

Interactions of Active Carbon with Low- and High-Molecular Weight Polyethylene Glycol and Polyethylene Oxide

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ABSTRACT: Composites of active carbon in a polymeric matrix composed of polyethylene oxide (PEO) and polyethylene glycol (PEG) having different molecular weight distributions were obtained by melt mixing. Characterization of the amount of bound polymer in the whole range of composition for the polymeric matrix has been performed after dissolution of the matrix in water. Size exclusion chromatography of the solution has been used to determine the composition of the polymeric bound layer. It has been shown that in these conditions of mixing, the amount of

bound polymer slightly decreases from a pure PEG to a pure PEO matrix. Furthermore, PEO is preferentially bound to the active carbon. A simple model is used to show that bonding occurs preferentially by monomeric units rather than by chain ends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3490–3497, 2006

Key words: adsorption; fillers; active carbon; polyethylene oxide; molecular weight distribution

INTRODUCTION

Addition of fillers into polymers is a common industrial practice. Beside their use for cost reduction purposes, fillers also enable to create new materials and bring new properties to polymers. For instance, carbon black is used to reinforce elastomers and also to enhance the electric conductivity of polymers. At least four factors are basically determining the properties of filled polymers: the intrinsic characteristics of the filler and polymer, the composition of the blend, the structure of the filler, and the interfacial interactions.¹

Among these factors, interactions between polymer and filler are known to be of extremely high importance. In the course of the study of interactions, bound rubber or bound polymer is considered to be the most interesting sensor because it depends on both the nature and the strength of the polymer–filler interactions. Therefore, it can be considered as a good measure of the surface activity of filler. In principle, it is also easily measurable, since it corresponds to the fraction of polymer that cannot be extracted from filled compounds by a good solvent of the elastomer or polymer.

Interactions between rubber and fillers such as carbon black and silica have received deep attention be-

cause of their major role in the process of reinforcement for tire applications. Most of the studies dealing with polymer–filler interactions consider an equilibrium between physisorption, chemisorption, and mechanical interactions. In the case of silica, chemisorption is the dominant mechanism because hydrogen bonds² and covalent bonds³ are formed between the matrix and the particles because of hydroxyl groups located on the surface of the filler. In the case of carbon black, contradictory results are found in the literature. For example, according to Wolff et al.,² the strong dependence of bound rubber with temperature in carbon black–styrene–butadiene copolymer (SBR) or in carbon black–natural rubber (NR) indicates physical interactions, whereas Roychoudhury and De⁴ invoke a chemical free radical process.

Any study on the interactions is complicated by other factors such as the surface area of the filler. Because of the increase of the adsorbed polymer chains, bound rubber logically increases with surface area.^{2,5} Though surface activity is generally a rough notion, its effects on interactions are significant. From a physical point of view, surface activity can be expressed through the amount of bound rubber per surface unit or by the surface energy (γ_s) of the filler.^{6,7} The dispersive component of the surface energy is sometimes preferred, since the measure of bound rubber can be misleading because of multiple-segment adsorption. In their study of the dispersive component of the surface energy of carbon black and silica with

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comparable surface areas and structures dispersed in NR, Wolff et al.³ have shown that carbon black exhibits stronger interactions than silica, with NR in agreement with the measured amount of bound rubber. The filler structure is also a key parameter. The crystalline structure of carbon black is correlated to the dispersive component of free energy⁸; small crystals having a higher surface energy because of crystal edges. Relation between the microstructure and the surface activity⁶ of fillers is proved by the large difference between the dispersive component of the surface energy of carbon black (257 mJ/m²) in comparison to that of the same carbon black after graphitization (189 mJ/m²).

The influence of the nature of the polymer on its interaction with fillers has been widely investigated in the case of carbon black. The effect of the polarity of double bonds together with their reactivity explain their activity towards bound rubber.⁹ The amount of bound polybutadiene is higher for silica than for carbon black owing to the high polarity of silica.¹⁰ Wang et al.⁶ have proposed a classification of elastomers in relation to their affinity with carbon black or silica, which stresses the influence of polar groups in the decreasing order: nitrile-butadiene rubber (NBR), SBR, NR, polybutadiene, and finally saturated rubbers and branched polymers. Similar results have been found on measuring bound rubber^{5,7,11} or through mechanical measurements.⁷ Recently, Leblanc^{12,13} has proposed a picture of the conformation of the chain segment of elastomer on the filler surface. For unsaturated elastomers, this model shows that the local conformational stiffness brought by double bonds is more critical than the location or the amount of double bonds. Saturated elastomers with high flexibility have low interactions with highly structured carbon blacks having a tortuous void volume inside the aggregates. However, the classification reported above is contested by some findings. For instance, though NBR is more polar than NR, the amount of bound rubber is much higher in the case of NR.⁴ In this case, chemical interactions between double bonds and chemical groups on the filler surface may be suspected, and they might be strengthened by free radicals created during mixing.

