

Progress in polymer materials modelling in IPF

In diesem Beitrag demonstrieren wir, wie mittels verschiedener theoretischer Studien die Bedeutung polymerinduzierter Wechselwirkungen und deren Einfluss auf die Mikrostruktur sowie letztlich auf die makroskopischen Eigenschaften von Polymer-Füllstoff-Kompositen herausgearbeitet wurde. Im Rahmen unserer Forschungen untersuchten wir die statischen und dynamischen Eigenschaften ausgewählter gefüllter Polymersysteme. Auf der Basis eingehender Studien der Mechanismen der Polymeradsorption an ausgewählten uneinheitlichen Substraten diskutieren wir im ersten Teil dieses Beitrages die Wechselwirkungen, die sich zwischen Polymer und Partikeln ausbilden. Im zweiten Teil werden die erhaltenen Resultate für das quantitative Verständnis für die Partikel-Partikel-Wechselwirkung in einer Polymerlösung herangezogen, und es wird gezeigt, wie diese letztlich von den Polymer-Partikel-Wechselwirkungen abhängen. Die so erhaltenen Ergebnisse dienen als Ausgangspunkt für den dritten Teil, der sich den statischen und dynamischen makroskopischen Eigenschaften ausgewählter polymerer Verbundmaterialien widmet. Das erste Beispiel dazu ist der Berechnung der Mehrkörper-Korrektur zur Verarmungs-Wechselwirkung (depletion interaction) in Kolloid-Polymer-Systemen gewidmet. Als zweites Beispiel untersuchen wir, wie die scherinduzierte Agglomeration-Deagglomeration und Orientierung von Füllstoffpartikeln die rheologischen und elektrischen Eigenschaften von Polymer-Nanokompositen beeinflusst. Des Weiteren zeigen wir, welche Änderungen polarisiertes Licht in der Mikrostruktur azobenzolhaltiger Polymere hervorruft, und diskutieren dessen Auswirkungen auf die Orientierungsverteilung und das photomechanische Verhalten der Polymere. Am Beispiel von vernetzten hochgefüllten Elastomersystemen untersuchen wir, wie sich große Deformationen auf die dynamischen Moduln dieser Systeme auswirken. Zuletzt zeigen wir, dass unsere theoretischen Ergebnisse in guter Übereinstimmung mit vorhandenen experimentellen Resultaten stehen.

Introduction

Static and dynamic properties of a variety of industrially important polymer-particle composites are known to be very sensitive to their microscopic structure. This fact calls for the need to develop theoretical approaches that rely on the detailed information on the density structure of the polymers in the presence of filler particles and relevant specificities of the polymer-mediated interaction among these fillers. This information can in turn be obtained only based on understanding the mechanisms of the polymer adsorption onto the filler surface and its effect on the interaction among fillers. According to the results of the present study, the polymer-filler adsorption interactions are directly related to the strength of the polymer-mediated interaction between fillers that can cause essential rearrangement of the filler particles in the host polymer system. For a quick example, the depletion interaction between filler particles results in their agglomeration that essentially affects rheological and electrical properties of the composites considered in the present work. As a second example, also addressed in the

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present study, one can mention the decisive influence of the microscopic structure of the azobenzene polymers on their orientation distribution that affects the macroscopic photomechanical behavior of this system. In most cases, the presence of fillers significantly alters the native unperturbed structure of the host polymer systems, which effect is especially pronounced in crosslinked polymer materials. One of the manifestations of this effect is the deformation-induced changes in the material microstructure of filled rubbers that is known to result in peculiar behaviour of their dynamic moduli (e.g. Payne effect). The need to take the filler-induced altering of the rubber microstructure into account poses the problem of calculating the dynamic moduli under excessive stretching conditions that can be imposed by high filler loadings. This problem is addressed as a final stage of the present work.

