IGC Study of Filler–Filler and Filler–Rubber Interactions in Silica-Filled Compounds

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ABSTRACT: A modification of the existing methods for evaluating the dispersive and specific components of surface free energy (γ_d and γ_s, respectively) was made to investigate filler–rubber and filler–filler interactions by inverse gas chromatography. Four silicas as fillers and various probes that mimic elastomers were employed in this study. It was shown that the pretreatment of silicas with helium could increase γ_d and decrease γ_s. Modification of the silica surface with silane could enhance the dispersive interaction and weaken the specific interaction. The temperature dependence of the interfacial interaction was also investigated, and it was found that lower temperatures favored filler–rubber interactions and mixing efficiency. Tests on different sizes of agglomerates demonstrated the existence of a filler–rubber and filler–filler network. It was also found that γ_d played a role in agglomeration or filler–filler interaction. Our study showed that the larger the specific surface area was, the stronger the dispersive and specific interactions were. The effectiveness of various fillers and elastomer probes was also compared. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2517–2530, 2001

Key words: surface free energy; filler; silica; polymer; rubber; interaction; inverse gas chromatography (IGC); agglomerate; temperature; silane; pretreatment; network

INTRODUCTION

Fillers have been widely used since the discovery of rubber vulcanization for the reinforcement of rubber compounds to enhance their tensile strength, stiffness, tear, and abrasion resistance. In general, the reinforcing ability of a filler depends on its nature, the type of elastomer it is used with, and the filler loading.

It has been widely recognized that the filler nature influences the effect of reinforcement by the following factors:[1] (1) the particle size or specific surface area, (2) the structure or degree of irregularity of the filler, and (3) the filler's surface activity.

The particle size contributes significantly to reinforcement. Smaller particle size (or larger specific surface area) provides more contact area between filler and elastomer and, therefore, leads to stronger reinforcement. The structure, mainly the primary one, which describes the degree of particle aggregation, plays a role in the restrictive motion of elastomer molecules under strain. The previous two factors have been well studied and are understood.[1,2] Surface activity provides a physicochemical contribution to reinforcement because the chemical nature of a particle's surface determines the filler–elastomer and filler–filler interactions. These interactions, accompanied by a change in surface energy, highly affect the elastic modulus, tensile strength, and abrasion properties of rubber compounds. The detachment of rubber from the filler surface requires the energy of an applied external field (e.g., stress) to overcome the filler–rubber in-

Table I   Properties of the Fillers

Name	BET Surface Area (m^2/g)	DBP/Adsorption, (mL/100 g)	Ph	Physical Form
Hi-Sil 132	200	195	7	Powder
Hi-Sil 233	150	190	7	Powder
Hiptane I (treated with mercapto silane)	135	170	7	Pellet
Hi-Sil 532EP	60	185	7	Powder

BET, Brunauer–Emmett–Teller; DBP, dibutylphthalate.

teraction. Thus, the knowledge of the filler's surface characteristics, among which surface energy is one of the most important, and of the change when filler particles contact rubber molecules is important for the understanding of rubber reinforcement and processing.

The value of surface energy for a solid can be found through the measurement of the contact angle.[3,4] However, this method is not that easy to use for filler particles, mainly because of their small size and the difficulties in accessing their surface. Many efforts have been made in recent years to investigate surface energy and its effect on reinforcement. Inverse gas chromatography (IGC) has proven to be one of the most sensitive, reliable, and convenient methods for studying surface energy and filler–rubber and filler–filler interactions.[5–12]

Chromatography has developed quickly since its discovery and now is one of the most useful analytical methods. IGC was introduced first in 1967.[13] Its development, principles, and applications are now well documented.[14]

In the area of IGC study of filler–polymer interactions, significant contributions have been made by Wang, Wolff, and their colleagues.[5–12] They measured the surface energies of various carbon blacks and silicas by IGC and compared filler–rubber and filler–filler interactions by measuring the bound rubber content with rheological and mechanical measurements. The information obtained from these previous studies has significantly enhanced the understanding of the role of surface energy in the rubber reinforcement.

Although many results were obtained by previous researchers, some practical problems still remain unsolved, such as (1) how the treatments of silicas with inert gases and organosilanes affect surface energies, (2) how temperature influences surface energies, and (3) how information about surface energies can help us to understand filler agglomeration. This study attempted to answer these questions through the use of the IGC method at infinite dilution to examine the surface energies for four silicas with various elastomeric probes. As the outcomes of these studies, the classifications of fillers and elastomers will be given with respect to surface energies measured by IGC. The difference between carbon black and silica was also studied and can be found in Wenjin Zhang's thesis.[15]

EXPERIMENTAL

Instrument

A Gow-Mac 69-550P (Bround Brook, NJ) gas chromatograph (GC) with a thermal conductivity detector was used in this research. Our experimental data, demonstrated later, showed very good sensitivity and repeatability for this instrument.

Fillers

Four precipitated silicas, including Ciptane I, which is silane-treated, were selected from PPG. Industries (Pittsburgh, PA) Their properties are summarized in Table I.

Probes

The following probes were used as low-molecular-weight analogs of various rubber elastomers:

1. *n*-Alkanes.
2. 1-Alkenes.
3. Aromatics (benzene and alkyl benzenes).
4. 2-Methyl-alkanes.

All the probes were reagent-grade hydrocarbons used without further purification.

Procedure

To reduce flow resistance through the columns, the filler particles were agglomerated by a press and then sieved to 250–500 and 1000–2000 μm. The agglomerated particles were then put into 25-mm-long stainless steel columns 6.2 mm in diameter. The columns were installed in a GC oven, in which helium pretreatment was carried out at 180°C for 24 h. Helium was also used as a carrier gas with a speed of 30–45 mL/min. The pretreated columns were tested at various temperatures (120–180°C), so the retention times were 0.5 min to 2 h. The probes, low-molecular-weight analogs of rubber elastomers, were injected into the column at infinite dilution, and the retention times, pressure drops applied to the columns, and flow rates were recorded. Air was used as an inert gas. It was assumed that the air was not absorbed on the surface of the filler particles. The net retention time, net retention volume, and the free energy of adsorption (ΔG) of the probes were then calculated with a well-developed procedure.[5]

Surface Free Energy

Surface free energy (γ), or surface tension, consists of two components: the dispersive (γ_d) or London component, stemming from the London forces, and the specific component (γ_s), originating from all other intermolecular forces, such as polar, H-bonding, and metallic forces:

$$\gamma = \gamma_d + \gamma_s. \qquad (1)$$

In rubber reinforcement, γ_s dominates the filler–filler interaction, and γ_d is mainly responsible for the filler–rubber interaction.