Among carbon fillers, active carbon¹⁴ has a particular behavior. This filler is used as an efficient adsorbent in water and wastewater treatment or filtration of contaminated air, because of its large porosity and surface area. For these reasons, the adsorption of small molecules on active carbon has received more attention in comparison to its activity towards macromolecules. In the case of polymers, the size of the molecules is a key parameter that may influence the adsorption on active carbon, since adsorption generally takes place in the order of increasing sizes.¹⁵ However this effect is balanced by the low desorption rate of long chains. Polydispersity is also reported to be an

TABLE I
Properties of Active Carbon

Ash content	3.7%
pH	10
Surface area: BET (N ₂)	1100 m ² /g
Acid functions	830 μmol/g
Basic functions	760 μmol/g
Mineral impurities	85 μmol/g
Surface tension	50 mJ/m ²
Microporous volume, <2 nm	0.27 cm ³ /g
Mesoporous volume, 2–50 nm	0.57 cm ³ /g
Macroporous volume, 50–200 nm	0.06 cm ³ /g

important parameter for adsorption of macromolecules.¹⁶ Arbuckle and Osman¹⁷ have shown that in the case of polyethylene glycol (PEG) and active carbon, there exists a limiting size of the pores that defines the amount of adsorbed molecules. For polyethylene oxide (PEO), it has been shown that the number of monomer units per chain, bounded on the filler surface, depends on the chain length. This number could range from one unit for short chains (11,000 g/mol) to nine units for long chains (480,000 g/mol). PEO chains are mainly adsorbed inside or near micropores on hydrophilic sites. Indeed, interactions of PEO with active carbon are similar to those of active carbon with water. Molecular modeling has also shown that interactions between PEO and active carbon interactions are mainly Van der Waals forces, electrostatic forces, and hydrogen bonding on the graphitic plans of active carbon.

This work focuses on the interactions of active carbon with a polymer matrix consisting in a miscible blend of PEG and PEO. The objective of this study is to compare the strength of interactions of active carbon with one of the other component, and to infer the existence of a preferential bonding of the PEO or the PEG chains. In the first part, the amount of polymers adsorbed on active carbon has been evaluated. In the second part, a simple model has been proposed to elucidate the nature of the preferential adsorption.

EXPERIMENTAL

Materials

The active carbon used in this study is produced from pine tree activated by vapor. It is available in powder form. The physicochemical properties of the active carbon are presented in Table I. Specific area and porosity have been assessed by nitrogen sorption isotherms at 77 K. The amount of acid and basic groups on the surface of the active carbon has been measured by titration. Acid groups have been titrated by pHmetry with three different bases of increasing strength: sodium hydrogensulfate for strong carboxylic acids, sodium carbonate for lactones, and weak carboxylic

TABLE II
Molecular Weights of the Polyethylene Oxide
and the Polyethylene Glycol

	PEO	PEG
M_n (g/mol)	21,000	7,400
M_w (g/mol)	194,000	7,800
I_p	9.2	1.05

acids and sodium hydroxide for phenols. Basic groups such as chromene and pyrone have been titrated by back titration: active carbon was first reacted with decinormal hydrochloric acid and the excess of acid was then titrated by decinormal sodium hydroxide. Mineral impurities also contribute to the basicity of the active carbon. The surface tension has been determined from the observation of the location of the filler in two immiscible solvents, using Young's equation.

To investigate the effect of chain length on the adsorption of polymer on active carbon, PEO and PEG blended in various proportions were used as a polymer matrix. The polymers are commercial grades available from Union Carbide. The molecular weight distribution of the polymers was measured by size exclusion chromatography in water at 30°C, using a Waters® Alliance® GPCV 2000 system. Two Ultrahydrogel™ columns in the range 1000 to 8×10^5 g/mol

and 10^4 – 10^6 g/mol were used. The calibration was performed with PEO standards from 1050 to 8×10^5 g/mol. Molecular weights are reported in Table II. The two polymers show excellent solubility in water.

Mixing

Two types of blends have been prepared. PEO/PEG blends were used to validate the analytical methods and PEO/PEG/active carbon blends were used to investigate the effect of chain length on polymer adsorption. In the filled polymers, the filler loading is 26.4% in volume of dry active carbon. Because the active carbon contains water adsorbed on its surface, the moisture content was measured using a Sartorius Infrared Dryer MA40 at 140°C prior to sample preparation. All blends have been prepared by melt mixing at 140°C in an internal mixer (Rheomix® 600P Haake) equipped with roller rotors and a 70 cm³ chamber. The rotor speed was 32 rpm, the corresponding shear rate was ~ 14.4 s⁻¹. Mixing for 10 min enabled the stabilization of the torque.