By developing and making use of the several independent theoretical approaches described below, we intend to demonstrate that understanding of the relationship between the microscopic structure and macroscopic behaviour of the polymer-particle composites is a key to the adequate description of their properties. This core conclusion of our studies is proven by the overall good agreement between the developed theories and experimental data for a wide variety of systems described in what follows.

Adsorption of polymers onto regularly and randomly patterned substrates

The performed study has been aimed at identifying the main factors that influence the reversible adsorption [1] of polymers onto selected chemically non-uniform substrates [2] of high practical importance. In addressing the aforementioned adsorption problems, we have developed two independent theoretical methods that are described in what follows. The first method, the self-consistent perturbation expansion [2, 3], relies on constructing the virial-type expansion of the polymer surface excess Γ that self-consistently couples Γ with the non-uniform structure of the density of adsorbed polymers. The second method, the transfer operator formalism [4], is suited to describe the adsorption of homo-polymers onto periodic or nearly periodic (e.g. weakly disordered) substrates. Mathematically, this method solves the Edwards equation that describes the polymer density structure in the presence of the periodically patterned adsorbing boundary in terms of the eigenproblem for the corresponding transfer operator. The both approaches make it possible to calculate the polymer surface excess as a function of the substrate surface structure and parameters describing the polymer system of interest. Comparing the findings of the above two independent methods provides a convenient tool for verification of the results, which increases their credibility. By making use of the described methods, we have successively investigated the density structure of homo-polymers adsorbed onto selected chemically non-uniform substrates, as follows: (i) periodically patterned rigid surface [3] (e. g. surface formed by phase-separated diblock copolymers); (ii) randomly patterned rigid surface [4, 5]; (iii) surface that bears an array of periodically distributed adsorbing centres [4] (e. g. carbon surface that bears perfectly aligned carbon nanotubes); (iv) different morphologies of the mixed brush [6, 7].

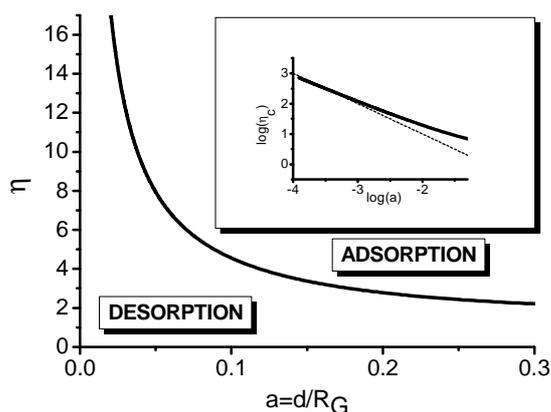


Fig. 1: Adsorption-desorption diagram of polymers adsorbed onto the hard surface that bears a periodic array of adsorbing centers. Inset shows the log-log plot of the adsorption-desorption diagram. The following notations are used: η the effective affinity of the center, d the separation between centers, R_G the radius of gyration

An illustrative example of the performed analysis is given in Fig.1 that shows the adsorption-desorption diagram of polymers adsorbed onto the periodic array of adsorbing centres, expressed as a dependence of the effective affinity of the centres on the reduced separation between them.

Our quantitative studies revealed the following main qualitative trends in the adsorption of polymers onto chemically patterned surfaces:

