Rheological Properties of Polymers: Structure and Morphology of Molten Polymer Blends

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ABSTRACT

The article reviews a brief literature on the rheological properties of polymer melts and blends. Experimental results on polymer blends are summarized. Technically, vital types of multi-phase polymers such as compounds and blends are discussed. The importance of the rheological properties of polymer mixtures in the development of the phase structure is discussed. And the importance of considering the stress and/or strain history of a material sample in a rheological investigation is discussed. Finally, the outlook on the past, present and future developments in the field of polymer rheology are given. The review concludes with a brief discussion on the opportunities and challenges in the field of polymer blends and blend rheology.

Keywords: Polymer Melts, Polymer Blends, Miscible Polymer Blends, Immiscible Polymer Blends, Compatibilization, Rheological Properties and Phase Structures

1. Introduction

Rheology is a branch of physics that deals with the deformation and flow of matter under stress. It is particularly concerned with the properties of matter that determine its behaviour when a mechanical force is exerted on it. Rheology is distinguished from fluid dynamics because it is concerned with the three traditional states of matters rather than only liquid and gases. Rheological properties have important implications in many and diverse applications. Often, an additive is used to impart the desired flow behaviour. Among these, organoclay products, formed by the reaction of organic cations with smectite clays, are the most widely used additives for solvent-based coatings. The often used cation, usually a quaternary ammonium salt, influences the performance of the resultant organoclay. Criteria to consider in the choice of a cation are molecular size, compatibility with the fluid in which the organoclay is to be used, stability and reactivity. Applications of rheology are important in many areas of industries involving metal, plastic, and many other materials. The results from rheological investigations provide the mathematical description of the viscoelasticity behaviour of matter. An understanding of the rheology of a material is important in the processing of composites, whether the task is designing an injection molded part or determining the cure cycle for a prepregs.

For many years, rheology has been used as semi-quantitative tools in polymer science and engineering. The relationship between the structure and rheology of a polymer is of practical interest for two reasons: firstly, rheological properties are very sensitive to certain aspect of structure and they are simpler to use than analytical methods, such as nuclear magnetic resonance. Secondly, it is the rheological properties that govern the flow behaviour of polymers when they are processed in the molten state. Considering the structures of polymers by means of the size and shape of molecules and the distribution of these characteristics among the molecules, structure formation and controlled assembly are the focus of joint simulations and various experiments. Neves et al. [1] investigated the main rheological features of vaginal hydrophilic polymer gels and elucidated the relationship between these characteristics, gels composition and their general influence in therapeutic/usage purpose. In their studies, two vaginal gels were studied by the cone-and-plate rheometry, at body temperature. Several parameters (apparent viscosity, complex viscosity, storage modulus, loss modulus, critical oscillatory stress, tan δ, thixotropy...
and yield stress) were measured and/or calculated. They found that the rheological behaviour of vaginal gels strongly depended on the type of gelling agent used; which potentially influences their spreading and retention properties when administered in the vaginal canal. Small variations in gels composition can result in substantial changes in their features, namely: viscosity, yield stress and thixotropy. Rheological properties of tested gels appeared to have correlated strongly with their therapeutic/usage purpose.

Early investigations of the solution properties of polymers are primarily responsible for proving that the high polymers are not association of colloids, but are macromolecules held together by covalent bonds. Methods of measuring the molecular weight of polymers were necessary to prove the truth (or otherwise) of this hypothesis [2]. It is striking that the rheology of macromolecules and suspensions reflects their size, shape, and interactions in a flowing field. For nearly a century, solution properties of polymers, such as their viscosities, collo-gative properties, solubility and light scattering behaviour have been studied. Materials with totally new property combination may be achieved by blending together, two or more polymers. In many polymer-polymer alloys, immiscibility has been observed by shearing an initially (static) phase-separated blend. A theoretical prediction shows that shear mixing occurs at low and high shear rates, with a demixing region at the intermediate shear rates [3]. While immiscible blend often follows predictable rheology pattern (since they exhibit single phase behaviour), the rheology of phase-separated system is much more complex. Its phase morphology is a major factor, since it critically affects the size and shape changes in shear flow, as observed by viscosity. The continuous phase of the phase-separated blend is determined by two important factors, viz: the volume fraction and the viscosity of the components. High volume fraction and low viscosity favour phase continuity [3]