Amount of bound polymer

To characterize the amount of bound polymer and the nature of the adsorbed species, a piece of ~ 50 mg of a

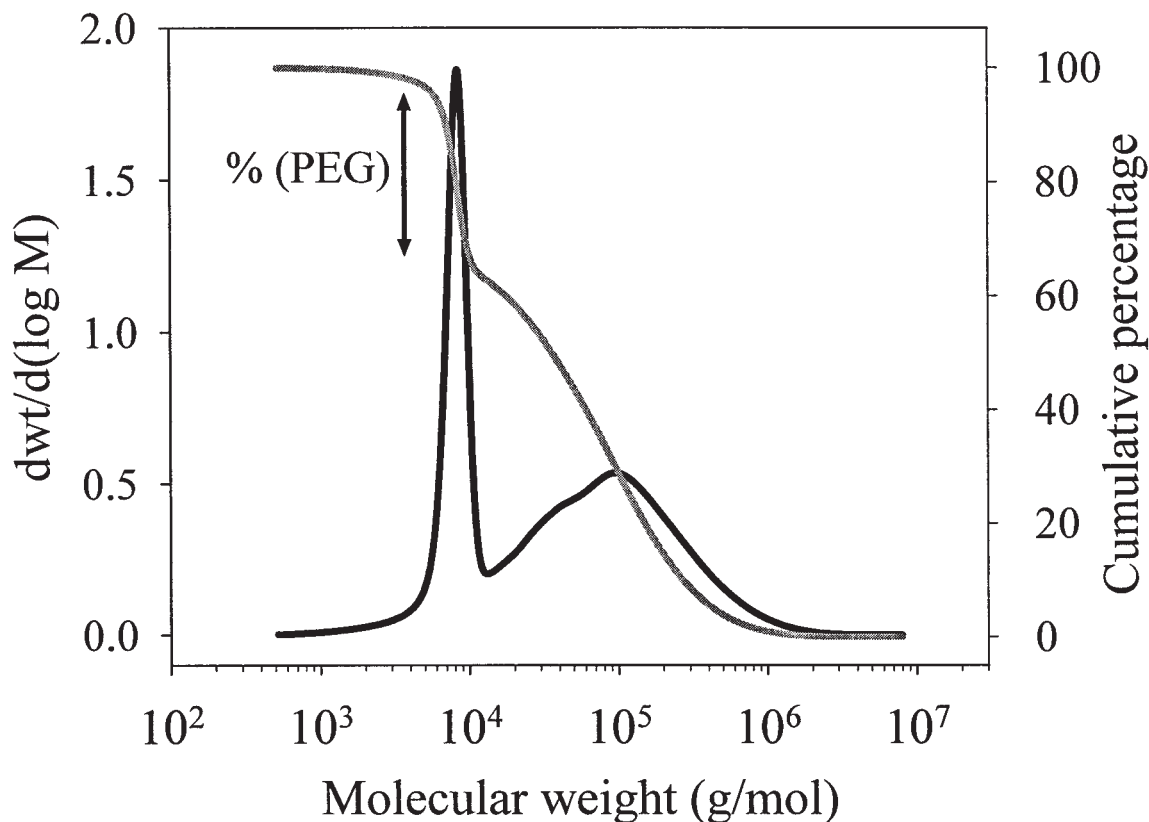


Figure 1 Typical chromatogram of a PEO/PEG blend (70 wt % of PEO).