The method of calculation of γ_d is well established.[5,12] If ΔG varies linearly with the number of carbon atoms when n-alkanes are used as probes, γ_d can be calculated as follows:

$$\gamma_d = \frac{(\Delta G_2)^2}{4a^2 N^2 \gamma_{CH_2}} \qquad (2)$$

where ΔG_{CH2} is ΔG of one —CH$_2$— unit in n-alkane molecules and is evaluated as the slope of the straight line of ΔG versus the carbon number of the n-alkanes. In eq. (2), N is Avogadro's number, a is the surface area of an adsorbed —CH$_2$— group (0.06 nm^2), and γ_{CH_2} is the surface energy

of a —CH$_2$— group as constituted by closely packed groups within polyethylene. It is given by

$$\gamma = 35.6 + 0.058(20 - T)\text{mJ/m}^2 \qquad (3)$$

where T is the experimental temperature (°C).

Analyzing γ_d with the use of the previous formula requires, however, a high accuracy of experimental data. One can see from eq. (2) that a small change in the slope (ΔG_{CH2}) of the straight line of ΔG versus the carbon number of n-alkanes will result in a large variation of γ_d. Sometimes, it may also be difficult to compare the values obtained for similar fillers. Therefore, we used another method to evaluate γ_d, as discussed next

Because the purpose of knowing surface energies is to obtain the information of filler–rubber and filler–filler interactions and the work of adhesion (W_a) directly reflects the interactions between the surface of filler particles and the probe molecules (elastomer analogs), in our investigation we used W_a of the surface energies of solid fillers. Accordingly, the absolute value of γ became less important.

When adsorption occurs, W_a can be expressed similarly to eq. (1) as a sum of contributory molecular interactions:[16]

$$W_a = W_{a-d} + W_{a-sp} \qquad (4)$$

where

$$W_a = 2[(\gamma_{d1}\gamma_{d2})^{0.5} + (\gamma_{sp1}\gamma_{sp2})^{0.5}] \qquad (5)$$

sp represents the polar (specific) contribution, and γ_1 and γ_2 are the surface free energies of the substances in contact.

Because alkanes can exchange only dispersive interactions (W_{a-d}'s) with the surface of filler particles, eqs. (4) and (5) for the adsorption of n-alkanes on solid fillers become

$$W_a = W_{a-d} = 2(\gamma_{d1}\gamma_{d2})^{0.5} \qquad (6)$$

where γ_{d1} is γ of the probe molecules (n-alkanes) and γ_{d2} is γ of the solid filler. The value of W_a can be obtained from ΔG of a series of n-alkanes as follows:

$$W_a = W_{a-d} = \Delta G/aN \qquad (7)$$

where ΔG is ΔG of the alkane molecule, whose value can be obtained from an IGC experiment,

and a is the surface area of the adsorbed alkane molecule.

One can see from eq. (6) that the work of adsorption $W_{a\text{-}d}$ is proportional to $(\gamma_{d1})^{0.5}$ and $(\gamma_{d2})^{0.5}$. For the same probes of n-alkanes with certain values of γ_{d1} and under the same conditions, the higher the value of $W_{a\text{-}d}$ is, the higher the value of γ_{d2} is. Therefore, the value of W_a or $W_{a\text{-}d}$ can represent γ_d.

From the previous argument and from a comparison of eqs. (2) and (7), one can see that if a filler has higher γ_d than other fillers, the plot of ΔG versus n (the carbon number of the n-alkanes) should (1) have a larger slope than others and (2) lie above the lines that characterize the other fillers. Besides, the plot of W_a versus n should also lie above those of others. Either the slope or the relative position of the plots can be used to evaluate the $W_{a\text{-}d}$'s.

Employing $W_{a\text{-}d}$ instead of the absolute value of γ_{d2} also has another advantage. When one calculates γ_{d2} from eq. (2), the only useful information is the slope of the straight line of ΔG versus n (the carbon number of the n-alkanes). An error in the experiment with one or more n-alkanes would result in an error in the slope of ΔG_{CH2}, and therefore, would lead to a bigger error in the calculation of γ_{d2} through $(\Delta G_{\text{CH2}})^2$. That is, one point of the plot would affect the whole calculation. However, $W_{a\text{-}d}$ can be easily calculated with eq. (7). Sometimes, it is even unnecessary to calculate $W_{a\text{-}d}$ because just a comparison of ΔG can provide enough information about $W_{a\text{-}d}$. When W_a is used to evaluate γ_d, all of the adsorption data of the n-alkanes can be useful to obtain the information of $W_{a\text{-}d}$; and inaccuracy in adsorption data would not affect the overall evaluation of $W_{a\text{-}d}$ and γ. With this modification, the evaluation of $W_{a\text{-}d}$ and γ becomes much easier.

For probes that have specific interaction ($W_{a\text{-}sp}$) with the fillers, we used a method similar to the determination of the γ_d. We chose benzene and a series of alkyl benzenes as the testing probes. For these molecules, W_a consists of both dispersive and specific components. The specific component ($W_{a\text{-}sp}$) is correlated with W_a and $W_{a\text{-}d}$ because of eq. (4) and additionally as follows:

$$W_{a-sp} = W_a - W_{a\text{-}d}, \; W_{a\text{-}d} = \Delta G /(aN). \quad (8)$$

where ΔG_{ref} is ΔG of an alkane molecule (real or hypothetical) with a surface area identical to that of the aromatic molecule. Some of the surface-area data of the probe molecules can be obtained from the literature;[12] more can be extrapolated by a surface area of 0.06 nm^2 of each —CH$_2$— group. Employing this method, we were able to obtain accurate and comparable information about filler–rubber and filler–filler interactions in silica-filled rubber compounds.

RESULTS AND DISCUSSION

Effect of Pretreatment on Surface Energy

The pretreatment was carried out at 180°C with helium flowing through the column for 24 h. Figure 1 shows the results obtained for ΔG on Hi-Sil 233 as a function of the carbon-atom number for the three families of hydrocarbons [n-alkanes, 1-alkenes, and aromatics (benzene and alkyl benzenes)] at 180°C. The figure shows that the pretreatment with helium could increase $W_{a\text{-}d}$ (i.e., filler–rubber interaction), represented by the adsorption of n-alkanes. However, the pretreatment almost did not affect the adsorption of benzene and alkyl benzenes on the filler. According to eq (8), this means that the specific component of W_a (i.e., filler–filler interaction) was decreased by the pretreatment. For the other three types of silica, the results were similar. This shows that the pretreatment removed the water physically adsorbed on the particle surface. The adsorbed water delivers high-energy sites (—OH— groups) that contribute more in polar, hydrogen-bonding, and metallic forces and, thus, favors the specific or filler–filler interaction but hinders the dispersive or filler–rubber interaction. The removal of water could expose more particle surface to elastomer macromolecules (here, the probe molecules) and, therefore, enhance the filler–rubber interaction. This confirms the known effect[5] that the concentration of the —OH— groups as high-energy sites can only contribute to $W_{a\text{-}sp}$. A small amount of adsorbed water could act as an adhesive agent between filler particles, but when silica particles were put in water, the particles tended to disperse in water.[17]

To maintain stable experimental conditions, all the silica fillers mentioned in the following experiments and discussions were 250–500 μm in size and pretreated with helium, except for some specific cases that are discussed separately.

