

Monte Carlo Simulations of Polymer Melts Filled with Solid Nanoparticles

Michele Vacatello[†]

Dipartimento di Chimica, Università di Napoli, Via Cinthia, I80126 Napoli, Italy

Received September 5, 2000; Revised Manuscript Received December 15, 2000

ABSTRACT: The results of realistic computer simulations of dense polymer melts filled with solid nanoparticles are compared with results obtained for similar systems near planar solid surfaces and with those of Monte Carlo calculations performed for single chains in the presence of spherical solid obstacles. The polymer units at the interface with the filler particles are arranged in densely packed and ordered shells analogous to those found near planar solid surfaces. The polymer chains, reduced in size compared to the unfilled melt, are constituted of sequences of surface segments, totally contained in the interface shell of a given particle, and of bridge segments, connecting different particles. Each chain visits the interface shell of several filler particles, and each particle is in contact with many different polymer chains, such that the filler particles behave as highly functional physical cross-links.

Introduction

Understanding the interface between polymer melts and solids is of fundamental importance in all practical applications where the properties of interest of polymer-based materials are primarily regulated by the presence of solid components. This is the case, for instance, of industrially important systems such as composites, lubricant films, adhesives, etc. Therefore, the polymer/solid interface has been the subject of several simulation studies in recent years (for a recent, comprehensive review, see ref 1). Monte Carlo (MC) and Molecular Dynamics (MD) simulations performed for various model polymers near planar solid surfaces indicate that molecular arrangements, conformations and dynamics of the polymer are strongly perturbed with respect to the isotropic bulk.^{1,2} In particular, it is found that (a) the chain segments in contact with the surfaces are arranged in densely packed and ordered layers, and this perturbation of density and order extends into the liquid two or three times the transverse diameter of the chains; (b) the chain conformation is perturbed to a scale length on the order of the root-mean-square (rms) radius of gyration of the polymer, and chains with center of mass at a distance from the surface less than the unperturbed rms radius of gyration are flattened against the planar surfaces like pancakes and present a substantial fraction of trains of units running in the first densely packed layer; (c) the component of the apparent diffusivity perpendicular to the surfaces is substantially smaller for chains in contact with the surfaces than for bulk chains, while the parallel components are slightly higher than in the bulk¹ or are practically unchanged.²

A technologically important process where the polymer/solid interface plays a major role is the reinforcement of elastomers with solid fillers, giving extensively utilized composite materials with enhanced mechanical properties.³ In the acceptable hypothesis that the polymer/solid interface is not substantially changed in the cross-linking step, this interface can be studied by simulating filled polymer melts. When the filler particles are large spheres with volume fraction small

enough to ensure that each polymer chain be in contact with the surface of a single particle at most, the molecular arrangements and conformations are obviously expected to be similar to those found in the proximity of planar solid surfaces.^{1,2} However, with filler particles of 10–100 nm diameter at a volume fraction on the order of 30%, as in most real systems, the surface shells of adjacent particles can be partly superimposed and each chain is likely to visit the surface shells of several particles. For instance, it may be easily checked with simple Monte Carlo calculations that in a random system of hard spheres of 30 nm diameter at a volume fraction 30%, the average distance of a sphere surface from the closest neighbor surface is as short as 1.6 nm. The resulting overall picture of the molecular organization in these composite systems is therefore quite different from that near a single planar surface.

This paper presents the results of realistic computer simulations of a dense polymer melt containing solid nanoparticles. These are compared with results obtained for similar dense systems near planar solid surfaces^{1,2} and with those of Monte Carlo calculations performed for single chains in the presence of spherical solid obstacles.⁴

Models and Methods

The systems simulated in this work consist of three dimensionally periodic arrays of cubic cells containing N_p polymer chains and N_f filler particles. The chains are modeled as unbranched sequences of 100 isodiametric units connected by links of length σ (i.e., σ coincides with the transverse diameter of the polymer chains), while the filler particles are modeled as spherical entities with diameter σ_f (Figure 1). The composition of the simulated systems is shown in Table 1 (systems M_{16a} and M_{16b} differ only for the initial placement of the filler particles; see later). For all systems, (a) the isodiametric units interact through a 12–6 Lennard-Jones potential $E_{uu} = \epsilon[(\sigma/r_{uu})^{12} - 2(\sigma/r_{uu})^6]$, where r_{uu} is the distance between the interacting units; the minimum distance allowed between units is $r_{uu,\min} = 0.70\sigma$; (b) the filler particles interact with the isodiametric units through the potential $E_{uf} = \epsilon[(\sigma/r_{uf})^{12} - 2(\sigma/r_{uf})^6]$, where r_{uf} is the distance of the given unit from the surface of the particle and $r_{uf,\min} = 0.70\sigma$; (c) the filler particles interact with other filler particles through the potential $E_{ff} = \epsilon[(\sigma/r_{ff})^{12} - 2(\sigma/r_{ff})^6]$, where r_{ff} is the distance between the surfaces of the two interacting particles and $r_{ff,\min} = 0.70\sigma$; (d) the

[†] E-mail: vacatello@chemistry.unina.it. Fax: (+39)-81-674325.