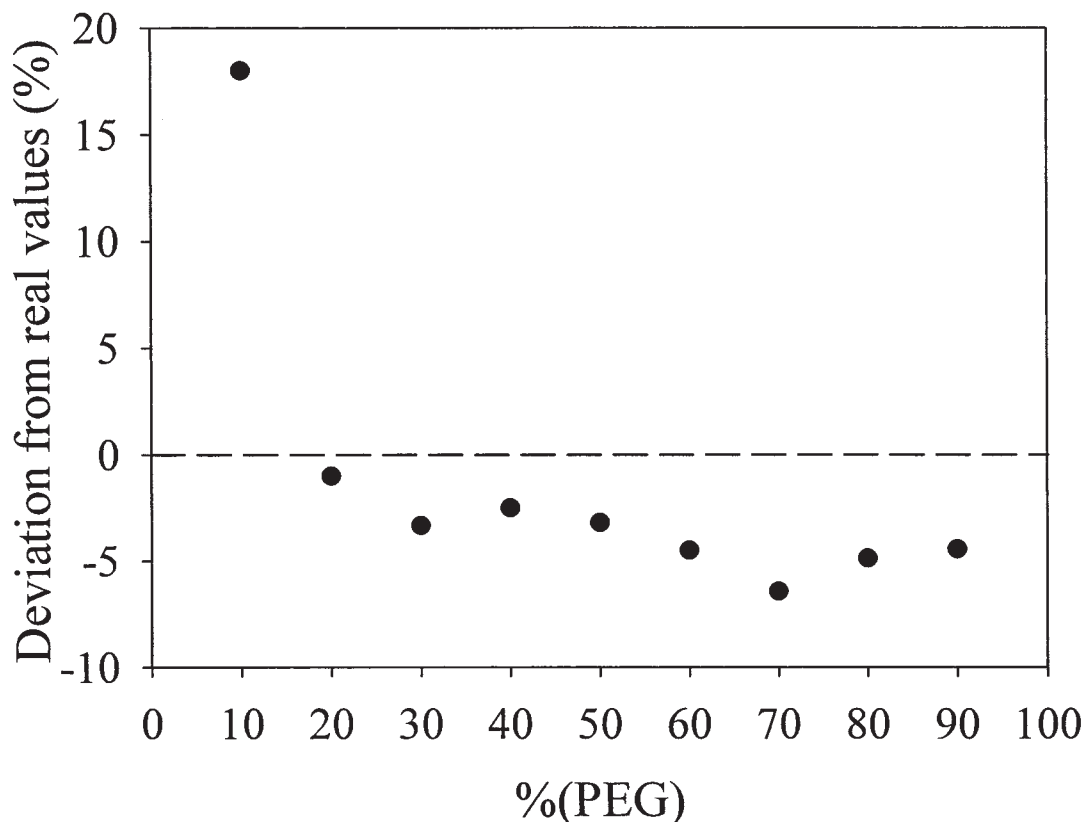


Figure 2 Deviation between the initial PEG fraction and the PEG fraction measured by SEC in PEO/PEG blends.

compact sample was weighed and immersed in 20 mL of water at room temperature. The solution was stirred mechanically to extract the larger amount of PEO and PEG. After 24 h, a suspension of active carbon in water was obtained. The suspension contains PEO and PEG dissolved in water and particles of active carbon on which polymer chains are attached. The suspension was filtered through a filter made of cellulose ester with $0.45 \mu\text{m}$ porosity. The active carbon on the filter was dried under vacuum at 42°C and then weighed. The amount of bound polymer was calculated as follows:

$$w(\text{bound polymer}) = 1 - \frac{m_i - m_f}{(1 - w_{ac})m_i} \quad (1)$$

where m_i is the initial mass of the sample, m_f is the mass of the material on the filter, and w_{ac} is the weight fraction of active carbon in the blend.

Nature of bound polymer

The analysis of the solution after filtration allowed to quantify the amount of each polymer bounded on the filler. This analysis was carried out by size exclusion chromatography (SEC). Chromatograms with two peaks similar to that of Figure 1 were obtained. The

broad peak corresponds to PEO while the narrow peak corresponds to PEG. The PEO/PEG ratio was measured on the cumulative weight fraction at the inflection point. Blends of PEO and PEG of known composition were used for the validation of the technique. A fair agreement between the known PEG fractions and those measured by SEC was obtained as shown on Figure 2. Except for the blend containing a low amount of PEG (10 wt %), the measured error does not exceed 10% and remains within the limits of accuracy of SEC. At low PEG contents, because of the broadness of the molecular weight distribution of PEO, the distribution can hardly be separated and the method is not accurate. The method can only be used with reasonable accuracy for PEG contents higher than 10%.

The PEG fraction adsorbed on the active carbon is determined through the following equation.

$$w(\text{bound PEG}) = \frac{[w_{\text{PEG}}(1 - w_{ac})m_i] - [(m_i - m_f)w_{\text{PEG,sol}}]}{m_f - w_{ac}m_i} \quad (2)$$

where w_{PEG} is the PEG fraction in the blend and $w_{\text{PEG,sol}}$ is the PEG fraction in the solution as measured by SEC.