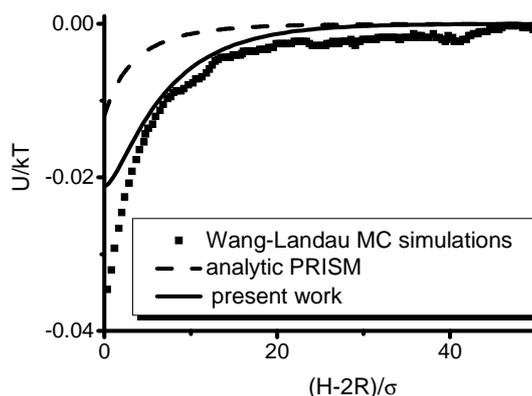
- (i) In all the cases studied, the main factor that affects the adsorption of polymers onto chemically non-uniform substrates is found [8] to be the relation between the polymer correlation length (e. g. radius of gyration for Gaussian polymers) and the typical size of patterns of the adsorbing substrate.
- (ii) Effect of the excluded volume interactions among polymers is found [9] to substantially reduce their adsorption in all the investigated cases.
- (iii) 'Softness' of the adsorbing surface of the mixed brush is proven [7] to suppress the depletion effect that comes from the entropic repulsion between the polymers and this surface.
- (iv) Switching between the ripple and random morphologies of the mixed brush can be effectively used to enhance or reduce the adsorption of polymers of a given degree of polymerization [7].

Potential theory of the depletion interaction in colloid-polymer mixtures

By developing and making use of the novel potential theory [10] of the polymer-mediated interaction between spherical colloids, we have investigated the many-body effects on the depletion interaction among these colloids in the colloid-polymer mixture. As central results of our study, we obtain analytic expressions for the coordinate dependent polymer density in the presence of the colloids and the many-body depletion potential acting between these colloids in the nano-particle limit. Our theoretical result for the pair polymer mediated potential acting between nano-particle colloids immersed in the dilute/semidilute polymer solution proves to show much better agreement with recent Monte Carlo simulations than previous PRISM theory. This point is illustrated in Fig. 2 that shows the comparison among Wang-Landau Monte Carlo simulations, results of PRISM theory, and our findings.

As our main result achieved through making use of the developed method, we directly obtain [10], for the first time, the suppression of the depletion force caused by the presence of many-body correlations.

Fig. 2:
 Comparison among the results of the Wang-Landau Monte-Carlo simulations of M. Doxastakis et al. [J. Chem. Phys. 123 (2005), 034901], analytic PRISM theory [J. Chem. Phys. 109 (1998), 10464], and present theory. The following notations are used: U the depletion potential, T the temperature, k the Boltzmann constant, R the colloid radius, H the separation between colloid centers, σ the statistical segment length.



Modelling rheological and electrical properties of polymer nanocomposites

These studies have been carried out in the frame of BMBF-Project "Eigenschaftsvorhersage von CNT-Polymer-Compositen durch Modellierung und Simulation des Perkolationsnetzwerks beim Verarbeitungsprozess".

1. Rheological properties. Theoretical description of rheological properties of polymer nanocomposites is still a very challenging topic. Here, one must take into account that most filler particles possess an active surface, tend to build agglomerates and at higher loadings form a network structure. This network is very fragile and can be easily broken in external flow fields. However, in the quiescent state the filler particles agglomerate again, slowly restoring a network structure. If the polymer melt is filled with anisometric nanoparticles (layered silicates, carbon nanotubes), additionally to the de-agglomeration process, in strong flows one observes noticeable orientation effects, as the particles tend to orient along the flow direction. For the sake of simplicity, it is usually assumed that all changes in the viscoelastic properties of such complex systems happen either due to agglomeration of particles with a frozen orientation state [11] or solely due to their reorientation, neglecting the agglomeration effects. Recently, we proposed a unified superposition approach which describes the time evolution of a stress tensor in polymer melts filled with attractively interacting anisometric particles [12].

In this approach the total stress is decomposed in three contributions: the viscoelastic stress arising in the polymer matrix, the pure hydrodynamic reinforcement due to the presence of filler particles and the viscoelastic stress arising in the filler network. To describe the first contribution, we probed a number of the rheological constitutive models proposed for the commercial polymer melts. The second contribution has been described by the Folgar-Tucker model for the time evolution of the anisotropic stress tensor in suspensions of non-interacting rod-like or disk-like particles. The third contribution is represented by a nonlinear modification of the Maxwell model. It is combined with a kinetic equation for the structural parameter that reflects the state of the filler network at particular flow conditions.