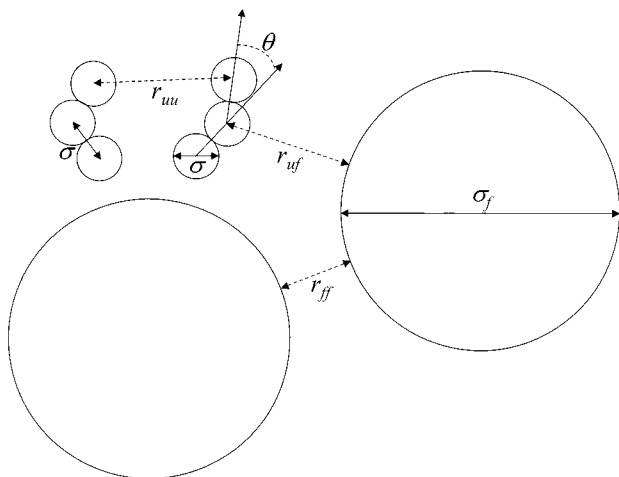


Figure 1. Model polymer segments and filler particles and definition of symbols.

Table 1. Composition of the Simulated Systems (N_p = Number of Polymer Chains of 100 Units; N_f = Number of Spherical Filler Particles; σ_f = Diameter of the Particles; φ = Volume Fraction of Filler)

system	cell edge	N_p	N_f	σ_f	φ
M_0	40σ	640	0		0
M_{10}	40σ	409	34	10σ	0.36
M_{16a}	40σ	409	9	16σ	0.36
M_{16b}	40σ	409	9	16σ	0.36

distribution of angles between consecutive links in the same chain is regulated by a bending potential of the form $E(\theta) = (1/2)k_\theta\theta^2$.

All interactions are truncated at a distance 2σ , where they are practically negligible. Calculations have been performed with $\epsilon/RT = 0.125$ and $k_\theta/RT = 1.00 \text{ rad}^{-2}$. If the chain units are considered to be polymethylene isodiametric units (3.5 CH_2 , $\sigma = 0.45 \text{ nm}$, see ref 5), a force field with these values in E_{uu} and $E(\theta)$ has been shown⁶ to lead to models approximating quite well conformational distribution and packing in polymethylene melts.

System M_0 (Table 1), containing no filler particles, represents the reference polymer melt, constituted by chains that would correspond in the polymethylene case to 350 CH_2 groups, with approximate density 890 kg/m^3 . This system has been initialized by placing the 640 molecules in the base cell at random in such a way that the distance between any two units is not smaller than $r_{uu,\min}$. The system has been then equilibrated in the canonical (NVT) ensemble by Monte Carlo methods, using the reptation technique. At each step, a new isodiametric unit was added to a randomly chosen chain end (the newly generated bond angle being selected according to the distribution dictated by the value of k_θ/RT), while the unit at the opposite end of the same chain was deleted. The trial configuration was immediately rejected when the new unit was closer than $r_{uu,\min}$ to any other unit; otherwise, the total energy change was evaluated and the new configuration was accepted or rejected according to the outcome of a standard Boltzmann test.

System M_{10} simulates the behavior of the reference polymer melt in the presence of filler particles with diameter smaller than twice the root-mean-square radius of gyration of the chains ($\approx 6.5\sigma$, see later). A total of 34 particles with $\sigma_f = 10\sigma$ have been initially placed at random in the base cell in such a way that the minimum distance of their surfaces was not smaller than $r_{ff,\min}$. Since the first layer of chain units in contact with the filler surfaces is expected to be found at $r_{uf} \approx \sigma$, the effective diameter of the filler particles is close to 11σ and the volume fraction occupied by the filler (φ in Table 1) can be estimated to be on the order of 0.36. As a consequence, the number of polymer chains was reduced to 409. The chains have been added as before, with the additional condition that

the minimum distance between polymer units and filler surfaces was not smaller than $r_{uf,\min}$. The system has been then equilibrated using reptation for the chains and local displacements for the filler particles. In the first case, the mechanism was identical to that described for the M_0 system, with the additional constraint that the trial configuration was rejected when the new terminal unit was closer than $r_{uf,\min}$ to the surface of a filler particle. In the second case, the center of a randomly selected particle was reallocated at random inside a sphere of radius 0.2σ . After checking that no distances smaller than the minimum allowed values were generated in the process, the new position of the particle was accepted or rejected on the basis of a Boltzmann test. The same methods were utilized to initialize and equilibrate systems M_{16a} and M_{16b} (Table 1), each containing in the base cell nine filler particles with $\sigma_f = 16\sigma$ (effective diameter $\approx 17\sigma$, $\varphi \approx 0.36$ as in system M_{10}), that is with diameter greater than twice the rms gyration radius of the chains.