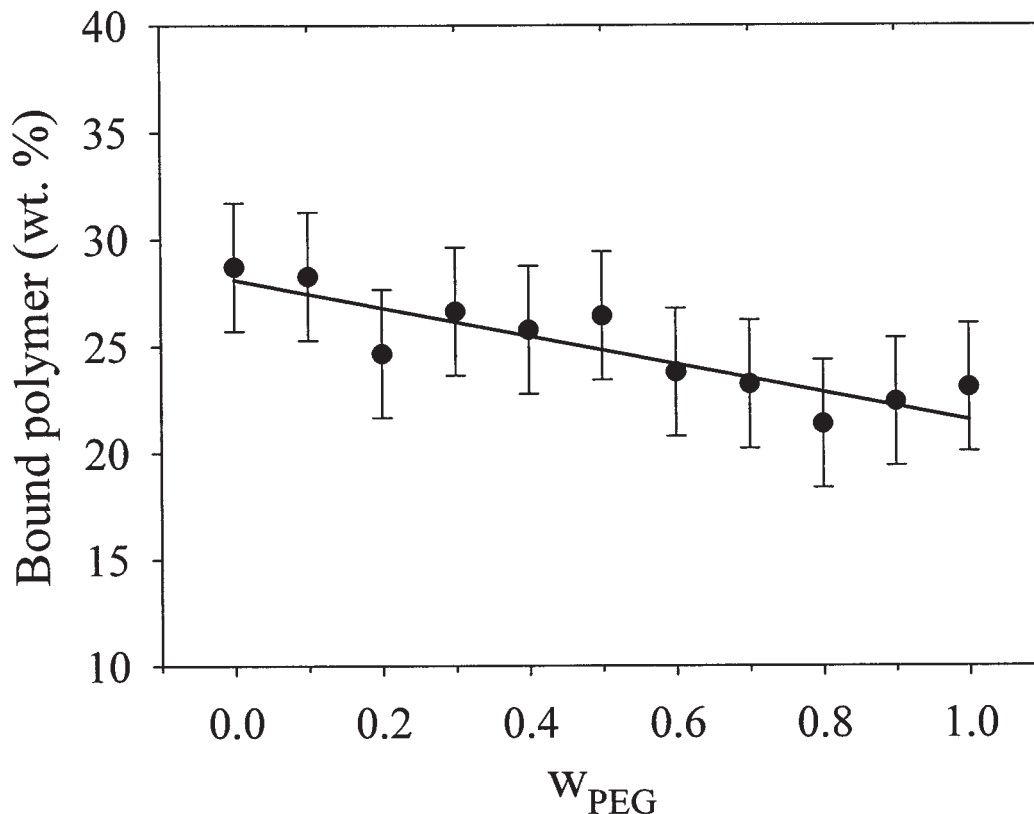


Figure 3 Bound polymer as a function of the matrix composition.

RESULTS AND DISCUSSION

In Figure 3, the percentage of bound polymer, calculated from eq. (1), is presented as a function of the PEG fraction in the polymer matrix. The fraction of bound polymer, PEO and PEG, on the filler surface ranges from 20 to 30 wt % of the whole polymeric material, indicating a strong adsorption phenomenon. The amount of bound polymer slightly decreases when the amount of short chain increases.

Figure 4 presents the fraction of PEG bounded on the active carbon as a function of the PEG fraction in the polymer, and it gives an indication of the composition of the PEO/PEG layer adsorbed on the filler surface. The position of the curve in relation to the bisector of the graph indicates that adsorption of PEO is favored. The fraction of bound PEG is always lower than the PEG fraction in the polymer blend. For instance, when the matrix contains 50 wt % of PEG, the polymeric layer on the filler particles contains only 38 wt % of PEG.

These results clearly indicate that the long chains of PEO are preferentially adsorbed. Considering the high volume fraction of mesopores and micropores of the active carbon under investigation (Table I), there is no limiting size of pores¹⁷ that favors the adsorption of short chains. In these conditions, the preferential bonding of long chains may have another origin. It can be explained in several ways. If bonding occurs by the chain ends or by a single site, then long-chain PEO molecules

interact with less surface area per molecule compared to PEG. In this case, the pore volume can be used by the nonabsorbed part of the PEO and more molecules can be absorbed compared to smaller PEG. On the other hand, if bonding occurs by the monomeric units, long chains have a low desorption rate, because of the weak probability of a simultaneous breakage of the multiple bonds. Because of this low desorption rate, the absorption of PEO molecules is almost definitive and the steric hindrance of the PEO chains, already bound on the filler, prevents any further bonding of short chains.

A simple model was developed to investigate these assumptions by considering the probability of the adsorption of a chain. It is assumed that the number of bonding sites on the surface of the active carbon is N augmented by N' additional sites that are only accessible to PEG chains. These N' sites take into account the small-size porosity of the active carbon. Thus, the mass of adsorbed chains on filler particles can be expressed by

$$m(\text{bound polymer}) = NM + N'M_{\text{PEG}}w_{\text{PEG}} \quad (3)$$

or, using k defined as the ratio between N' and N

$$m(\text{bound polymer}) = N(M + kM_{\text{PEG}}w_{\text{PEG}}) \quad (4)$$

where M_{PEG} is the molecular weight of PEG and M is some average molecular weight of the chains in the blend.