The effect of viscosity ratio on the morphology of immiscible polymer blend has been studied by several researchers. To achieve fine phase morphology during the processing of immiscible polymer blends, it is often required to add compatibilizers [4]. Mayu et al. [5] studied the morphology of blends of PS/PMMA, PC/SAN24 and PMMA/EVA and compared the morphologies with and without modified organoclays Cloisite 20 A or Cloisite 6 A. In each case, they found a large reduction in domain size and the localization of the clay platelets along the interfaces of the components. Increase in miscibility was accompanied in some cases, with the reduction of the system from multiple values of the glass transition temperatures to one. In addition, the modulus of all systems increased significantly. They proposed a model where the in-situ grafts were forming on the clay surfaces during blending and the graft had to be localized at the interfaces. This mechanism reflects the composition of the blend and is rather fairly nonspecific [5]. Young and Kim [6] investigated the effect of the amount of in-situ formed graft copolymers on the blend morphology for immiscible polymer blends of poly (butylenes terephthalate) (PBT) and polystyrene (PS) with various amount of poly (styrene-ran-glycidy methacrylate) (PS-GMA) as in-situ compatibilizer. This article surveys published literature which were concerned with the rheology, polymer melts and blends. Also included are some studies of blend of different polymers. The aims are:

- To highlight the importance of polymer melts and blends.
- To highlight the rheological properties of polymeric materials in the molten state, in order to gain fundamental understanding of the processability of such materials.
- To highlight the importance of considering the stress or strain history of a material sample in rheological investigations.
- To review the past, present and possible future developments in the field of polymer blend rheology.
- To discuss the current research issues.
- To highlight the opportunities and the challenges thereof.

### 2. Polymer Melts

In the last three decades, considerable progress has been made in the rheology of polymer solutions and polymer melts. The measurement of rheological properties of any polymeric material in the molten state is crucial in order to gain fundamental understanding of the processability of that material. This is because rheological behaviours are strongly influenced by the material structure and the interfacial characteristics. The rheology of polymer melt is crucially essential for two reasons. Firstly, it has helped to resolve many polymer problems, such as wide gauge variations in films, poor optical quality of sheet and films, slow production rates, dimensional instability and poor mechanical properties. Secondly, it has been employed for the analysis of parameters, such as: molecular structures, branching type and extent of branching, content, entanglements and crosslink density [2]. Since polymer melts are viscoelastic, both viscosity and elasticity must be measured. This information is easily obtainable from viscoelastic spectrum. Data can be treated in many different ways. Master curves can be produced from where retardation and relaxation spectra can be generated. To include the wide range of relaxation times-from the largest molecules to the smallest subsegments, it is necessary to make measurement over a wide
range of temperature and frequency (or shear rates). Nichetti and Manas-Zloczower [7] employed a simple superposition model to define the relationship between molecular weight distribution and shear viscosity for linear polymeric systems. Gel permeation chromatography data for molecular weight distributions were fitted using statistical distribution functions. A simple superposition model was then employed to calculate the shear viscosity for the systems investigated. The effect of polydispersity on the shape of the flow curves was calculated. The simplicity of the model makes feasible its use in numerical simulations of complex geometries as encountered in polymer processing equipment. Their study also sheds some light on the relationship between entanglement and disentanglement phenomena in polymeric systems. Soskey and Winter [8] measured stress relaxation after rapid extensional strain, in order to obtain the extensional relaxation modulus. Their research had the objectives of developing the lubricated squeezing technique for molten polymers, by applying the technique to two different polymers, and testing the “separability hypothesis.” The time-dependence of the relaxation modulus was found to be the same in extension as in shear, giving the relaxation modulus of linear viscoelasticity.

3. Polymer Blends and Melts

3.1. Polymer Blends

Recently, there has been pronounced interest in polymer blends. The enhanced activities are related to the hope of producing advanced high performance materials based on well known products and the need for basic knowledge on their phase behaviour, which in turn offers some flexibility for the control of morphology during processing. Polymer blends are mixtures of different homopolymers, copolymers, and terpolymers. They can be homogeneous (miscible) or heterogeneous (multiphase). This includes both crystalline and amorphous polymers. Whether a mixture of two chemically dissimilar polymers is miscible or not depends on the thermodynamics of mixing. In order to understand what governs polymer-polymer miscibility on a molecular scale, it can be approached via the polymer solution theory. The unique factor affecting the thermodynamics of polymer blends compared with polymer solutions is the large molecular weight of both components [2]. Polymer blending has been identified as the most versatile and economical route to producing new multi-phase polymeric materials that are able to satisfy the complex demands of performance [9]. Over the past few decades, polymer blend has grown tremendously in leaps and bonds. In fact, the design and development of these multi-phase polymer blend materials are strongly dependent on two major parameters; which are:

- The control of interface bonding.
- The control of morphology.