In the case of the filled systems, a MC cycle is defined to consist of 5×10^8 attempted reptation moves and 5×10^5 randomly distributed attempted filler displacements. Approximately 1.0×10^7 (2.0%) and 1.2×10^7 (2.4%) reptation moves were accepted per cycle in the M_{10} system and in the M_{16} systems, respectively, while the fraction of accepted filler displacements was 9.4% in the M_{10} system and 6.4% in the M_{16} systems. Since the number of chains in the M_0 system is 1.5 times higher than in the filled systems, a MC cycle has been defined in this case to consist of 7.5×10^8 attempted reptation moves, with approximately 2.3×10^7 attempts accepted (3.1%). Each calculation has been performed on a dedicated PC equipped with a 450 MHz Pentium II processor, a cycle taking approximately 7 h for the filled systems and 9 h for the M_0 system. As far as efficiency is concerned, the reptation technique is found to be very efficient for the M_0 system, in which all units are displaced in 10 cycles (i.e., no units are left having the same coordinates of any unit of the same chain before the 10 cycles), with more than 95% of the units displaced in five cycles. Because of the presence of the filler, the efficiency is diminished in the M_{16} systems, where 95% of the units are displaced in 10 cycles and only 81% in five cycles. Reptation is even less efficient in the M_{10} system, where it takes five cycles to displace 62% of the units and 10 cycles to displace 81%. On the other hand, although the fraction of accepted filler displacements was quite high in all cases, the size of the particles is such that their mean square displacement in five cycles is as low as $0.002\sigma^2$ in the M_{10} system and even smaller in the M_{16} systems. In other words, the filler particles are practically frozen in their initial positions. It is concluded that the methods utilized in the present calculations are intrinsically unable to investigate the equilibrium behavior of the filler particles. Considering that the purpose of this paper is to study the behavior of the polymer in the presence of the filler, this is probably not a severe problem for the M_{10} system, where the number of particles is high enough so that chain segments can experience several different local situations, representative of those found in bigger systems. However, the results obtained with only nine particles in the base cell may depend on the particular arrangement assumed by these particles. Hence, two systems with the same composition have been independently initialized and equilibrated in this case (M_{16a} and M_{16b} , respectively). The results of these two calculations, showing minor and scarcely significant differences only in the case of the chain dimensions, have been averaged in the following section.

Starting from the initial configuration, the equilibration process has been followed by monitoring various properties, such as the radial distribution function of the polymer units with respect to other polymer units or to the filler particles, the mean square end to end distance and the mean square radius of gyration of the polymer chains, etc. It was observed that all the properties of interest reach a stationary value after 20 cycles for the M_0 system and after approximately 40 cycles in the other cases. The statistical samples utilized for evaluating the average values reported in the following section for the various properties consist of 40 configurations obtained

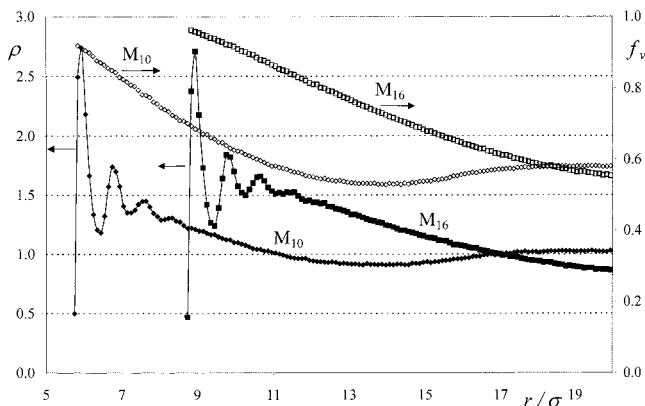


Figure 2. Radial distribution function of the polymer units with respect to the filler particles (ρ , full symbols, left scale) and the volume fraction of spherical shells not occupied by filler particles (f_v , open symbols, right scale) for cells of edge 40σ as a function of the distance r of the shell from the center of a filler particle.

at the end of cycles 51–90 for the M_0 system, and of 50 configurations obtained at the end of alternate cycles from 52 to 150 for the filled systems. Calculations were long enough that segments of adjacent chains could exchange their position several times during the sampling cycles. Hence, one can confidently assume that averages obtained from these MC samples are representative of the equilibrium state of the polymer in the systems under study. In the following section, standard errors of the averages are explicitly indicated when appropriate. In the plots, standard errors are comparable to the vertical size of the data markers, or smaller.

Results and Discussion

The Filler/Polymer Interface: Packing of the Chain Units. Adding filler particles to a polymer melt is expected to modify molecular arrangements and conformations of the polymer chains on a global scale, and those of shorter segments of the polymer chains on a more local scale. In particular, as found for polymer melts near planar solid surfaces, chain units in contact with the spherical filler particles are expected to be arranged in densely packed shells. Figure 2 shows (full symbols, left scale) the radial distribution function, $\rho = \rho_r/\rho_a$, of the polymer units with respect to the filler particles for systems M_{10} and M_{16} . ρ_r has been calculated as the average number of polymer units found in a spherical shell at a distance between $r - 0.05\sigma$ and $r + 0.05\sigma$ from the center of a filler particle, divided by the volume of this shell. Therefore, for large values of r , ρ_r is expected to be coincident with the average density of polymer units in the simulated systems, $\rho_a (= 0.64\sigma^{-3})$, such that $\rho = 1$. Starting from the surface of a filler particle, ρ shows at least three well-developed maxima separated by two intervening minima, the distance between consecutive maxima or minima being approximately 0.8σ . Not unexpectedly, this behavior is qualitatively similar to the corresponding behavior found in a previous investigation of a polymer melt near planar solid surfaces.² The differences observed in the intensity of the maxima (much higher here than in ref 2), are simply due to the fact that the polymer is obviously confined in the regions of the simulated systems not occupied by the filler, where its average density is coincident with the density in the reference polymer melt (system M_0). On the other hand, the overall behavior of the ρ curves in Figure 2 is quite peculiar, since the curve for the M_{16} systems shows a monotonic decrease following the initial series of maxima

