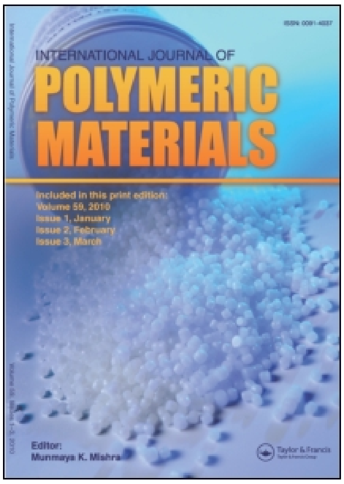

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Kunihiro Osaki[a]
[a] Institute for Chemical Research, Kyoto University, Kyoto, Japan

To cite this Article Osaki, Kunihiro(1991) 'Polymer Dynamics and Rheology', International Journal of Polymeric Materials, 15: 3, 221 — 225

To link to this Article: DOI: 10.1080/00914039108041087

URL: http://dx.doi.org/10.1080/00914039108041087

Intern. J. Polymeric Mater., 1991, Vol. 15, pp. 221–225
Reprints available directly from the publisher

Printed in the United Kingdom

POLYMER DYNAMICS AND RHEOLOGY

KUNIHIRO OSAKI

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.

This article is a summary on 4 topics from the "Polymer Dynamics and Rheology" session which contained 88 papers.

Computer Simulation of Concentrated Colloid Systems

Rheological properties of a suspension of solid particles are highly related to the state of dispersion. The particles may form aggregate structures of various shapes and sizes depending on the interparticle force. The suspension state and its effect on rheological properties are undoubtedly one of the important problems facing the polymer industry.

D.H. Chen, M. Doi *et al.* have been studying for sometime the structure and properties of dispersions of spherical particles by computer simulation. In their first paper (890), they dealt with non-sticking spherical particles dispersed in a Newtonian liquid with the lubrication force approximation. No interparticle force was introduced except for the hard core repulsion term. The hydrodynamics were appropriately simplified and probably correspond to the free-draining approximation in polymer dynamics. The Brownian motion was not taken into account. At the beginning, the particles were placed at randomly chosen places in a vessel. The boundary was moved to simulate a simple shear flow. The location of particles were registered from time to time and the viscosity was calculated. The cyclic boundary condition was employed to circumvent the limited size of the vessel. They observed that the particles gradually formed network structures and the viscosity increased with time. The viscosity in steady state increased with the particle volume fraction at relatively low particle contents. At higher contents, the particles were aligned in layered structures (2-dimensions) or straw-like structures (3-dimension). The viscosity did not increase significantly with particle content in these cases.

In their second paper (891), Chen and Doi studied a more interesting case of sticky particles. They assumed that two particles in contact should move together until a force larger than a certain critical value separate them from each other. In a flow field, the particles collide with one another and aggregate in clusters. On the other hand, the hydrodynamic force generates a large separating force in the case of large clusters. Thus the cluster size in the steady state is determined by the rate of shear and the content of particles. The results of simulation in 2-dimensions were as follows. The average number of particles in a cluster decreased in proportion to the –2/3 power of the rate of shear. The viscosity decreased in the same manner. The average radius of the cluster was proportional to the square root of the average number of particles in the cluster; the fractal dimension of the cluster was 1/2. Thus the structure of the aggregate was not like a network but like a circular floc. The simulation in 3-dimensions, comparable with real systems, may be completed in a matter of a year.

Dielectric Measurements in Entangled Polymers

The concept of polymer chain entanglement is strongly related to the viscoelastic behaviour of polymeric materials. The measurements of diffusion coefficient and dielectric relaxation are new techniques for studying the molecular motion in polymer concentrates. The longest dielectric relaxation time is equal to the longest viscoelastic relaxation time for a certain type of polymer. Suppose each segment of a polymer has a component of dipole moment parallel to the chain axis and is aligned in a regular head-to-tail structure. Then the polymer molecule has a dipole moment proportional to the end-to-end vector and the dielectric relaxation time represents the global motion of the chain. K. Adachi, T. Kotaka *et al.* have been studying the dielectric properties of polyisoprene in the entangled state and have published several results mostly in Macromolecules. They now investigated more sophisticated systems in the polymer symposium.