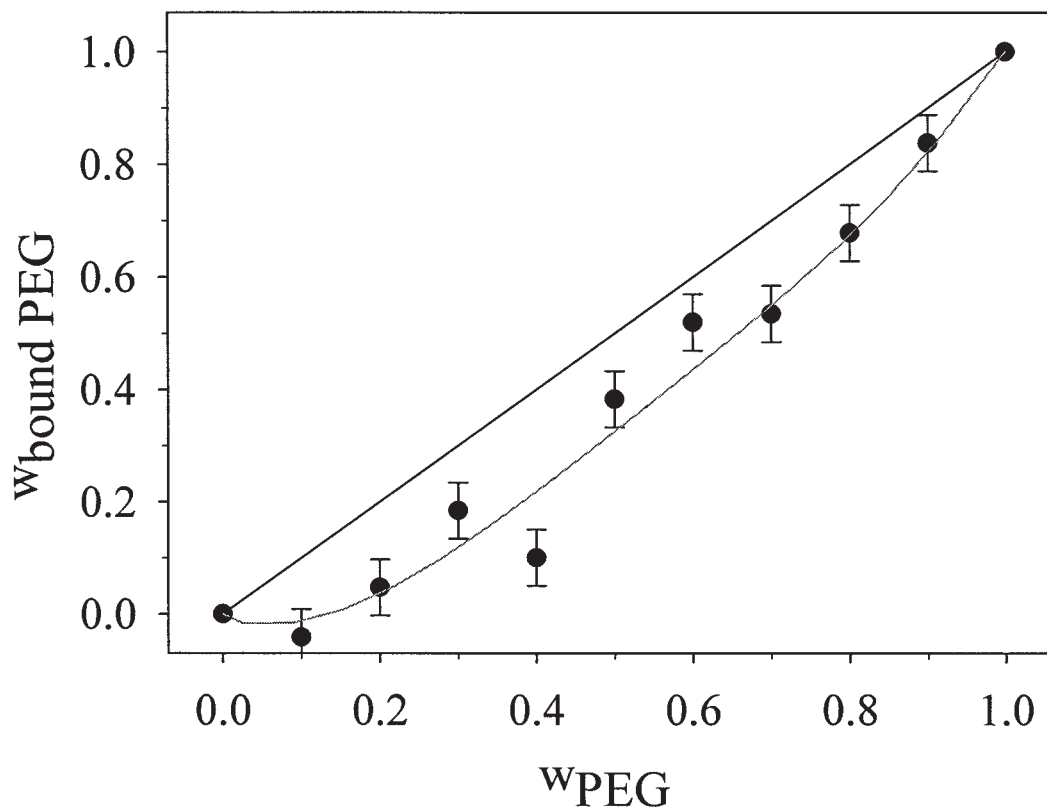


Figure 4 Composition of bound polymer as a function of the matrix composition.

A decrease of k means that there are fewer supplementary sites devoted exclusively to PEG chains. From eq. (4), the weight fraction of nonbonded chains can be calculated.

$$w \text{ (dissolved polymer)} = 1 - \frac{N(M + kM_{\text{PEG}}w_{\text{PEG}})}{m_i(1 - w_{\text{ac}})} \quad (5)$$

where N is unknown in the general case. Nevertheless, it may be easily evaluated from experiments with PEO as the matrix, because in this case $w_{\text{PEG}} = 0$ and the weight fraction of dissolved polymer is 71%, as obtained experimentally (see Fig. 4). Then, eq. (5) becomes

$$w \text{ (dissolved polymer)} = 1 - \frac{0.29}{M_{\text{PEO}}}(M + kM_{\text{PEG}}w_{\text{PEG}}) \quad (6)$$

The weight fraction of PEG bound on the filler surface in relation to the total amount of adsorbed polymer can also be calculated.

$$w \text{ (bound PEG)} = \frac{m \text{ (bound PEG)}}{m \text{ (bound polymer)}} = \frac{\mu_{\text{PEG}}M_{\text{PEG}} + kM_{\text{PEG}}w_{\text{PEG}}}{M + kM_{\text{PEG}}w_{\text{PEG}}} \quad (7)$$

where μ_{PEG} is the (weight or number) fraction of PEG in the blend, with $\mu_{\text{PEG}} = w_{\text{PEG}}M/M_{\text{PEG}}$.

If bonding on the filler surface occurs only through the monomer units, then the number of monomers of the chains must be the key parameter defining the probability of bonding rather than the number of chains. Consequently, in the calculation, weight average molecular weights must be used and μ_{PEG} equals the weight fraction of PEG in the blend w_{PEG} . For a mixture of PEG and PEO containing a PEG weight fraction, w_{PEG} , the weight average molecular weight of the PEO/PEG matrix is

$$M_w = w_{\text{PEG}}M_{w(\text{PEG})} + (1 - w_{\text{PEG}})M_{w(\text{PEO})} \quad (8)$$

If chain adsorption takes place by the chain ends, the number average molecular weights must be used in the calculation, because the larger the number of chains, the higher the probability that a chain is bound on the active carbon. The number average molecular weight, M_n , is expressed by

$$M_n = \left(\frac{w_{\text{PEG}}}{M_{n(\text{PEG})}} + \frac{1 - w_{\text{PEG}}}{M_{n(\text{PEO})}} \right)^{-1} \quad (9)$$

In this case, μ_{PEG} equals the number fraction of PEG in the blend.