Interactions of Silica Particles with Low-Molecular-Weight Elastomer Analogs

In this part of our study, a series of n-alkanes was employed to model the macromolecules of satu-
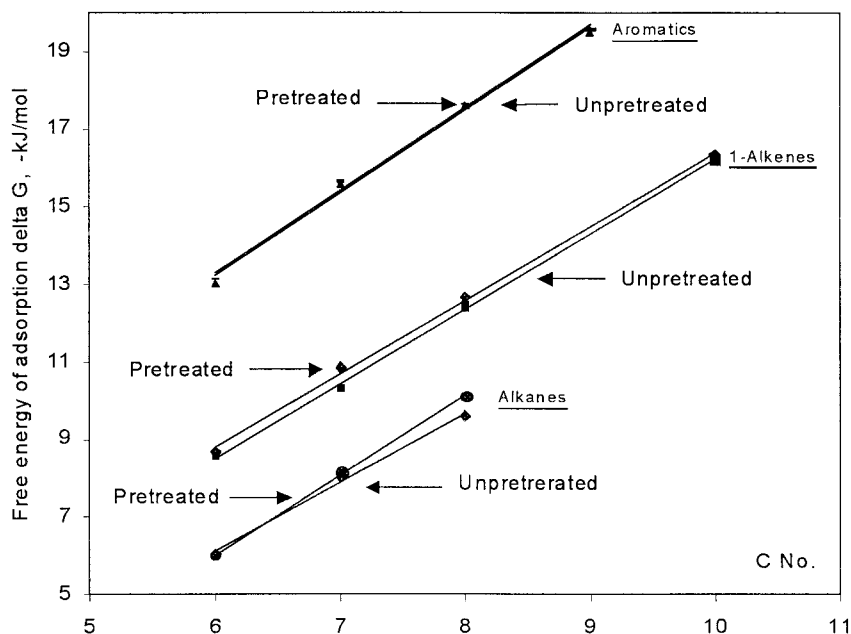
Figure 1 ΔG's of probe molecules on unpretreated and pretreated Hil-Sil 233 versus their carbon numbers at 180°C.

rated rubbers, such as ethylene–propylene rubber (EPR) and butyl rubber, with 1-alkenes used as probes for unsaturated rubbers, such as natural and polybutadiene rubbers. A series of alkyl benzenes were used to investigate the contribution of an aromatic ring in the elastomers (e.g., Styrene–butadiene rubber [SBR]) in the filler–rubber interaction. We investigated the effect of side chains in elastomer molecules by comparing 2-methyl alkanes with n-alkanes.

We obtained the standard enthalpy and entropy of adsorption of the probes by plotting Gibbs' potential ΔG versus temperature (T) according to the following thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

The intercept of the straight line with the Y axis is the enthalpy ΔH, and the slope is the entropy of adsorption ΔS.

Figure 2 shows ΔG for various rubber analogs on silica Ciptane I. All the other silicas showed similar results. All the plots of ΔG versus carbon number for the homologous probes were represented by straight lines. The differences between n-alkanes and the other given elastomer analogs could then be considered the contribution of the functional groups. As shown in Figure 2, the double bonds in the 1-alkenes contributed to $W_{a\text{-}sp}$

because of the so-called induced polar–polar interactions with the silica surface. The presence of the benzene ring led to an even larger such interaction because the conjugated π-bond was more easily polarized by the polar surface of silica particles. When a side methyl group was introduced in the probe molecules, the filler–rubber interaction became weaker because of the steric effect of packing.

As shown in Figure 3, the plots of ΔH versus carbon number for the homologous probes were represented by straight lines. The enthalpies of adsorption of elastomer analogs led to the same conclusions as those from ΔG's. If one compares Figures 2 and 3, one can see that both the enthalpy and entropy significantly contribute to the ΔG values of the probe molecules. The free energies and enthalpies of adsorption were all negative; the enthalpy changes indicated exothermic interactions, and the free energy changes yielded a spontaneous process. From Table II, one can see that for the silica–probe interactions, the entropy changed from -0.0628 to -0.1086 kJ mol^{-1} K^{-1}, indicating that the probe molecules changed from the less-ordered gas phase to a more-ordered adsorbed phase on the surface of the filler particles. Compared with the probe molecules, real rubber molecules had lower entropy, and the entropy contribution differed from that of the probe mol-
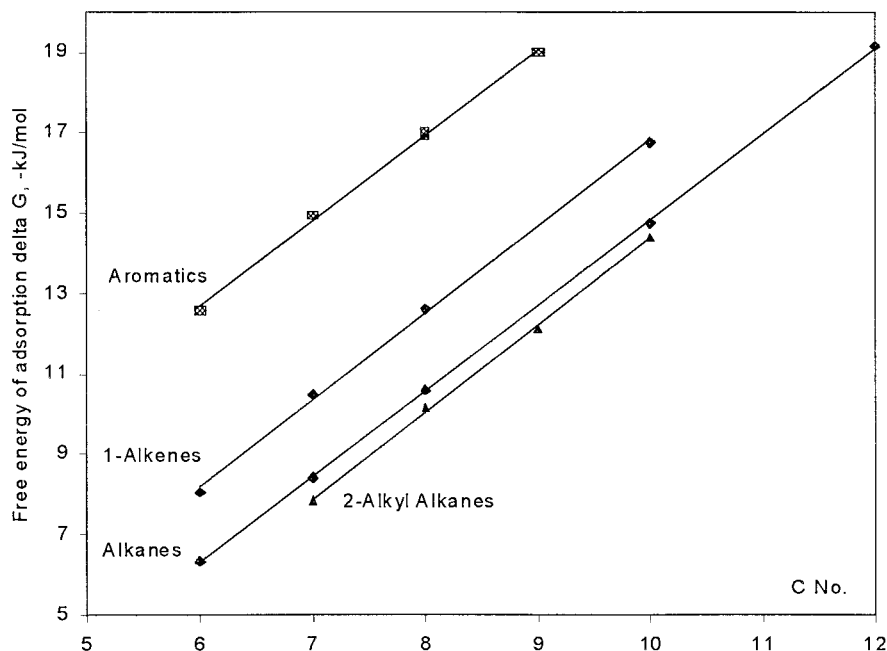
Figure 2 ΔG's of probe molecules on pretreated Ciptane I versus their carbon numbers at 180°C.

ecules. The interactions between fillers and real rubbers included many factors (e.g., molecular weight, molecular weight distribution, molecular structure, configuration, and mixing and processing conditions), which may be very different for various types of rubbers. In this study, when the interactions of probes with fillers were extended to real rubbers, it was assumed that the differences between various rubbers were due to the functional groups, such as double bonds, aromatic rings, and degree of branching.