They combined f polyisoprene chains of molecular weight M_P at one point and synthesized a star-branched polymer (884, 2076). The number of arms, f, was 6 or 2. The precursor molecules had the regular head-to-tail structure and they were combined at their heads: The dipole moment was arranged in a manner radiating from the branch point. The polymer with $f = 2$ was thus a linear block copolymer in the sense of dipole structure. Theories for dilute solution tell that the longest dielectric relaxation time for such polymers is much shorter than the viscoelastic relaxation time and is equal to that of the precursor, a linear polymer with $M = M_P$. They showed that when M_P was small (3.5×10^3), the dielectric relaxation time of a 6-armed polymer was slightly higher but close to that of the precursor linear polymer. When M_P was large (2.07×10^4), the dielectric relaxation time of a 6-armed polymer was about 10 times as large as that of the precursor and the relaxation spectrum was rather diffuse. This result may be in qualitative agreement with the dynamic theories in entangled systems.

They studied (884, 2073) also block copolymers of isoprene (I) and butadiene (B); poly B-block-poly I and poly B-block-poly I-block-poly B. In these cases, the polybutadiene block does not have a dipole moment proportional to the end-to-end vector and behaves in a neutral manner in dielectric measurments. The relaxation time will represent the motion of the particular range of the chain where the isoprene block is located. The preliminary results seemed to be more complicated than the above-mentioned results for branched homopolymers.

Another new application of the dielectric method was in a blend of polyisoprene samples with different molecular weights (885). A weakness of the viscoelastic method in the study of molecular motion in the blend is the difficulty in evaluating the relaxation time of the short chain in the mixture; any viscoelastic function has a considerable contribution from the glass-to-rubber relaxation mechanism in the time range in question. On the other hand, the peak of the dielectric loss corresponding to the global motion of the short chain turned out to be a rather sharp process. Thus the relaxation time of the short chain was evaluated with high precision. The relaxation time of the short chain was approximately proportional to the 3rd power of the molecular weight in accord with the tube model theory of entanglement. This method may be very promising for the detailed examination of the entanglement theories.

Microheterogeneous Polymer Liquids

The relation between the rheological properties and the morphology or structure of inhomogeneous systems is always one of the main subjects in the Polymer Symposium. Following materials were reported this year: chitosan in weak acid (893); alginate aqueous solution (894); styrene-butadiene block copolymer in various solvents (877, 896, 2091, 2100); polyamides and styrene-acrylonitrile copolymer (2190); epoxy resin with filler (2118); polyurethane (2121, 2124); and liquid crystals (907, 908, 2127, 2130, 2133, 2136, 2139). The structures such as microphases, aggregates, and liquid crystal domains are diverse and the rheological properties are very much affected by the details of the structure.

Among these systems, T. Masuda *et al.* found a group of systems with rather simple and common behaviour and named them "Microheterogeneous polymer liquids (MHPL)" (2094, 2097). According to their definition, the MHPL is an entangled polymeric system in which small particles are very well dispersed without any aggregate structures. The MHPL systems they investigated so far were: highly branched polystyrenes with more than 6 branches sticking out from one branch point; highly branched tree-like polystyrenes; specially prepared high impact polystyrenes and ABS resins.

The stress relaxation of such a material was revealed to proceed through the entanglement relaxation and an additional relaxation mechanism with a longer relaxation time. This relaxation mode was evidently not originated by the aggregated structure of particles but by the existence of well-dispersed particles. They asserted that the relaxation time was approximately equal to the time for a particle to drift 1/2 of the average interparticle distance through diffusion. The relaxation time could then be estimated from the particle size, the average distance, and the local viscosity. The estimated values for a series of star-branched and tree-like polystyrene samples were in semiquantitative agreement with the observed values. Thus they asserted that the relaxation mode corresponded to the recovery of equilibrium due to the diffusion of particles after a disturbance in a randomly distributed particle system.