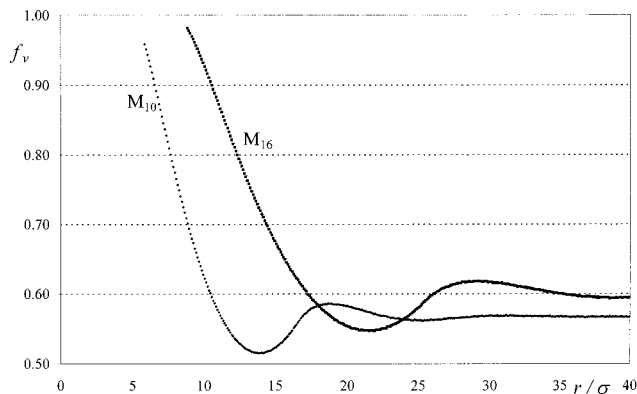


Figure 3. Volume fraction of spherical shells not occupied by filler particles, f_v , for cells of edge 80σ as a function of the distance r of the shell from the center of a filler particle.

and minima, while the curve for the M_{10} system shows at first a similar decrease and then a broad minimum centered around $r = 14\sigma$. Also, the value of ρ_r for $r = 20\sigma$ is seen to be approximately equal to the expected value $0.64\sigma^{-3}$ (i.e., $\rho \approx 1$) for the M_{10} system, but is substantially lower for the M_{16} systems. For comparison, curves of ρ for polymer melts in contact with planar solid surfaces show only the initial series of maxima and minima, these oscillations being rapidly damped such that the value of ρ becomes equal to unity at relatively short distances from the surface ($<5\sigma$).²

One could suspect that the peculiar behavior of ρ revealed in Figure 2 is related to the particular arrangements assumed by the filler particles in the three performed simulations, such that repeating the simulations with different arrangements would lead to different results. Figure 3, plotting the volume fraction f_v of spherical shells not occupied by filler particles as a function of r , clarifies that this is not the case. The f_v curves have been obtained by simulating a very large number of configurations of a base cell of edge 80σ containing 272 spherical particles in the case of the M_{10} system and 72 such particles in the case of the M_{16} system, respectively. To evaluate f_v , after introducing the filler particles with the methods already described, these have been assumed to be hard spheres with diameter $\sigma_f + 1.6\sigma$. The two curves shown in Figure 3 are practically coincident, when properly scaled. The fraction of empty volume is obviously very high near the surface of a filler particle. It shows then a decrease up to a minimum located at approximately $1.4\sigma_f$, followed by a maximum around $1.8\sigma_f$. Since the f_v curves have been obtained for random distributions of filler particles at the given density, it is concluded that the similar behavior shown by ρ in Figure 2 is not related to the particular arrangements assumed by the particles in the systems investigated in this work but is a general feature of these filled systems. In other words, when the distribution of the space left empty by the filler particles is properly taken into account, the behavior of ρ is seen to be both qualitatively and quantitatively very similar to the behavior observed in polymer melts near planar solid surfaces.

Figure 3 requires a further comment. In fact, for all filled systems, f_v reaches the featureless asymptotic limit at distances much higher than the value 20σ corresponding to half the edge of the base cell utilized in the simulations. In other words, when the cell edge is 40σ , the distribution of the filler particles could be not identical to the limiting distribution expected for

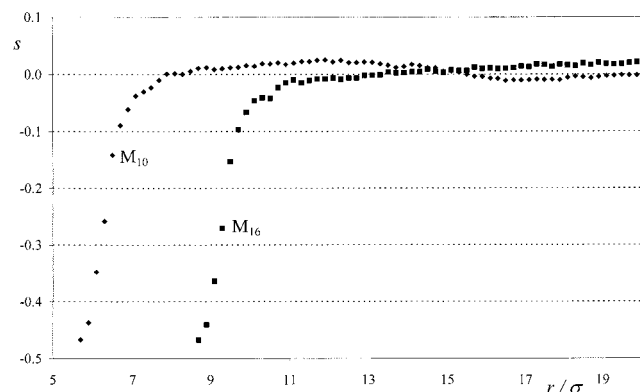


Figure 4. Order parameter of chain segments comprising five consecutive units (s ; for a definition, see text) as a function of the distance of their center of mass from the center of the closest filler particle.

much larger systems. Therefore, one could speculate that the base cells utilized in the simulations are too small to be truly representative of infinite systems and that the results reported in this section may be affected by the imposed fictitious periodicity. To clarify this point, the calculation of f_v has been also performed with the same methods for smaller cells of edge 40σ . The resulting curves, shown in Figure 2 (open symbols, right scale), are practically indistinguishable up to $r = 20\sigma$ from those shown in Figure 3. It is concluded that the influence of the 40σ periodicity imposed in the simulations of the M_{10} and M_{16} systems is negligible for properties with characteristic length shorter than 20σ . On the other hand, simulating larger base cells would require equilibrating systems containing an extremely large number of polymer units (more than 325 000 for a cell edge 80σ). Although calculations of this kind are not unfeasible today, the computer time required for the equilibration and sampling would be in the latter case at least eight times higher. Since the molecular arrangements and conformations of the polymer molecules are likely to be very well approximated in the 40σ base cells adopted in this work, simulating such exceptionally large systems is not worth the effort.