Experimental data of the amount of dissolved polymer and bound PEG for the whole range of matrix

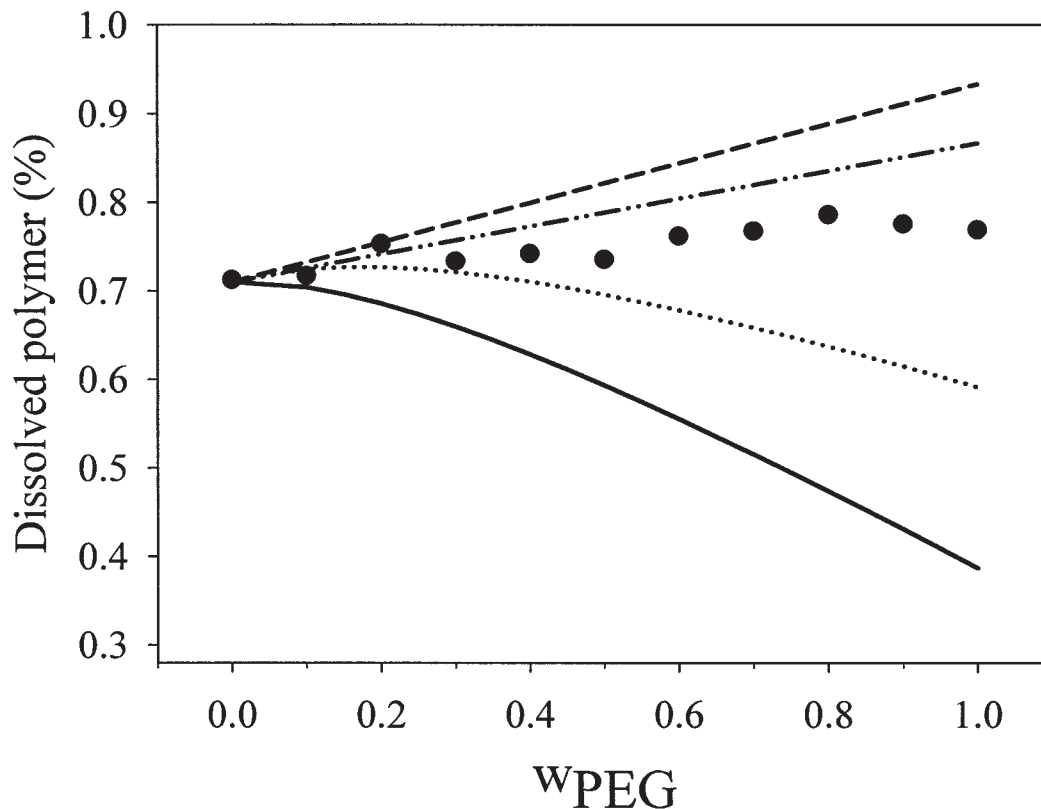


Figure 5 Dissolved polymer as a function of matrix composition. (Symbols: experimental data, lines from eq. (6); —: adsorption by chains ends, $k = 5$;: adsorption by chain ends, $k = 3$; ---: adsorption by monomeric units, $k = 5$; -·-·-: adsorption by monomeric units, $k = 11$).

composition have been compared with the results of the calculation, using eqs. (6) and (7) for various values of k and assuming that bonding occurs by either the monomeric units or by the chain ends. The results are given in Figures 5 and 6. As can be seen in Figure 5, with the assumption of bonding by the chain ends, the predicted amount of dissolved polymer (full and dotted lines) displays a maximum at low PEG content and then it decreases, whatever the value of k is. The monotonic increase that is observed experimentally can only be described with the assumption of bonding by the monomers (dashed and dash-dotted lines). Besides, as can be seen on Figure 6, bonding by the chain ends overestimates the bonding of PEG chains; the predicted curve being systematically over the bisector (full and dotted lines). Conversely, the assumption of bonding through monomeric units enables the description of the experimental data (dashed and dash-dotted lines). From these results, the assumption of chain end bonding must be definitely considered as not valid. Indeed, in this case, the variation of both the bound polymer and the bound PEG amounts with the matrix composition are off. On the opposite, the calculated variation with the assumption of adsorption by monomeric units, are in qualitative agreement with experimental results.

Though it helps explaining the nature of the interactions between PEO and PEG and active carbon, the

model remains qualitative because the same value of k cannot describe accurately the evolution of both the amount of bound polymer and the amount of bound PEG. Moreover, the description of the evolution of the fraction of bound PEG requires a high value of k ($k = 11$). This indicates that the assumptions of the model do not take into account some features of the adsorption. In particular, some chains may also be adsorbed on the filler surface by their ends, especially because the chemical nature of PEG chain ends (hydroxyl groups) may be different from that of PEO chain ends (methyl groups).

