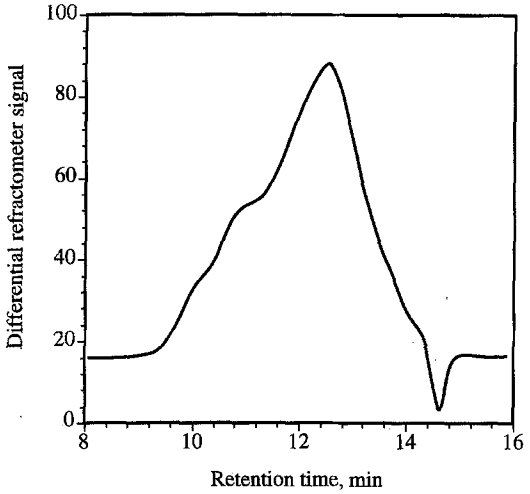

Fig. 2. Gel permeation chromatographic analysis of styrene-butadiene rubber in asphalt. (10% devulcanized rubber tire in asphalt)

polyethylene-asphalt emulsions were prepared by slowly adding a known amount of stabilizer in addition to pure polyethylene to fresh asphalt at approximately 150 °C. Employing a high shear laboratory mixer, the polyethylene was dispersed for at least 15 to 30 min.

For the determination of particle concentrations in a stable polyethylene emulsion, known amounts of asphalt (between 3 and 10 mg) were weighed out to an accuracy of 0.1 mg and subsequently dissolved in approximately 50 mL toluene, filtered through a Nuclepore polyester membrane filter (0.2 μm pore size and 25 mm diameter), rinsed twice with approximately 10 mL fresh toluene and gold coated for scanning electron microscopy (SEM) examination. The SEM negatives were enlarged through a projector directly onto a white screen to measure the number of particles. Taking into account the number of particles counted on each negative, the magnification by the SEM, the total weight of asphalt mixture filtered and the area of the filter paper, the particle concentrations can be calculated with a reasonable accuracy. Similar procedures were followed to measure the average and maximum particle sizes in emulsions stabilized with different polybutadiene contents. For each individual sample, between 100 and 600 particle diameters were measured. The distributions were computer-fitted to a three parameter log-normal distribution function using the *Simplex* subroutine as described previously [1].

4. Results and discussion

Stabilization with virgin polybutadiene

The particle concentrations for a 2% polyethylene emulsion stabilized by virgin polybutadiene are given in Table 3b for eight different incubation times at 150 °C. The composition of this stabilized system is given in Table 4. It is obvious from these results that the system shows long-term storage stability without any change in particle concentration or particle size.

If we ignore any swelling effects for the purpose of simplicity then the average particle concentration of 3.0 $10^9\,\mathrm{mL}^{-1}$ for this system corresponds to an average particle radius of approximately 1 μm. If all the maleic anhydride groups on the functionalized polyethylene could attach themselves to a single polybutadiene chain on the particle surface then this would result in a concentration of steric stabilizer at the interface of 3.5 10^{18}

Table 3b. Particle concentrations for in situ stabilized polyethylene emulsion in a Bow River 290 penetration grade asphalt

Incubation time, *h*	Particle concentration, $10^9\,\mathrm{mL}^{-1}$
0	7.5
1	3.6
2	3.4
3	4.3
4	3.5
5	2.6
12	5.2
24	4.5
50	4.2

Table 4. Composition of in situ stabilized emulsion

Ingredient	Concentration, wt%
Bow River 290	97.4
PE-g-MA	0.5
LPBD	0.6
ATBN	0.3
Sulfur	0.2
Polyethylene	1.5

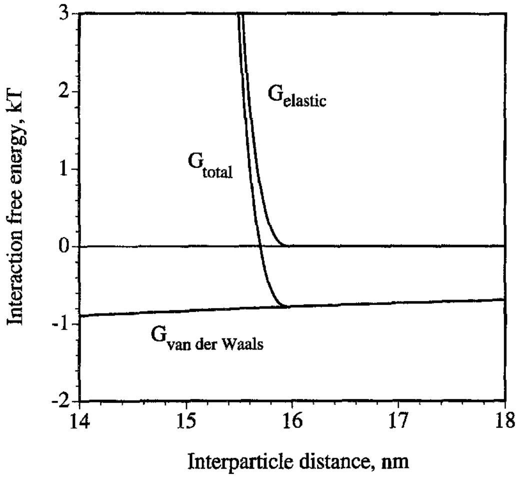

Fig. 3. Interaction free energies for in situ stabilized polyethylene particles. ($A^* = 8.6\,10^{-20}$ J, $a = 1\ \mu$m, $L = 16$ nm, $v = 3.5\,10^{18}\ \text{m}^{-2}$)