The superposition approach has been verified on the polycarbonate composites filled with 5 wt% multi-wall carbon nanotubes [12, 13]. The samples were produced by injection moulding Bayer Technology Services. Satisfactory agreement between the predicted and measured data have been achieved for a number of shear experiments as illustrated in Fig. 3.

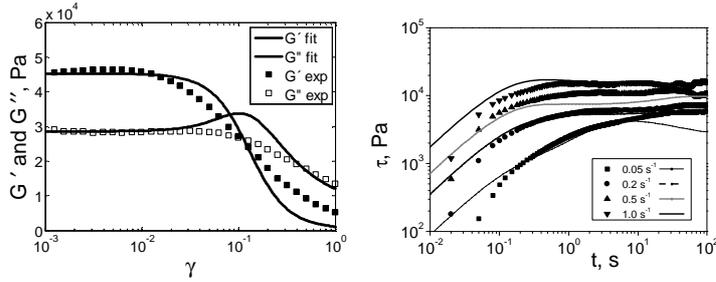


Fig. 3: Strain sweeps of the storage and loss moduli (left) and shear growth curves (right) for polycarbonate composites filled with 5 wt% multi-wall carbon nanotubes. Symbols – experiment, lines – modelling using the unified superposition approach. The matrix contribution is described by the Doi-Edwards model.

II. Electrical properties. Similar to the rheological properties, electrical properties of polymer nanocomposites, filled with attractively interacting conductive anisometric particles strongly depend on the morphology of filler network as well as on the orientation state of individual particles. To model the electrical properties of isotropic composites, a percolation approach is usually applied. In this approach one considers composites in which conductive filler particles are randomly distributed in a non-conducting polymer matrix. The insulator-to-conductor transition in such systems is induced by the formation of a percolation path, once the filler content has reached a threshold critical value.

To describe the shear-induced changes in the electrical conductivity, we have recently proposed to couple a kinetic equation for the structural parameter, representing the state of conductive network, with one of the percolation theories (e. g., a generalized effective medium approximation or Bethe-lattice theory) [14]. The coupling is done by assuming that the percolation probability above the percolation threshold is proportional to the time-dependent structural parameter, i. e. to the fraction of nanoparticles constituting the filler network. This enables us to reproduce the “shear-thinning” behaviour of stationary electrical conductivity as well as the transient behaviour under steady shear for the polycarbonate melt filled with multi-wall carbon nanotubes (see Fig. 4).

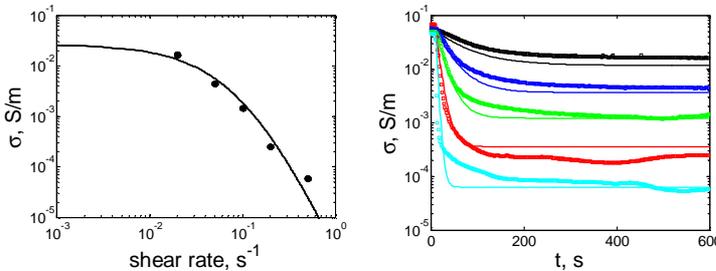
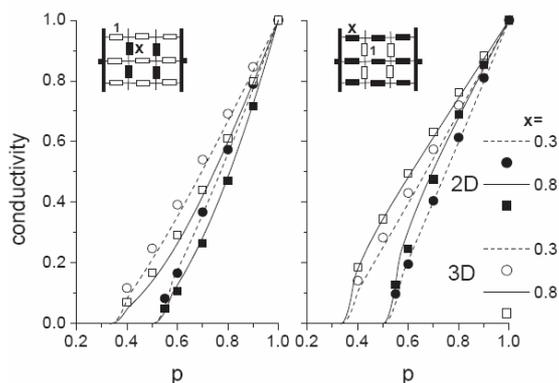


Fig. 4: Dependence of steady state electrical conductivity on shear rate for polycarbonate melt filled with 1 wt% multi-wall carbon nanotubes (left). Time dependencies of the electrical conductivity at five different shear rates for the same system (right): 0.02 (black), 0.05 (blue), 0.1 (green), 0.2 (red) and 0.5 s⁻¹ (cyan). T = 230 °C. Symbols – experimental data provided by T. Skipa (DKI Darmstadt), lines – modelling using the coupled model.