The Filler/Polymer Interface: Order Parameters of the Chain Segments. Figure 2 evidences that the interface between filler particles and polymer melt is characterized by the presence of several consecutive high density layers of polymer units, separated by layers with lower density. Such high densities, specially high in the first layer, are necessarily associated with orientational correlations among spatially neighboring chain segments and/or among these segments and the surface of the filler particles. This is shown in Figure 4, plotting the order parameter of chain segments comprising five consecutive units as a function of the distance of their center of mass from the closest filler particle. The order parameter, s , is defined to be $(3\langle\cos^2\tau\rangle - 1)/2$, with τ the angle between the end-to-end vector of a segment (i.e., the vector from unit i to unit $i + 4$ of the same chain) and the vector radius of the filler particle through the center of mass of the segment; s is 1 for segments perfectly aligned along the vector radius, 0 for random disorder, and -0.5 for segments aligned perpendicular to the vector radius, respectively. Figure 4 indicates that segments in contact with the filler tend to run mainly parallel to the filler surface. Of course, the value of s for segments with center of mass at less than σ from the surfaces is negative for obvious geo-

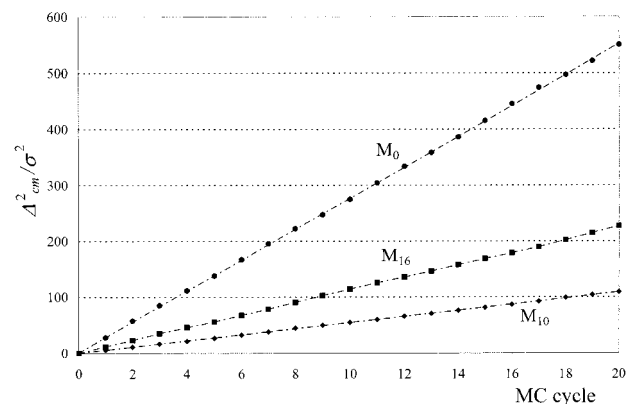


Figure 5. Mean square displacement of the center of mass of the chains as a function of the number of Monte Carlo cycles.

metrical reasons. However, the average value found for s in the first high-density layers, i.e., for distances of the segments from the filler surface less than $1.5-2\sigma$, is very low, indicating in all cases a strong additional tendency of chain segments in contact with the filler particles to run parallel to their surfaces. It is interesting to note that the behavior of the order parameter at high values of r is somehow opposite to that observed for ρ in Figure 2. In particular, s shows a monotonic increase from $r = 11\sigma$ to $r = 20\sigma$ in the case of the M_{16} systems, while a broad maximum is found for r between 8σ and 14σ for the M_{10} system, followed by a barely discernible minimum in the $15-18\sigma$ region. By analogy with the results shown in Figures 2 and 3, it is likely that the curve for the M_{16} systems would show a behavior similar to that for the M_{10} system, if extended to distances higher than 20σ . Features of this kind are not observed for polymer melts near planar solid surfaces, where the orientational distribution of the chain segments becomes isotropic at less than 5σ from the surfaces.² Even after a detailed exam, they cannot be explained on the basis of single and well-defined effects. For instance, approximately 50% of the chain segments giving a high positive contribution (>0.5) to the order parameter at r between 8σ and 14σ for the M_{10} system belong to chains that are not in contact with the given particle. Therefore, these features appear to be related to the general topology of filled systems having particle size and density comparable to those simulated here.

Mobility of the Polymer Chains. Since the filler particles are practically frozen in their initial positions and since the polymer segments in contact with their surfaces are well packed and ordered, the filler particles can be considered equivalent to highly functional *physical* cross-links. At variance with *chemical* cross-links, where the polymer chains are linked by chemically stable bonds, these physical cross-links cannot prohibit the diffusion of the polymer chains. However, even in the absence of strong attractive interactions between filler and polymer, they can slow considerably the diffusion in filled polymer melts. Figure 5 plots the mean square displacement of the center of mass of the chains as a function of the number of Monte Carlo cycles for all simulated systems. It is seen that the diffusion coefficient is strongly reduced in the presence of filler, being in the M_{16} systems approximately half and in the M_{10} system five times smaller than in the unfilled melt. Hence, for a given volume fraction of filler, smaller particles are more efficient in reducing the mobility of

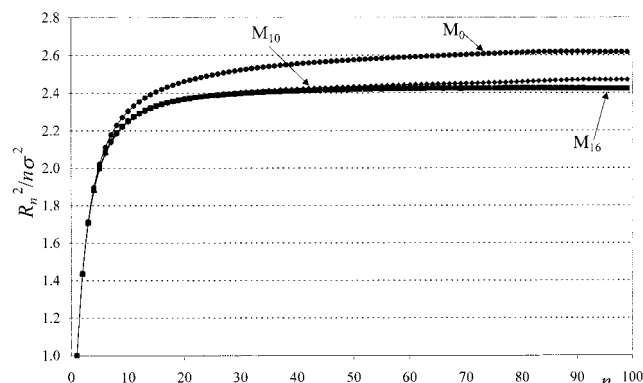


Figure 6. Plot of $R_n^2/n\sigma^2$ vs n , with R_n^2 the mean square distance of units belonging to the same chain and separated by n links.

the polymer chains (for an explanation, see the end of this section). However, one obviously expects that upon decreasing more and more the size of the particles, the diffusion coefficient passes through a minimum and then increases up to the point where the diameter of the particles is on the order of σ .