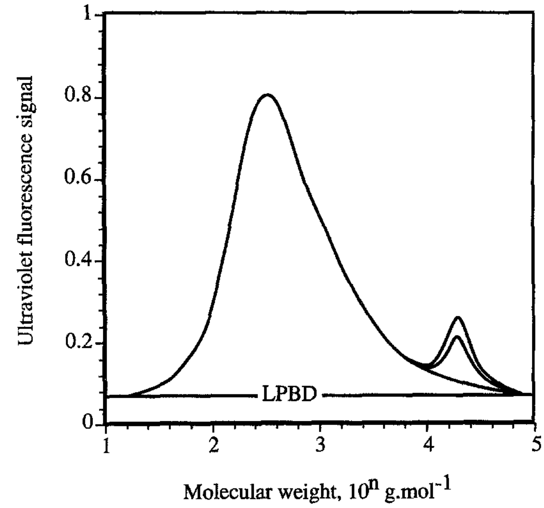

Fig. 5. GPC curves for in situ vulcanization of liquid polybutadiene. (10% LPBD, 1% sulfur, $T = 150\,°$C, after 0, 1 and 4 hours of reaction)

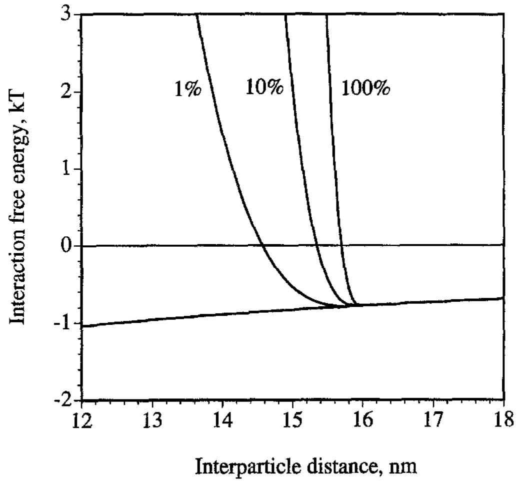

Fig. 4. Interaction free energies for in situ stabilized systems with different stabilizer efficiencies. ($v = 3.5\,10^{16}$, $3.5\,10^{17}$ and $3.5\,10^{18}\ \text{m}^{-2}$ respectively)

chains·m^{-2}. Due to the high molecular weight of the asphalt phase, these chains will attain unperturbed dimensions and the steric barrier thickness, L, can be estimated as 1.5 times the unperturbed end-to-end distance [22]. If we assume that the asphalt grafted onto the polybutadiene chain does not affect its dimensions very much, we may then use the unperturbed rms end-to-end distance for a polybutadiene of molecular weight 12 000 g·mol^{-1} to calculate L.

The van der Waals and elastic interaction free energies in this sytem can now be calculated from Eqs. (2) and (6). The total interaction free energy given in Fig. 3 shows, as was expected, that the 1 µm particles stabilized by the LPBD chains should be stable against phase separation since the minimum in the interaction free energy curve is only shallow.

In Fig. 4 the van der Waals and total interaction free energies according to Eqs. (4) and (7) are given for in situ stabilized systems with *lower* grafting efficiencies. It is clear from these results that for the system given in Table 4 more than ample LPBD has been added to prevent coalescence. These curves also show that the stability of the 1 µm particles is not very sensitive to the attached amount of steric stabilizer in this concentration range. One would expect that only few polybutadiene chains adsorbed at the emulsion interface should suffice to produce a stable system. However, it has been our experience that if we dilute the stabilizer much below 0.5% LPBD for a 3 to 8% polyethylene concentration, then the emulsion often coalesces. This suggests that most likely a large fraction of the LPBD is free in the asphalt phase and is not being utilized as a steric stabilizer.