For all the silicas, the elastomers could be classified in the order of interaction with silica fillers:

$$SBR > NR \geq BR > EPR \qquad (10)$$

where NR is material rubber and BR is butyl rubber.
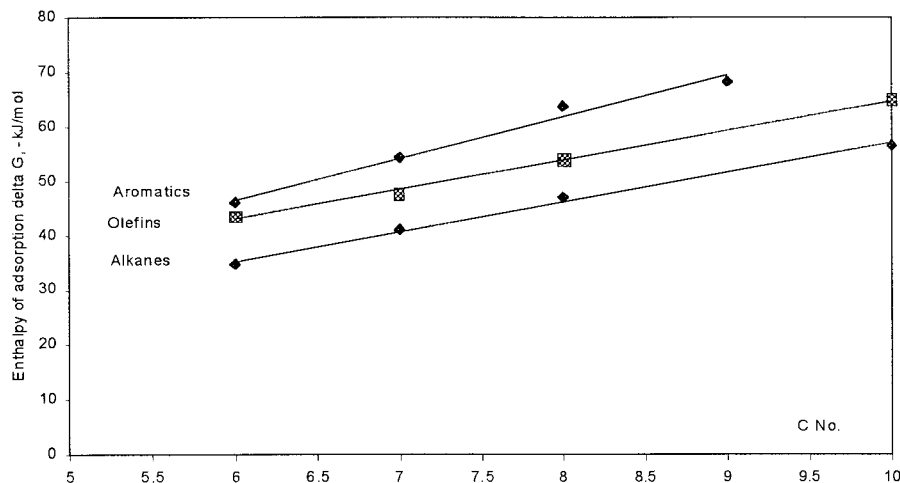
Figure 3   Enthalpies of the adsorption of probe molecules on pretreated Ciptane I versus their carbon numbers.

Table II   Entropy of Adsorption of Probes on Silica Ciptane I

Probe	ΔS (kJ mol^{-1} K^{-1})
Hexane	−0.0628
Heptane	−0.0719
Octane	−0.083
Decane	−0.0924
Hexene	−0.0783
Heptene	−0.082
Decene	−0.1065
Benzene	−0.0705
Toluene	−0.0868
Ethylbenzene	−0.1034
Propylbenzene	−0.1086

Classification of Fillers by Their Interactions with Various Elastomers

Figure 4 shows ΔG of the three groups of elastomer analogs on the surface of various fillers. Because n-alkanes had only W_{a-d} with filler particles, Figure 4(a) demonstrates the comparisons of the fillers with respect to W_{a-d}'s and γ_d's. The classification of W_{a-d} and γ_d was as follows:

$$\text{Hi-Sil } 132 > \text{Ciptane } I > \text{Hi-Sil } 233$$
$$> \text{Hi-Sil } 532\text{EP}. \quad (11)$$

If one compares the specific surface areas of the silicas in Table I, one can see that the larger the specific area was, the stronger the filler–rubber interaction was (Ciptane I, which is a silane-treated silica, was an exception). This confirms the well-known fact that finer particles display stronger filler–rubber interactions and rubber reinforcement. For 1-alkenes, which represent such elastomers containing double bonds as NR and BR, the order of the silicas was about the same [see Fig. 4(b)].

Figure 4(c) compares the interactions of aromatics with fillers. Benzene and alkyl benzenes were used to evaluate the contribution of aromatic rings to the interaction of SBR with the fillers. The silicas' interaction with SBR elastomers could be classified as follows:

$$\text{Hi-Sil } 132 > \text{Hi-Sil } 233 > \text{Ciptane } I$$
$$> \text{Hi-Sil } 532\text{EP}. \quad (12)$$

Again, the finer particles showed a stronger interaction with SBR elastomers. In chain inequal-

ity (12), the interactions between fillers and SBR elastomers included both W_{a-d} and W_{a-sp}. The latter contributed to the interaction between the fillers' surfaces and the polar or polarizable parts of the elastomer molecules and also to the filler–filler interactions. During processes such as mixing and reinforcement, W_{a-sp} may play a complex role. Therefore, the investigation of W_{a-sp} was necessary for a better understanding of the rubber reinforcement.

W_{a-sp}'s of Fillers with Low-Molecular-Weight Elastomer Analogs

A series of aromatic hydrocarbons were used to study W_{a-sp} or filler–filler interaction. The values of W_{a-sp} were calculated, and the results are shown in Figure 5. Finer silicas had stronger W_{a-sp}'s. The classification of W_{a-sp} for silicas was established as follows:

$$\text{Hi-Sil } 132 > \text{Hi-Sil } 233 > \text{Ciptane } I$$
$$> \text{Hi-Sil } 532\text{EP}. \quad (13)$$

If one compares Figures 4 and 5, one can see that when used in nonpolar elastomer reinforcement, finer silica demonstrated stronger filler–rubber and filler–filler interactions.

Figure 6 shows the W_{a-sp}/W_a ratio of the fillers. This ratio shows the part of the total surface energy that contributed to W_{a-sp}. According to the percentage of W_{a-sp}, the magnitude of interaggregate interactions, or filler–filler networking in hydrocarbon rubbers, could be classified as follows:

$$\text{Hi-Sil } 233 > \text{Hi-Sil } 132 > \text{Hi-Sil } 532\text{EP}$$
$$> \text{Ciptane } I. \quad (14)$$

By summarizing all classifications of the silica fillers shown previously, we can state that Hi-Sil 132 and Ciptane I had better filler–rubber interaction and less filler–filler interaction, and Hi-Sil 532EP was the worst among the fillers.