Conformational Distribution of the Polymer Chains. The presence of the filler particles also modifies the conformational distribution of the polymer chains with respect to the unfilled melt. This is shown in Figure 6, plotting for all systems simulated in this work the values of $R_n^2/n\sigma^2$ vs n , with R_n^2 the mean square distance of units belonging to the same chain and separated by n links. The curve for the M_0 system is in excellent agreement with the results of previous simulations.² In particular, $R_n^2/n\sigma^2$ with $n = 99$ is found for this system to be equal to 2.62 ± 0.02 , slightly higher (as expected) than the corresponding value 2.57 ± 0.02 obtained for shorter chains of 50 units in ref 2. If the model units are assumed to correspond to polymethylene isodiametric units (3.5 CH_2 , $\sigma = 0.45 \text{ nm}$, $l_{C-C} = 0.154 \text{ nm}$) and the centers of units 1 and 100 of the model chains are considered to be separated by 345 C–C bonds, the characteristic ratio of the simulated polymer would be approximately 6.4. Figure 6 also shows that the mean square end-to-end distance in the presence of filler is always smaller than in the unperturbed melt. In particular, $R_n^2/n\sigma^2$ with $n = 99$ is 2.46 ± 0.02 and 2.42 ± 0.02 for the M_{10} and M_{16} systems, respectively. It is worth noting that the mean square radius of gyration follows exactly the same trend, being $42.42 \pm 0.24\sigma^2$ for the M_0 system, $40.20 \pm 0.22\sigma^2$ for the M_{10} system and $40.01 \pm 0.21\sigma^2$ for the M_{16} systems, respectively. Therefore, the ratio of the mean square end-to-end distance to the mean square radius of gyration is always very close to the value 6 expected for Gaussian coils. Last, it is seen that the dimensions of the chains are reduced with respect to the unfilled melt both on the global and on the local scale, in the sense that also chain segments consisting of 10–20 links are on the average shorter than the corresponding segments in the unfilled melt.

A decrease of chain dimensions in the neighborhood of relatively large particles was not unexpected, since the same behavior has been observed in ref 2 for similar chains with center of mass close to planar solid surfaces. Such a decrease has been also predicted theoretically,^{4,7} and found in recent SANS experiments⁸ on filled polymer melts with particles having approximately the same size of the polymer molecules. In particular, it is

interesting to compare the results reported in this section with those obtained by Yuan et al.⁴ from Monte Carlo calculations on single poly(dimethylsiloxane) (PDMS) chains generated in the presence of fixed impenetrable spherical obstacles. With due care to the obvious differences, some of the systems studied in ref 4 can be considered analogous to those simulated in the present work. For instance, the unperturbed characteristic ratio of the PDMS chains of 200 skeletal bonds studied in ref 4 was 6.4 (at 400 K), coincidentally equal to the value calculated for the chains simulated in the present work by assuming polymethylene isodiametric units (see before). Keeping on with this assumption (i.e., taking $\sigma = 0.45 \text{ nm}$), the rms radius of gyration of the chains simulated here would correspond to 2.8 nm, with the radius of the spherical particles close to 2.5 nm for the M_{10} system and to 3.8 nm for the M_{16} systems. For comparison, the rms radius of gyration of the PDMS chains was approximately 2.4 nm, while the radius of the spherical obstacles was 2.0 and 4.0 nm. It is then seen that in both calculations the spherical particles are slightly smaller than the chains in one case, and much bigger in the other case. The calculations of ref 4 indicate an opposite trend in these two cases. That is, the dimensions of the chains were found to increase quite strongly with increasing volume fraction of the filler when the radius of the particles was 2.0 nm, and to decrease when this radius was 4.0 nm. As shown in Figure 6, this is in contrast with the results of the present simulations, always indicating a decrease of chain dimensions in the presence of filler. The origin of this discrepancy may be related to a number of different factors. First of all, the range of filler volume fraction examined in ref 4 for particles with radius 2.0 nm had to be restricted to 0–7.5%, because the method used for sampling the configuration space was inadequate at higher filler content. Since the volume fraction of the filler is as high as 36% in the systems simulated here, one can still make the hypothesis that, increasing the filler content, the initial rise of the chain dimensions is followed by a maximum and then by a subsequent decrease (a behavior of this kind is indicated by the SANS experiments of ref 8). On the other hand, the overall setup of the calculations performed in ref 4 is quite peculiar, since for computational convenience the chain was started at the center of a spherical cavity with radius at least equal to the radius of the spherical obstacles, giving rise to a situation infrequent in real systems, specially with small filler particles at high volume fractions. It is apparent that single chain calculations of this kind could be better performed in the framework of a reptation scheme, allowing one to sample efficiently systems with much higher filler volume fraction and with filler particles distributed completely at random. However, these calculations would be scarcely beneficial, not only because they are intrinsically unable to take into account the packing effects evidenced in Figure 2 but also because it is well-known that in dilute polymer solutions the polymer chains tend to avoid solid surfaces.^{9,10} Therefore, properties deduced from single chain calculations may be strongly different from those in systems where the polymer has the proper density.