In Fig. 5, gel permeation chromatograms for an in situ vulcanized system containing 10% polybutadiene and 1% sulfur are given for increasing

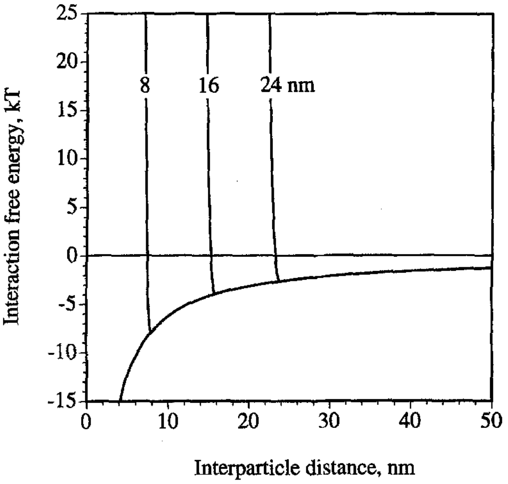

Fig. 6. Effect of steric layer thickness on interaction free energy between two 5 μm particles in asphalt. ($\nu = 2.6\ 10^{17}\ m^{-2}$)

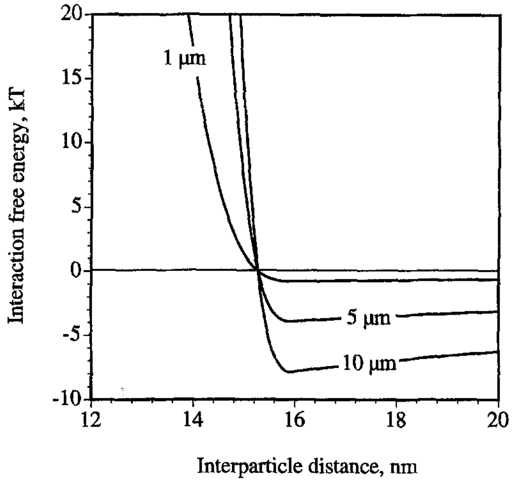

Fig. 7. Effect of particle size on interaction free energy. ($L = 16$ nm, $\nu = 2.6\ 10^{17}\ m^{-2}$)

reaction times. From these curves it can be concluded that at the polymer and sulfur concentrations used in this reaction, grafting of asphalt onto the polymer backbone chain is the main reaction which occurs. Crosslinking of the polybutadiene is not very significant. However, in order for the polybutadiene to attach itself to the polyethylene-asphalt interface, it has to react with at least one amine terminated-polybutadiene, which at some point in time has to react with the anhydride on the functional polyethylene. This crosslinking reaction will occur randomly along the polymer backbone and will therefore cut down the average chain length adsorbed onto the polyethylene particle surface. Most polybutadiene chains that are grafted onto the particles will have effective molecular weights of less than 12000 g·mol^{-1}.

From a comparison of the attractive free energies for particles covered with different steric layer thicknesses, as given in Fig. 6, it was shown that the stability of these particles is greatly reduced for steric layer thicknesses of 8 nm (a polybutadiene molecular weight of approximately 3360 g·mol^{-1}) and that such a system should fail. This was confirmed by experimental results since it has been impossible to stabilize these emulsions when only the amine functional polybutadiene with a molecular weight of 2400 g.mol^{-1} is reacted with sulfur in the asphalt phase. Moreover, attempts to substitute the polybutadiene of molecular weight 12000 g·mol^{-1} with more readily available hydroxy terminated polybutadienes of 2500 g·mol^{-1} proved also to be unsuccessful.

Table 5. Particle size data of in situ stabilized emulsions in a Venezuelan 85–100 penetration grade asphalt

Polybutadiene, wt%	d_{avg}, μm	d_{max}, μm
5	0.8	2.0
4	1.1	2.6
3	1.0	2.2
2	1.6	4.2
1	2.9	7.3
0.5	unstable	>100

To gain further understanding of the steric stabilization system, a number of emulsions of 3% polyethylene in 85–100 penetration grade asphalt were prepared with decreasing amounts of steric stabilizer. For these systems the average and maximum particle sizes were determined by scanning electron microscopy of which the results are given in Table 5.