W_{a-sp} is caused by polar, hydrogen-bonding, and metallic forces between surfaces. When used in rubber reinforcement, fillers with a stronger W_{a-sp} are more suitable for polar or polarizable elastomers than nonpolar elastomers. W_{a-sp} contributes to both the filler–rubber and filler–filler interactions. Some high-energy sites on the surface of filler particles can be attached by polar or polarizable groups in the elastomer molecules so that the interaction between the polar surfaces of
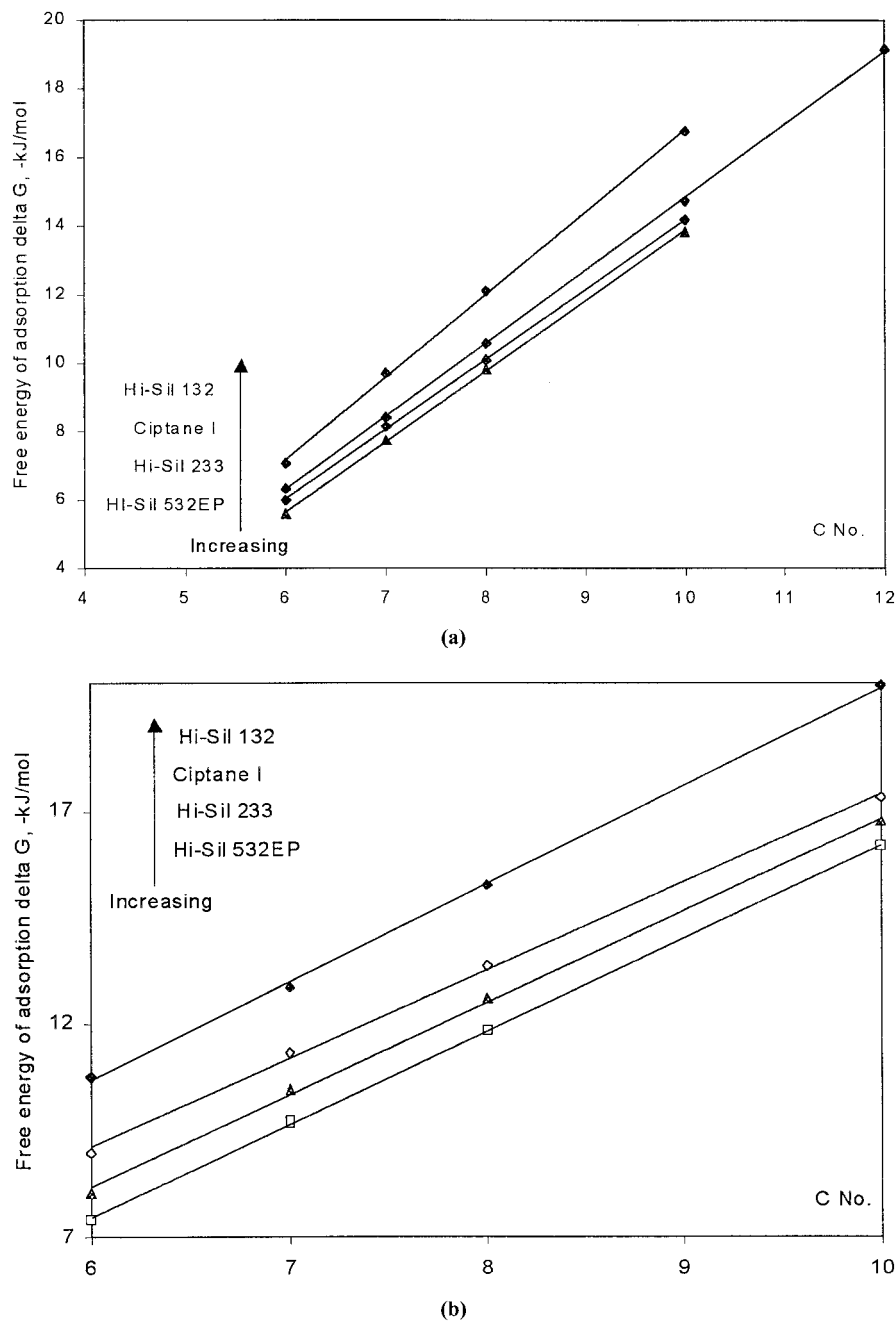
Figure 4 ΔG's of probe molecules on pretreated silicas versus their carbon numbers at 180°C: (a) n-alkanes, (b) 1-alkenes, and (c) aromatics.

the filler particles can be diminished to some extent. It is also easy to understand that polar fillers such as silicas have a higher tendency to agglomerate in nonpolar solvents such as hexane but a lesser tendency to agglomerate in polar solvents such as water or alcohol.[17] However, nonpolar fillers are more likely to agglomerate in polar solvents. Therefore, mixing silicas with po-

lar (or polarizable) elastomers is easier than mixing them with nonpolar elastomers.

Temperature Dependence of the Interactions

Figure 7 shows the temperature dependence of ΔG for Ciptane I. ΔG decreased with increases in temperature. The reason was that when the temperature increased, the degree of freedom of the

(c)
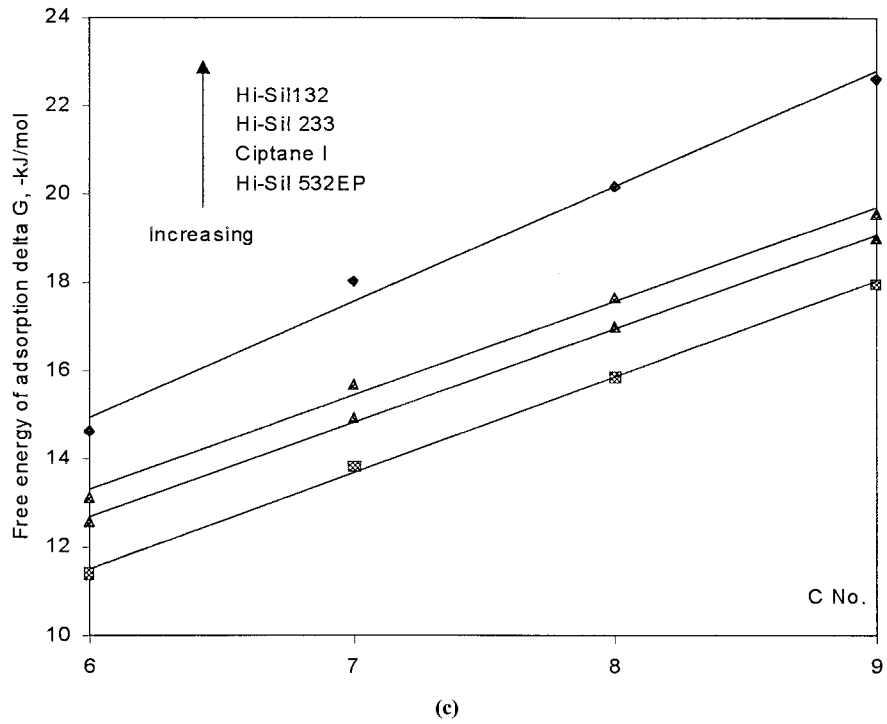
Figure 4 (*Continued from the previous page*)

probe or elastomer molecules increased and the adsorption became more difficult. The same was true for all other fillers. However, the dependence

of dispersive and specific components on the temperature was not so simple. Figure 8 demonstrates the decrease in $W_{a\text{-}sp}/W_a$ for Ciptane I