CONCLUSIONS

The evaluation of the amount of bound polymer on the surface of active carbon shows the existence of favorable interactions between polymers such as PEO and PEG and active carbon after melt mixing. Using a relatively high amount of active carbon (26.4 vol %), 20–30% of a composite matrix of PEG and PEO is adsorbed on the filler surface during mixing. These large values are due to the high surface area (1100 m²/g) and high porosity of the active carbon.

Moreover, the evolution of the amount of bound polymer as a function of matrix composition indicates

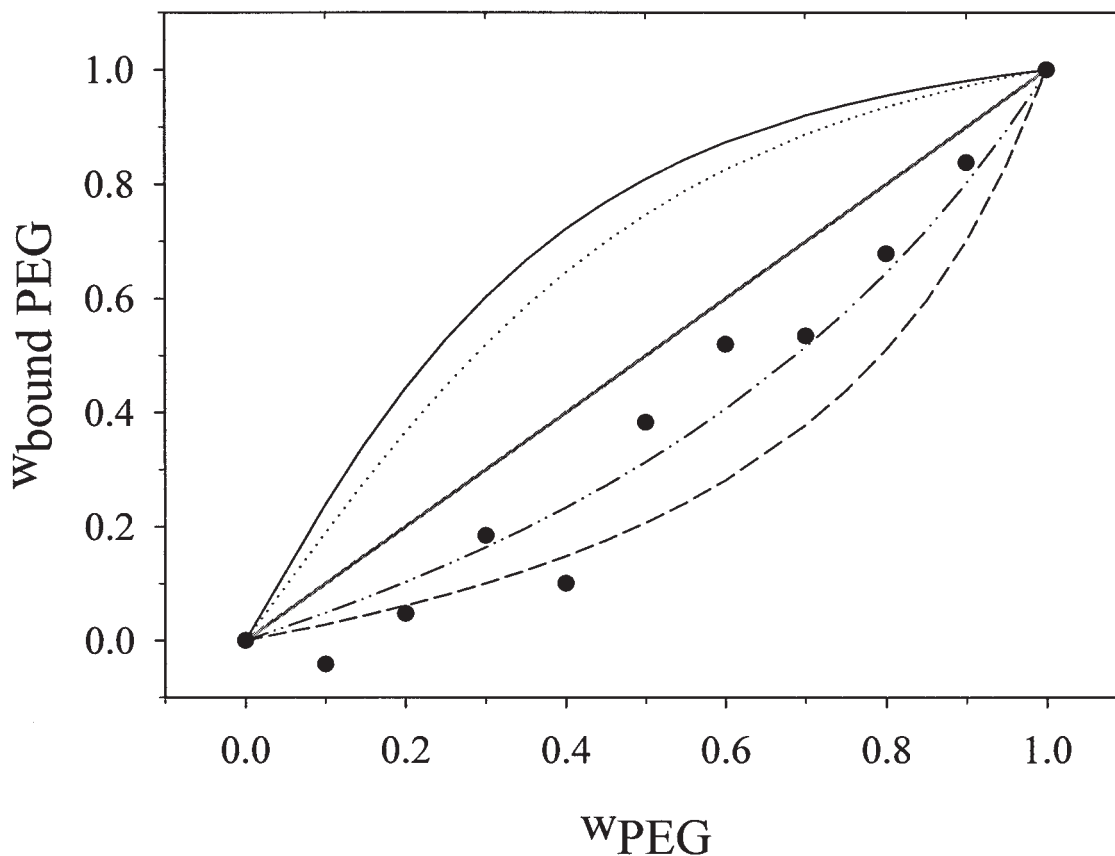


Figure 6 Bound PEG as a function of matrix composition. (Symbols: experimental data, lines from eq. (7); —: adsorption by chains ends, $k = 5$;: adsorption by chains ends, $k = 3$; ---: adsorption by monomeric units, $k = 5$; -·-·-: adsorption by monomeric units, $k = 11$).

preferential interactions between PEO and the active carbon. The determination of the composition of the polymeric layer surrounding the particles shows that the amount of long chains bound on the active carbon is higher than that of PEG in the whole range of composition.

Because of the large mesoporous volume of the active carbon, there is no indication of the limiting size of the bonded molecules. The preferential bonding of PEO chains may be related to the smaller surface area per molecule that is required by a PEO molecule when it is bonded through a single monomeric unit or through its chain ends. On the other hand, it may also be due to differences in the adsorption and desorption rates of long and short chains, if they are bonded through their monomeric units. Indeed, because of small desorption rates, long PEO chains may be definitively adsorbed and they may hinder further bonding of PEG chains by the screening of the sites.

A simple model giving the relation between the amount of bound polymer and the composition of the adsorbed polymeric layer was used to validate these assumptions. The assumption of adsorption by the monomer units rather than by the chain ends enables to fit, at least qualitatively, the experimental data. The

model shows that the adsorption of the PEO chains is favored.

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