In Fig. 7 the effect of the particle size on the colloidal stability shows that for these systems the maximum stable particle diameter should be less than 10 µm. For larger particles the magnitude of the van der Waals forces would cause the emulsion to irreversibly flocculate and eventually coalesce. These results are in good agreement with

Table 6. In situ stabilized polyethylene-asphalt emulsions using devulcanized rubber tire

Ecoflex, g	85–100, g	PE, %	PE-g-MA, %	ATBN, %	S, %	Stability
300	200	–	1.5	1.8	0.8	Stable
300	200	–	1.5	1.8	1.4	Stable
300	150	–	1.5	2.0	2.0	Stable
300	–	–	1.5	–	–	Stable
100	200	1.0	0.5	0.6	0.3	Stable
100	200	2.0	0.5	0.6	0.7	Stable*)
100	200	2.0	0.5	–	–	Stable*)
100	200	2.5	–	–	–	Unstable

*) Minor flocculation only

the experimentally observed maximum particle sizes as given in Table 5.

Stabilization with devulcanized styrene-butadiene rubber

The cost of any new polymer modifier for asphalt binders has to be low enough to be competitive with currently used products which may contain unstabilized PE, SBR, EVA or SBS polymers. In order to bring the cost of in situ stabilized polyethylene emulsions down to this competitive level, we should focus on two areas.

First of all the efficiency of the liquid polybutadiene stabilizer can be increased. As was concluded from Fig. 4, a large fraction of the stabilizer is not being utilized at the polymer-asphalt interface. This situation may be improved in a controlled manner through a functionalization of the polymer with for instance an anhydride group. Once the butadiene has been grafted with asphalt, the functional groups can be used to drive the 'asphalt polymer' to the emulsion interface.

Another possibility for reducing the cost of this system is to replace the virgin polybutadiene stabilizer with a low-cost, devulcanized styrene-butadiene rubber. Some promising results have been obtained. A 10% devulcanized styrene-butadiene concentrate in asphalt was reacted with amine functional polybutadiene (ATBN) and sulfur (S) in the presence of maleic anhydride modified polyethylene (PE-g-MA). The concentrate was subsequently diluted and additional pure polyethylene was added after which the stability was checked with a hot-stage microscope. The results of these limited trials are given in Table 6 and Fig. 8.

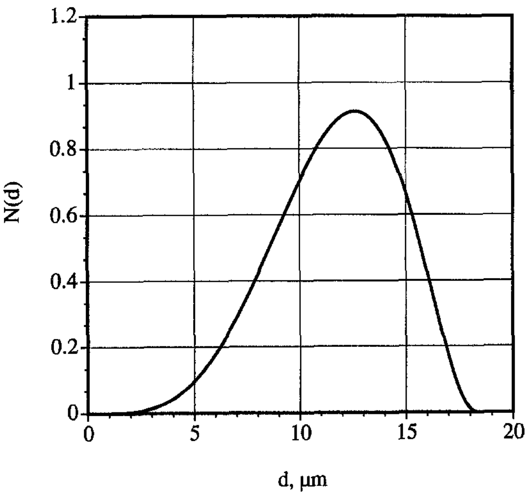

Fig. 8. Particle size distribution for a 2.5% polyethylene emulsion stabilized with recycled styrene-butadiene rubber (after heating for 1 h at 150 °C)

Surprisingly enough, the Ecoflex and PE-g-MA together formed a stable emulsion without any need for the addition of ATBN and/or sulfur. This indicates that the recycled SBR contains functional groups which can react with the anhydride on the modified polyethylene.

5. Conclusions

An approximate calculation on the elastic steric stabilization of polyethylene-asphalt emulsions shows that only a few high molecular weight polybutadiene chains would suffice to secure a stable system. From these findings it can be concluded that most likely a significant fraction of the polybutadiene, as it is currently used to stabilize polyethylene-asphalt systems, is not effectively being utilized at the emulsion interface.

The liquid polybutadiene can be replaced by an economically more attractive recycled styrene-butadiene polymer. An adjustment in the functionality and molecular weight of the devulcanized rubber can make this an ideal alternative to expensive virgin polybutadiene.

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