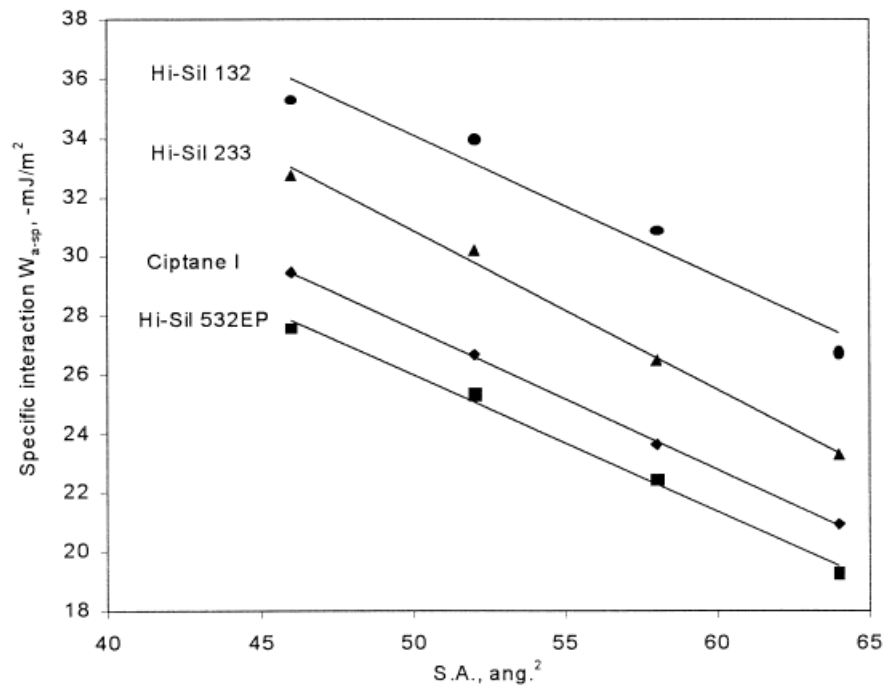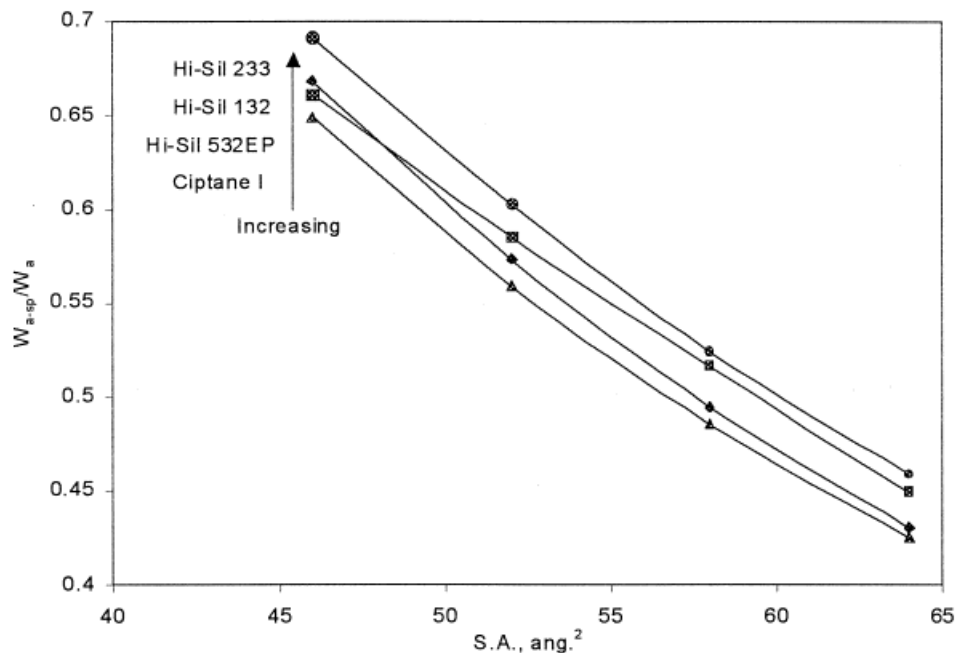**Figure 5** $W_{a\text{-}sp}$'s of aromatics versus their molecular surface areas of various fillers at 180°C.

Figure 6 $W_{a\text{-}sp}/W_a$'s of aromatics on various fillers versus their molecular surface areas at 180°C.

with the temperature decreasing. Although the two components increased when the temperature decreased, the increase of the specific component was smaller than that of the dispersive compo-

nent. This information may be useful for the mixing process. Because the filler–filler interaction is less dependent on temperature, at lower temperatures the stronger filler–rubber interaction can
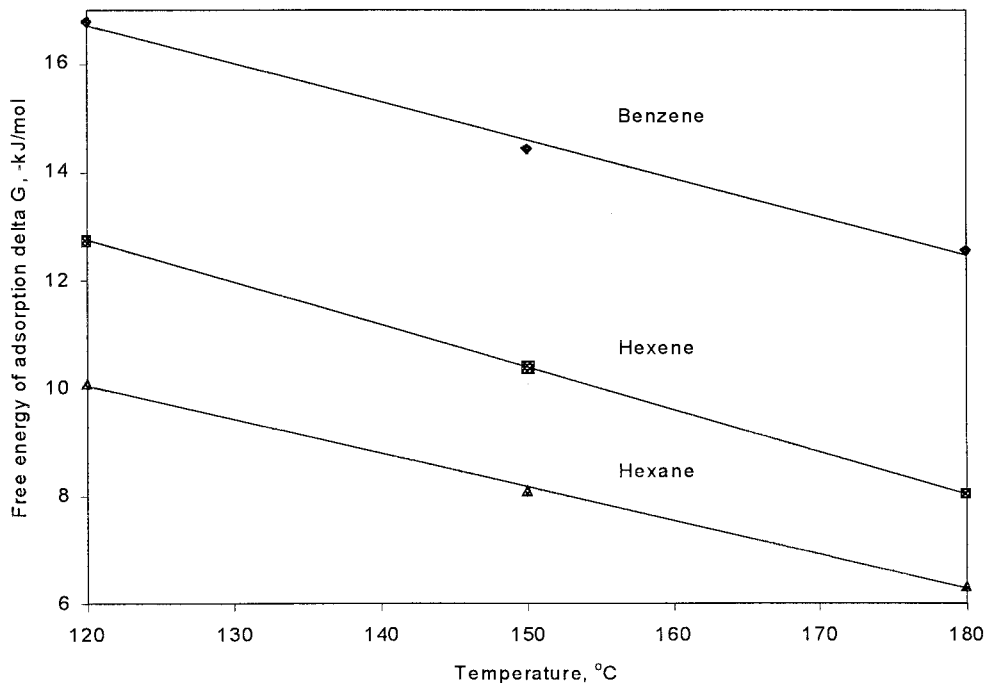

Figure 7 ΔG's of probe molecules on Ciptane I versus testing temperatures.