III. Anisotropic percolation theory of electrical conductivity.

For the modelling of the anisotropic network structures appearing under shear flow, no suitable theoretical model can be found in the literature. Therefore, recently we developed the first anisotropic percolation theory [15] which is aimed at describing the observed anisotropy in conductivity for composites filled with anisometric conductive particles. The problem has been solved with the help of a random resistor network model placed on an anisotropic Bethe lattice. This tree-like lattice differs from the usual isotropic one by the subdivision of its bonds into two categories, α and β . The number of bonds extending from each site is a constant referred to as the coordination number, z . The local conductivities of the resistors on the binary Bethe lattice are 'direction'-dependent, i. e. equal to σ or σ' for α and β occupied bonds, respectively. The advantage of the present theory is that the Bethe lattice approach can be used for an arbitrary coordination number z , and thus can be applied for nanocomposite systems with an arbitrary value of percolation threshold $p_c=1/(z-1)$.

Fig. 5: Comparison between the MC simulation on 2D and 3D square lattices and the Bethe lattice theory. The theory predictions with $z = 3$ and 4 for 2D and 3D, respectively, are shown by the curves. The inset shows a resistor network on a fully occupied regular lattice ($p = 1$). Resistors are shown by two colors to elucidate their orientation-dependent conductivities.



The most important outcome of the developed theory is the asymptotic expansion of the average conductivity near $z \rightarrow \infty$. To verify the anisotropic Bethe lattice theory, we computed numerically the electrical conductivity of statistical resistor networks on the regular lattices. The theory predictions were found to be in a very good agreement with the Monte Carlo data for the square and the cubic lattices if one takes $z = 3$ and 4 , respectively (see Fig. 5). Another result is the investigation near the percolation threshold, $p \approx p_c$, regarding the conductivity critical exponent. In particular, we investigated the anisotropy ratio $\sigma_{\parallel}/\sigma_{\perp}$, where $\sigma_{\parallel, \perp}$ are the bulk conductivities parallel and normal to the direction of an applied voltage. For the case of large z , it has been shown that $\sigma_{\parallel}/\sigma_{\perp} \sim p - p_c$. Hence, we found out that the critical exponent is equal to 1. This is in agreement with the experimental data on CNT/polymer composites oriented by strong shear flow [16].

Theory of light-induced deformations in amorphous azobenzene polymers

Azobenzene polymers are able to change their shape significantly under light irradiation. Photo-induced stress is so large that light irradiation of the intensity $I_p \sim 0.1 \text{ W/cm}^2$ is able to deform an amorphous polymer which is even in the glassy state. Due to this unique property, azobenzene polymers have a fascinating potential in such technical applications as data storage media, actuators, artificial muscles, etc. A number of theories have been proposed to explain the origin of the photo-induced force. However, all previous theories provide values of the light-induced stress much smaller than values of the yield stress which is necessary to deform irreversibly glassy polymers. Moreover, they do not describe the effect of chemical structure of azobenzene polymers on their photomechanical properties.