A remarkable feature of the long-time relaxation mode of MHPL was its behaviour in large deformation. It was revealed that the relaxation modulus corresponding to this relaxation mode was independent of the magnitude of strain. Thus the relaxation modulus of MHPL decreased with increasing strain at relatively short times corresponding to the entanglement relaxation but became independent of strain at long times. This behaviour is in a sharp contrast with that of a dispersed system with aggregated particle structures. The aggregated structures usually exhibits a second plateau in the relaxation modulus and the strain dependence is extremely strong in this time range. The property of the relaxation modulus at large strains of MHPL was rather unexpected and Masuda *et al.* did not give any idea of explanation. Neighbouring particles may slide together for several times the average particle distance. The drift mechanism proposed to estimate the relaxation time may be insufficient if the strain dependence comes into question.

Polymer Blend

Studies on polymer blends seemed to have continuing support from industry and appeared in many sessions of the symposium; Polymer solutions, Solid polymers, and Superengineering plastics. Two aspects of polymer blend were of special interest in the Polymer dynamics and rheology session.

One of the subjects was shear-induced homogenization of two polymers in solution. Takebe, Hashimoto *et al.* (2079) investigated the small angle light scattering from semidilute solutions of the mixture of polystyrene and polybutadiene in dioctyl phthalate in simple shear flow. The solution was homogeneous at high temperatures and was phase separated under a certain temperature, T_c. They observed that the homogenization temperature in a shear field with a rate of shear S, $T_c(S)$, was lower than that at rest, $T_c(0)$, and that the relative lowering of T_c, $[T_c(0)-T_{,c}(S)]/T_c(0)$, was proportional to the square root of S.The proportionality constant in this relation was orders of magnitude larger than that for mixtures of liquids of low molecular weights. They extended the scaling theory for the phase separation of materials of low molecular weight and suggested that the difference came from the long time for the equilibration of the concentration fluctuation in polymeric materials.

They also reported that the correlation length estimated by fitting the Ornstein-Zernike equation to the scattering intensity was inversely proportional to the change of the homogenization temperature, $T_c(0) - T_c(S)$. In their second paper (2082), they showed the variation of the two-dimensional scattering patterns at various rates of shear at a temperature slightly lower than $T_c(0)$. The liquid was a mixture of macroscopic droplets at low rates of shear. The droplets became smaller and were elongated in the flow direction as the rate of shear was increased. The streak scattering pattern due to elongated small particles became sharper and weaker as the rate of shear was increased and finally disappeared at $T_c(S)$. The scattering intensity distribution was expressed by q^{-4} at low rates of shear and by q^{-2} at high rates of shear, corresponding to the disappearance of the macroscopic domain structures with increasing shear. Here q is the magnitude of the scattering vector. Another rheological subject in polymer blend was the orientation of component polymers of a cosoluble polymer blend in stress relaxation processes. The degree of orientation was estimated by measuring the birefringence in the process of stress relaxation, Takahashi, Inoue *et al.* have been studying this problem for a few years. They reported the comparison of two extreme blend systems in the symposium(2106). They studied the blends of polystyrene (PS) and poly(phenylene oxide)(PPO) and of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF). The PS/PPO system was a system with a very small value of Flory chi parameter and PMMA/PVDF was a large negative value.: Thus the latter was a very good cosoluble system. They observed that the birefringence of the PS/PPO system could be explained if the PS and PPO chains were moving independently in the relaxation process. On the other hand, the PMMA/PVDF chains were moving in a highly cooperative manner. From the reported relaxation spectra and the maximum relaxation times, one can guess that their result on birefringence behaviour probably corresponds to that in the glass-to-rubber transition zone. On the other hand, Takatori, Osaki *et al.* (2103) studied the birefringence and the relaxation modulus of solutions of the mixture of PS and poly(vinyl methylether) (PVME) in the rubbery plateau region and the terminal flow region. They observed that the longest relaxation time increased with the increasing molecular weight of the PS and the plateau modulus at long times corresponded to entanglement among long PS chains. The birefringence in this time range could not be accounted for unless the PVME chains retained some orientation.