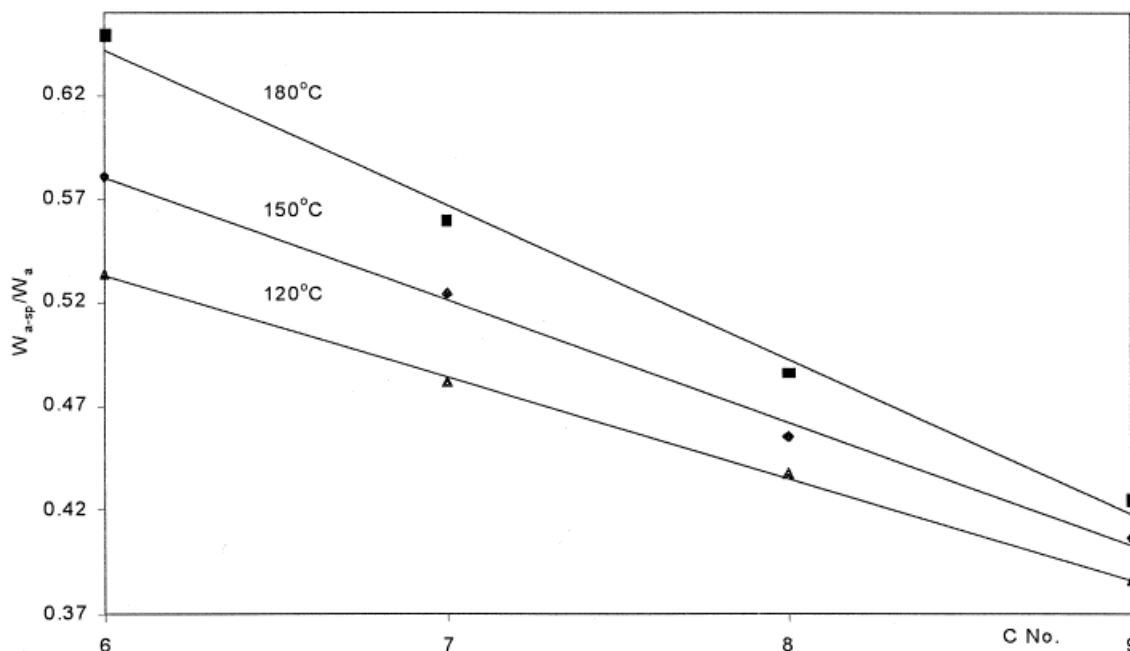**Figure 8** $W_{a\text{-}sp}/W_a$'s of aromatics on Ciptane I versus their carbon numbers at different temperatures.

overcome the filler–filler interaction and thus improve the mixing quality and reinforcement.

Although this result contradicts another observation,[6] this effect is easy to understand. $W_{a\text{-}sp}$, to some extent, can be interpreted as the interaction between opposite electric charges, where the attraction between the charges is almost independent of temperature. However, γ_d is highly dependent on temperature, so the ratio $W_{a\text{-}sp}/W_a$ decreases when the temperature decreases.

Effect of Silane Treatment of the Silica Surface

When comparing the specific areas of all the silicas, we noted that silica Ciptane I exhibited distinct properties among the four silicas. From chain inequalities [eqs. (11), (13), and (14)], one can see that Ciptane I had stronger $W_{a\text{-}d}$ but weaker $W_{a\text{-}sp}$ than Hi-Sil 233, with its $W_{a\text{-}sp}/W_a$ ratio being the lowest among all the silicas studied. This means that the proper treatment of the silica surface with silane (mercapto silane) significantly increased γ_d and the filler–elastomer interaction, decreased γ_s and the filler–filler interaction, and, hence, improved the mixing quality and rubber reinforcement. Knowing the mechanisms of the silane coupling reaction,[18] one can deduce that the silane treatment resulted in some of the high-energy sites such as hydroxyl groups on the filler surface, which exert polar and hydro-

gen-bonding forces to surrounding rubber molecules or other sites of the silica surface covered by silane molecules. This cover-up could prevent the surface of the silica from being attached by water molecules and other polar functional groups of the silica particles and rubber molecules. However, the sites occupied by silane molecules could have stronger interaction with nonpolar rubber molecules through the other part of the silane molecules and, thus, make the surface more compatible with hydrocarbon rubbers.

Test on Agglomerates

Two sizes of silica agglomerates ($\phi = 250$–$500~\mu$m and 1000–$2000~\mu$m) were used under the same experimental conditions in our studies. Figure 9 shows that W_a's for Hi-Sil 233 and Ciptane I were higher for larger agglomerates. This was because the interaggregate distances were smaller for larger agglomerates. Thus, when probe molecules (alkyl benzenes) penetrated the void, they had stronger interactions with the surface of the aggregates through multiparticle attachment, which formed a filler–filler network. This observation is consistent with rheological and mechanical tests on filled rubber[7] and explains the existence of filler–elastomer and filler–filler networks in the rubber compounds from the viewpoint of surface energy. From Figure 9, one can also see
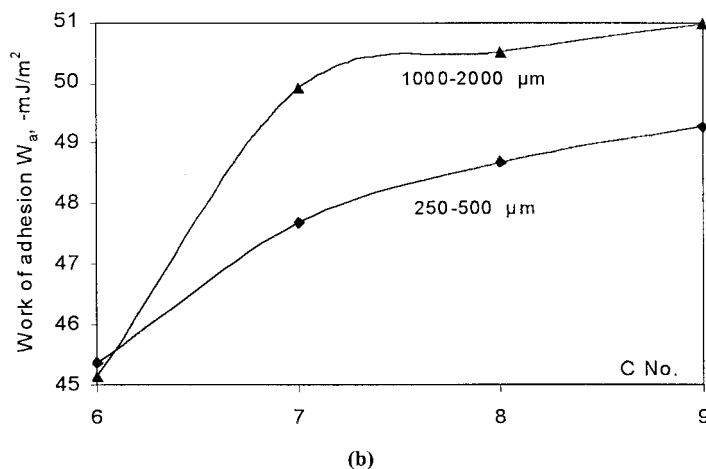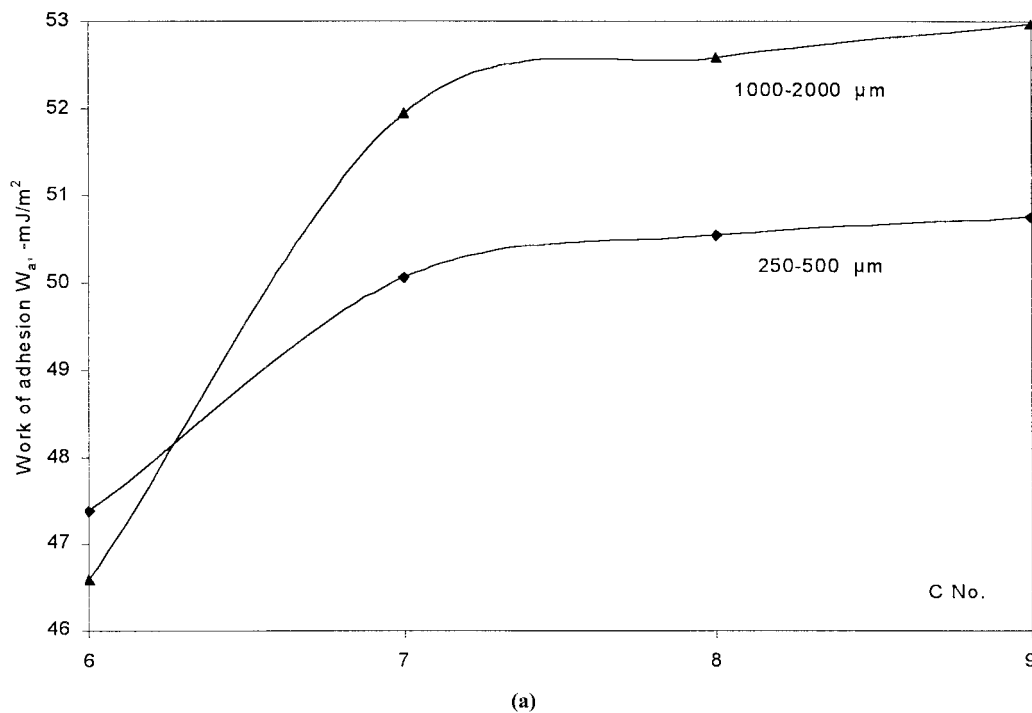
Figure 9 W_a's of aromatics on different sizes of silica agglomerates versus their carbon numbers at 180°C: (a) Hi-Sil 233 and (b) Ciptane I.

that it was difficult to demonstrate interfacial interactions for different sizes of agglomerates when benzene was used as the only probe. This was also true for the analysis of dispersive and specific components of W_a and γ.