Topology of the Simulated Systems. Figure 7 is a partial snapshot of a configuration of system $M_{16}b$ at thermal equilibrium. The size of the filler particles (with the exception of the one in the lower right corner) has

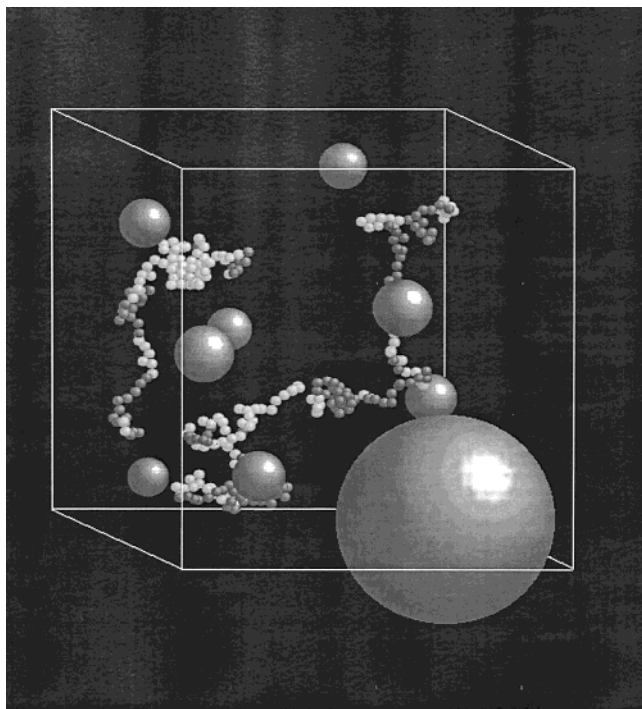


Figure 7. Partial snapshot of a configuration of the M_{16b} system at thermal equilibrium. The size of the filler particles (except the one in the lower right corner) has been reduced; chain units in white are at a distance from the surface of a filler particle less than 2σ .

been reduced in order to show the spatial arrangements of some selected chains (chosen to avoid superimpositions in the figure) with respect to the particles. The chain units in white are at a distance from the surface of a filler particle less than 2σ . It is seen that each chain visits the surface of several particles, and is practically constituted by a sequence of surface segments, i.e., chain segments running in the surface shell of a given particle, and bridge segments, i.e., chain segments connecting two different particles. In the case of the M_{16} systems, 33% of the units are contained in these surface shells of width 2σ , and the average lengths of the surface and bridge segments are 4.5 and 11 units, respectively. One expects that in the M_{10} system, where the particles are smaller and more abundant, the surface segments are possibly a little shorter, while the bridge segments are much shorter. Also, since the overall surface of the particles is higher, more polymer units are expected to be in the surface shells. In fact, 51% of the units are in the surface shells in the M_{10} system, and the average lengths of the surface and bridge segments are 3.9 and 5.4 units, respectively. For comparison, the average length of surface segments with all units within 2σ from a planar solid surface was found to be 5.1 in ref 2. It is also found that each chain visits on the average the surface shell of 4.9 filler particles in the M_{10} system and of 2.7 particles in the M_{16} systems. Conversely, the number of different chains visiting the surface shell of a given particle is approximately 60 for the M_{10} system and 120 for the M_{16} systems. One can see that both values are practically coincident with the total number of contacts per particle ($4.9N_p/N_f = 59$ and $2.7N_p/N_f = 123$). It is also interesting to mention that in the case of the M_{10} system many units belong to the surface layer of two or more different filler particles. In particular, the fraction of surface units belonging to the surface shells of two different particles turns out to be only 2%

in the M_{16} systems, while it is as high as 12% in the M_{10} system, showing that the surface shells of adjacent filler particles are largely superimposed in the latter case. The observations that the M_{10} system contains a larger proportion of surface units, and that each chain visits the surface shells of many more filler particles in the M_{10} system than in the M_{16} systems, are obviously in line with the behavior of the diffusion coefficient, much lower in the M_{10} system than in the M_{16} systems (Figure 5). Of course, all the numerical results reported here are strictly related to those particular systems that have been simulated. Changing the chain length, the size of the filler particles or their density would change most of them. More simulations are undoubtedly needed in order to clarify in full the behavior of these complex systems. Nonetheless, the general picture emerging from Figure 7 and from the other results reported in this paper represents a significant progress in this direction.