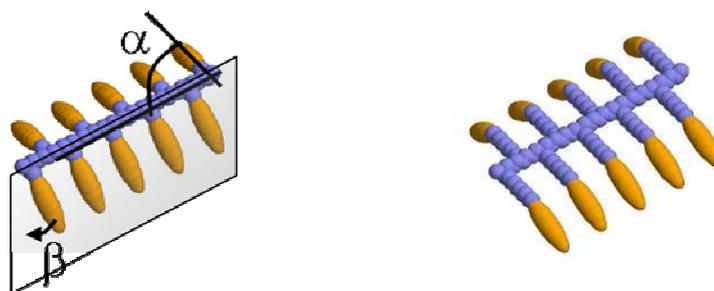


Fig. 6: Side-chain azobenzene molecules with (left) short spacers and with (right) long spacers

Recently, we have proposed a first theory which takes the chemical structure of azobenzene polymers explicitly into account [17,18]. The theory is based on the fact that interaction of chromophores with linearly polarized light leads to orientation ordering of azobenzene molecules which is accompanied by the appearance of mechanical stress.

Each side-chain azobenzene molecule is modelled in the theory as an oligomer which bears photoactive chromophores in side chains (see Fig. 6); α is the angle between a chromophore and the main chain; β is the angle between the plane of symmetry of the molecule and the plane formed by the chromophore and the main chain. The angle β characterizes rotations of chromophores around the main chain. The values of α and β are defined by potentials of internal rotations and by the lengths of spacers. We have found that photo-mechanical behaviour of azobenzene polymers is very sensitive to their chemical structure, as illustrated in Fig. 7.

- (i) If the spacers are short and the chromophores lie almost perpendicular to the backbone (area I in Fig.7), an azobenzene polymer demonstrates a monotonic stretching along the vector E with increasing light intensity.
- (ii) If the spacers are long and the chromophores lie almost along the backbone, $\alpha < 54.7^\circ$ (area II in Fig. 7) a sample shows monotonic compression with increasing light intensity. Note that stretching of a sample consisting of molecules with short spacers and uniaxial compression of a sample consisting of molecules with long spacers are confirmed by experiments and computer simulations [19].
- (iii) We have found specific structures (area III in Fig. 7) for which a sample demonstrates non-monotonic behaviour: a stretched sample starts to be uniaxially compressed at high light intensities. Such non-monotonic photo-elastic behaviour of azobenzene polymers has been also observed in experiments [20].

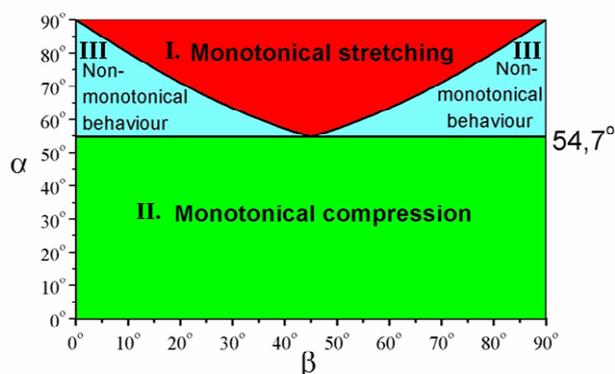


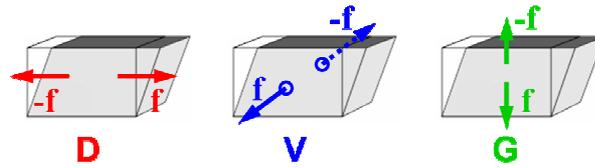
Fig. 7: Values of the structural angles α and β for three typical photo-mechanical behaviours of azobenzene polymers. See text for details.

Furthermore, we have found that at large intensities, $I_p = 0.1 \text{ W/cm}^2$, the light-induced stress becomes larger than the values of the yield stress (10 to 50 MPa) typical for glassy polymers [17, 18]. Under such stresses the deformation of an azobenzene polymer is fixed after the light is switched off. Thus, our approach explains for the first time the possibility of irreversible deformation of azobenzene polymers under light irradiation. This approach can be applied in the future for understanding photomechanical properties of azobenzene polymers of different structures, including azobenzene elastomers.