Figure 10 shows that both $W_{a\text{-}d}$'s and $W_{a\text{-}sp}$'s of the aromatics on Ciptane I increased when agglomerate size increased. This illustrates that in addition to the specific component, γ_d (represented by W_a) also played a role in filler agglomeration, at least when the agglomeration of the particles happened under the action of a

force. When the chain length of the aromatic molecules increased, the polarity (or polarizability) of the whole molecules decreased, and so $W_{a\text{-}sp}$ between polar sites of the silica and the polar part of the probe molecules diminished. Because experiments with IGC do not involve any strain and force, the results genuinely illustrate the influence of γ on the filler agglomeration. Because the probe molecules were very small compared with rubber molecules, the effect was not as big as that in rheological and mechanical tests of rubber compounds.[7]
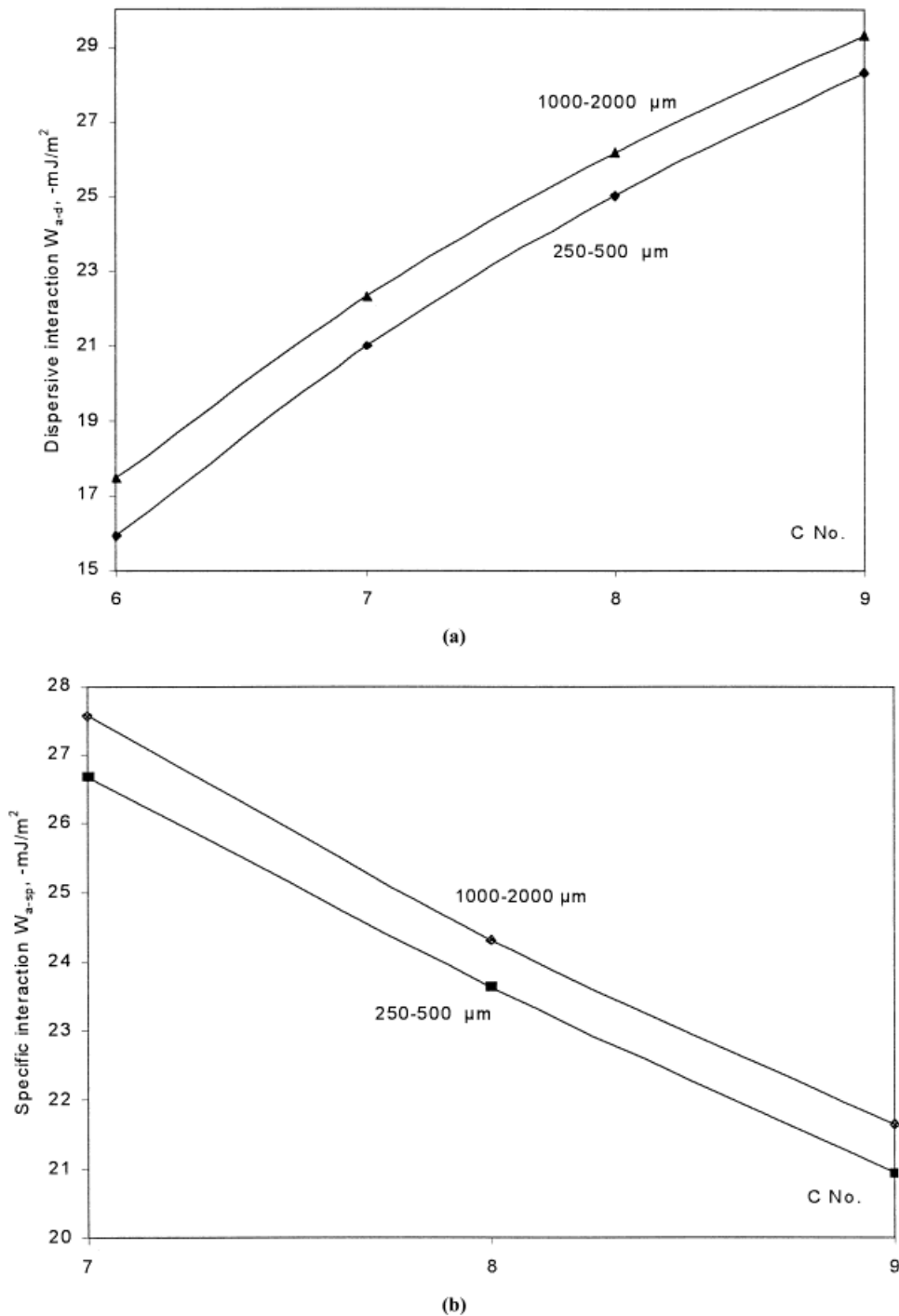
Figure 10 (a) W_{a-d}'s and (b) W_{a-sp}'s of aromatics on different sizes of silica agglomerates versus their carbon numbers (180°C, Ciptane I).

CONCLUSIONS

IGC has been proven to be a reliable and powerful tool for investigating the filler–elastomer and filler–filler interactions. With our modifica- tion for the evaluation of γ_d and γ_s, IGC can be used to obtain a variety of quantitative data. Our results indicate that the pretreatment of silicas with helium can improve the filler–rubber interaction and decrease the filler–filler in-

teraction. For all the silicas investigated, SBR had the strongest filler–rubber interaction, followed by NR, BR, and EPR, in that order. Silicas with higher specific surface areas had stronger filler–rubber and filler–filler interactions and a higher tendency of agglomeration. Treating the silica with silane can increase filler–rubber interaction and decrease filler–filler interaction, thereby decreasing the tendency of agglomeration and improving the mixing quality. $W_{a\text{-}sp}$ has less temperature dependence than $W_{a\text{-}d}$. The magnitude of the interaggregate interactions, $W_{a\text{-}sp}/W_a$, or the filler–filler networking in hydrocarbon rubbers decreases when the temperature decreases. Lower temperatures favor the filler–rubber interaction and decreases the filler–filler interactions, or $W_{a\text{-}sp}$. The test on different sizes of agglomerates showed the contribution of both γ_d and γ_s in agglomeration and confirmed the existence of the filler–elastomer and filler–filler networks.

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