Conclusions

Although filled polymers are utilized in several industrially important applications and have been extensively investigated from the experimental point of view in the past century, realistic computer models of filled polymer melts with proper densities of both filler and polymer have not been presented up to now. This is due, at least in part, to the fact that the filler particles are much larger than the transverse dimension of the polymer chains. Studies of this kind, requiring the explicit representation of a very large number of polymer units, were practically unfeasible with the limited computing power available before the last two decades. Therefore, literature simulations have been limited to systems in which the polymer chains are represented as random walks on simple lattices with no multiple occupancy of the lattice nodes.^{11–14} Though very useful to clarify the general aspects of the problem, these lattice models are obviously not well suited for investigating crucial properties such as packing and order at the polymer/filler interface. The models utilized here are realistic in the sense that the lattice approximation is avoided, and that the conformational distribution of the simulated chains is similar to that of real polymers. The principal results of the simulations performed in this paper, i.e., with filler particles of size comparable to the polymer chains, may be shortly summarized as follows: (a) The polymer units at the interface with the filler particles are arranged in densely packed and ordered shells analogous to the layers found near planar solid surfaces; the thickness of these shells is approximately twice the transverse diameter of the polymer chains, (b) Even in the absence of specific interactions with the polymer, the filler particles behave as highly functional physical cross-links, reducing the overall mobility of the polymer chains with respect to the unfilled melt; for a given volume fraction of filler, this effect is more pronounced when the particles are smaller. (c) The conformational distribution of the polymer is strongly perturbed by the presence of the filler both on the global and on the local scale; in particular, the average dimension of chain segments comprising more than a few units is reduced when compared to the unfilled melt in all three simulations performed. (d) The polymer chains can be thought as constituted by sequences of surface segments, totally contained in the interface shell of a given particle, and of bridge segments, connecting different particles; each

chain visits the interface shell of several filler particles, and each particle is in contact with many different polymer chains. (e) For the particular systems that have been simulated, the fractions of polymer units in the interface shells are 51% and 33% for the M_{10} and M_{16} systems, respectively; in the same order, the average lengths of surface segments are 3.9 and 4.5 units, the average lengths of bridge segments are 5.4 and 11 units, each chain visits on the average the surface shell of 4.9 and 2.7 filler particles, and the numbers of different chains visiting the surface shell of a given particle are as high as 60 and 120.

One could obviously comment that the filler particles simulated here are relatively small and that the chains are too short with respect to real polymer/filler systems. Unfortunately, a base cell with only 10 spherical particles of diameter 20 nm at a volume fraction of filler 0.3 should also contain more than 10^6 polymer units. Also, the reptation method, as well as all other known equilibration methods, is extremely slow for dense systems of chains longer than 100–200 units. In conclusion, simulations of properly scaled systems are presently out of reach. On the other hand, increasing both the size of the particles and the length of the polymer chains should not change dramatically the overall picture emerging from the present calculations. As far as the interactions are concerned, the calculations presented in this paper are not meant to simulate the behavior of a specific polymer/filler system, and their results, mainly determined by topology and entropy, should be of general validity. For instance, the structure and order of the interface shells and the conformations of the polymer chains are not expected to be substantially altered in the presence of (moderate) preferential interactions between polymer and filler. The picture can be quite different, however, when strong polymer/filler interactions are localized in specific parts of the (co)-polymer chains, or when the filler particles show a pronounced tendency to self-aggregate in the melt. Systems of this kind deserve special attention, and should be individually simulated using appropriate methods.

Acknowledgment. The financial support of the Ministero dell'Università e della Ricerca Scientifica of Italy and of the Italian Research Council (CNR, Progetto Finalizzato MST-A-II) is gratefully acknowledged.

Supporting Information Available: Text files containing the coordinates of well-equilibrated configurations of all simulated systems. This material is available free of charge via the Internet at <http://pubs.acs.org>. They are also available for downloading at URL <http://dichi.unina.it/vacatello>.

References and Notes

- (1) Yoon, D. Y.; Vacatello, M.; Smith, G. D. In *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*; Binder, K., Ed.; Oxford University Press: New York, 1995; p 433.
- (2) Vacatello, M. *Macromol. Theory Simul.*, in press.
- (3) Wolff, S.; Wang, M.-J. In *Carbon Black, Science and Technology*, 2nd ed.; Donnet, J.-B., Bansal, R. C., Wang, M.-J., Eds.; Marcel Dekker: New York, 1993; p 289.
- (4) Yuan, Q. W.; Kloczkowski, A.; Mark, J. E.; Sharaf, M. A. *J. Polym. Sci.: Polym. Phys. Ed.* **1996**, *34*, 1647.
- (5) Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules* **1984**, *17*, 862.
- (6) Vacatello, M.; Yoon, D. Y. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 349.
- (7) Baumgartner, A.; Muthukumar, M. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1996; Vol. XCIV, p 625.
- (8) Chen, W.; Nakatani, A. I.; Schmidt, R. G.; Gordon, G. V.; Han, C. C. Presented at a meeting of the Rubber Division, American Chemical Society, Orlando, FL, September 21, 1999.
- (9) Vacatello, M. *Macromol. Theory Simul.* **1994**, *3*, 325.
- (10) Klein, J. *J. Colloid Interface Sci.* **1986**, *111*, 305 and references therein.
- (11) Meijer, E. J.; Frenkel, D. *J. Chem. Phys.* **1994**, *100*, 6873.
- (12) Sevink, G. J. A.; Zvelindovsky, A. V.; van Vlimmeren, B. A. C.; Maurits, N. M.; Fraaije, J. G. E. M. *J. Chem. Phys.* **1999**, *110*, 2250.
- (13) Huh, J.; Ginzburg, V. V.; Balazs, A. C. *Macromolecules* **2000**, *33*, 8085.
- (14) Balazs, A. C.; Ginzburg, V. V.; Qiu, F.; Peng, G.; Jasnow, D. *J. Phys. Chem.* **2000**, *104*, 3411.

MA0015370