Theory of dynamic mechanical properties of highly stretched polymer chains and networks

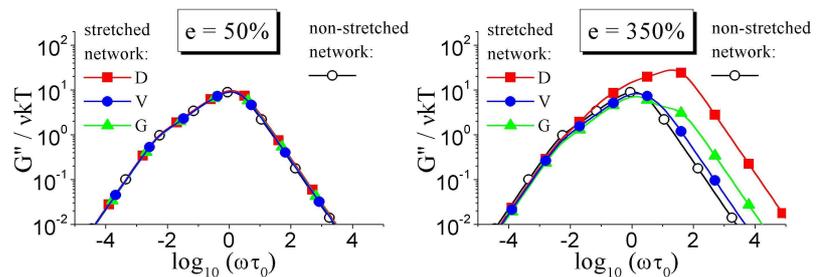
Investigation of the molecular mobility of polymer chains and networks under large static strains is one of the important topics in the modern physics of rubbers. On the one hand, superposition of large static and small oscillating strains has been proposed as a method for studying the molecular mobility and structure of polymer networks [21]. On the other hand, this topic is important for understanding the phenomenon of crack propagation, as the crack tip velocity is controlled by the viscoelastic parameters of highly stretched network fragments near to the crack tip [22]. Additionally, excessive stretching conditions can be caused by high filler loads in the reinforced rubbers.

Fig. 8:
Three principal geometries of periodic shear deformation with respect to the axis of a static stretching force, f :
D: displacement
V: vorticity
G: for f along the shear gradient



We have proposed a theory of dynamic mechanical properties of polymer chains and networks under large static strains [23]. We use an approach in which a polymer chain under static stretching force, f , is modelled as a sequence of Gaussian subchains whose elasticity constants (i) are different for motions parallel and perpendicular to the direction of f and (ii) are functions of the elongation ratio. This approach introduces a *modified* Rouse model. A polymer network is described by a regular cubic network model built from anisotropic Gaussian subchains. We have shown that both stretched polymer chains and stretched polymer networks are characterized by the anisotropy of the dynamic mechanical properties. Frequency dependent storage (G') and loss (G'') shear dynamic moduli are different for different geometries of applying small periodic shear deformation with respect to the direction of the static strain, f . We consider three principal geometries under shear deformation, denoted by D (displacement), by V (vorticity) and by G (for f along the shear gradient), see Fig. 8.

Fig. 9:
Three principal loss moduli for a stretched polymer network under D, V, and G-geometries of shear deformation (filled symbols) and the loss modulus for a non-stretched Gaussian network (open symbols) as functions of the frequency, ω . Relative elongation ratios are equal to $e=50\%$, when $h/L=0.3$, (left) and $e=350\%$, when $h/L=0.9$ (right). Number of segments in network strands, $N=25$ ($h_0/L=0.2$); τ_0 is the relaxation time of a single chain fragment; ν is the degree of crosslinking.



A broad region of elongation exists (both for stretched polymer chains and for stretched polymer networks) where the loss modulus and the relaxation part of the storage modulus do not display splitting with respect to the axis of deformation and their values are close to those for non-stretched Gaussian systems (see Fig. 9 left). This is a region in which $h/L < 0.4$, here h and L are the end-to-end distance and the contour length, respectively, of stretched polymer chains. Significant splitting of the moduli with respect to the axis of deformation and strong difference of their values from those for non-stretched Gaussian systems take place at limiting values of the elongation ratio, when $h/L > 0.4$, see Fig. 9 right.

Theoretically calculated frequency dependences of the storage and the loss moduli for polymer networks are in a qualitative agreement with experimental data for slightly crosslinked elastomers [21]. The results of the theory are useful for studying the phenomenon of crack propagation in filled rubbers.

Conclusions

The present work contributes towards comprehensive understanding the diverse effects of the polymer-induced altering of the microstructure of polymer-particle composites on their static and dynamic properties. We have quantitatively investigated these effects by relying on the detailed study of the polymer-mediated particle-particle and polymer-particle interactions in diverse polymer-particle-solvent systems. The obtained results have been used to study the many-body correlations in the colloid-polymer mixtures. Next we have studied how the polymer-flow induced agglomeration/de- agglomeration of fillers affects rheological and electrical properties of filled polymer melts. Along the same lines, we investigated the effect of chemical microstructure on the macroscopic photomechanical response in the azobenzene polymer systems. In addition, we calculated the dynamic modules of rubbers under high stretch conditions that can be potentially imposed by fillers. In all the cases studied, we found good agreement between our theoretical findings and the available experiments and simulations.

References

- [1] A.I. Chervanyov, G. Heinrich: *J. Chem. Phys.* 131 (2009), 104905
- [2] A.I. Chervanyov, G. Heinrich: *Pol. Mat.: Sci. Eng* 99 (2008), p. 763
- [3] A.I. Chervanyov, G. Heinrich: *J. Chem. Phys.* 125 (2006), 084703
- [4] A.I. Chervanyov, G. Heinrich: *J. Chem. Phys.* 129 (2008), 074902
- [5] A.I. Chervanyov, G. Heinrich: *Pol. Mat.: Sci. Eng* 101 (2009), p. 1773
- [6] A.I. Chervanyov, G. Heinrich: *Phys. Rev. E* 75 (2007), 021801
- [7] A.I. Chervanyov, G. Heinrich: *Pol. Mat.: Sci. Eng* 101 (2006), p. 273
- [8] A.I. Chervanyov, G. Heinrich: *Eur. Phys. J. E.* 24 (2007), p. 271
- [9] A.I. Chervanyov, G. Heinrich: *J. Chem. Phys.* 127 (2007), 014902
- [10] A.I. Chervanyov, G. Heinrich: *J. Chem. Phys.* 131 (2009), 244904
- [11] F. R. Costa, M. Saphiannikova, U. Wagenknecht, G. Heinrich: *Adv. Polym. Sci.* 210 (2008), p. 101
- [12] S. Richter, M. Saphiannikova, D. Jehnichen, M. Bierdel, G. Heinrich: *eXPRESS Polymer Letters* 3 (2009), p. 753
- [13] S. Richter, M. Saphiannikova, G. Heinrich: "Constitutive Models for Rubber VI", Taylor & Francis Group, London, eds. G. Heinrich et al. (2009), p. 205
- [14] T. Skipa, D. Lellinger, M. Saphiannikova, I. Alig: *Phys. Stat. Sol. B* 246 (2009), p. 2453
- [15] F. Semeriyarov, M. Saphiannikova, G. Heinrich: *J. Phys. A: Math. Theor.* 42 (2009) 465001
- [16] J. W. Xu, W. Florkowski, R. Gerhardt, K. S. Moon, C. P. Wong: *J. Phys. Chem. B* 110 (2006), p. 12289
- [17] V. Toshchevikov, M. Saphiannikova, G. Heinrich: *J. Phys. Chem. B* 113 (2009), p. 5032
- [18] V. Toshchevikov, M. Saphiannikova, G. Heinrich: *Proc. SPIE* 7487 (2009) p. 74870B
- [19] J. Ilytskyi, M. Saphiannikova, D. Neher: *Cond. Matter Phys.* 9 (2006), 87
- [20] S. Bian, J. M. Williams, D. Y. Kim, L. Li, S. Balasubramanian, J. Kumar, S. J. Tripathy: *Appl. Phys.* 86 (1999), p. 4498
- [21] E. Munch, J. M. Pelletier, B. Sixou, G. Vigier: *Polymer* 47 (2006), p. 3477
- [22] T. Horst, G. Heinrich: *Polymer Science Ser. A.* 50 (2008), p. 583
- [23] V. Toshchevikov, G. Heinrich, Yu. Gotlib: "Constitutive Models for Rubber VI", Taylor & Francis Group, London, eds. G. Heinrich et al. (2009), p. 435