Tol et al. [10] prepared (PPE/PS)/PA6 and PS/PA6 blends by means of melt-extrusion. They were compatibilized using the reactive styrene-maleic anhydride copolymer with 2 wt% maleic anhydride (SMA2). The effect of compatibilization on the phase inversion and the stability of the resulting co-continuous blend structures were investigated using scanning electron microscopy, dissolution and extraction experiments. Depending on the blend composition, the onset of co-continuity shifted towards the lower PA6 concentrations according to the change in blend viscosity ratio. The unmodified co-continuous blends were not stable and did break-up into droplet/matrix type of morphology upon annealing in the melt. Although the stability of the threads during annealing improved upon compatibilization because of the resulting lower interfacial tension, the decreased possibility for recombination and coalescence during flow reduced the co-continuous region for the compatibilized blends. It was proposed that a dynamic equilibrium between break-up and recombination phenomena after the initial network formation is necessary to maintain the network structure.

Processing of polymer materials has a large influence on the resulting mechanical and optical properties of the end product. For instance, dimensional stability in precision injection moulding or yield strength, Young’s modulus and even tear strength of blown films are affected by the viscoelastic properties of the polymer melt. In turn, the rheological behaviour is related to specific molecular structures and the molecular weight distribution [11]. In the manufacturing of polymeric objects, most of the shaping is carried out in the molten state, as it is an important part of the physical property development. Melt processing involves interplay between fluid mechanics and heat transfer in rheologically complex liquids, and taken as a whole, it is a relevant example of the importance of coupled transport processes. The viscoelastic character of polymer melts reflects the entangled microstructure and plays an important role in property development and in flow stability. Viscoelasticity has little effect on the evolution of many processing flows, however, where the mechanics are dominated by the temperature and shear-rate dependence of the viscosity; this statement is especially true of extrusion and some mold filling, but it equally applies to some extensional flows, even when the polymer is a relatively inelastic polyester or nylon.

Many investigations have been done on polymer melt. Seemann et al. [12] studied the stability conditions of
thin (3 to 300 nm) liquid polymer films on various substrates. The key role was played by the effective interface potential, $\phi$ of the system air/film/substrate, which determined the de-wetting scenario, in case, if the film is not stable. In their study, they described how to distinguish spinodal de-wetting scenario from heterogeneous and homogeneous de-wetting by analysing the emerging structures of the film surface, by e.g. Minkowski measures. They also included line tension studies of tiny droplets, showing that the long-range part of $\phi$ does affect the drop profile, but only very close to the three phase boundary line. The dynamic properties of the films are characterized via various experimental methods: the form of the de-wetting front, for example, was recorded by scanning probe microscopy that gave insight into the boundary condition between the liquid and the substrate. They further reported experiments probing the viscosity and the glass transition temperature of nm-thick films using e.g. ellipsometry. They found that even short-chained polymer melts exhibit a significant reduction of the glass transition temperature as the film thickness is reduced below 100 nm. Daoulas et al. [13] presented an atomistic modeling approach for simulating the interface between a polymer melt and a crystalline solid substrate. As a test case, a thin film of polyethylene (PE) melt confined between a semi infinite graphite phase on the one side and vacuum on the other, were considered. The simulation was carried out in the isothermal-isobaric statistical ensemble with an efficient Monte Carlo (MC) algorithm based on state-of-the-art variable connectivity moves. The atomistic simulations are conducted by describing the PE and PP chains with a united atom model, which considers each methylene (CH$_2$) and methyl (CH$_3$) group along the chain backbone as single interaction sites. To calculate the potential energy of interaction between polymer atoms and the semi-infinite graphite substrate, capable of incorporating the exact crystallographic structure of graphite, the method designed by Steele was implemented. The new approach has allowed the authors to analyze the structural and conformational properties on the length scale of just a few angstroms from both surfaces. Detailed results are presented for the local mass density, structure and conformation of PE at the two interfaces, obtained from simulations with model, strictly monodisperse PE samples of molecular length up to C-400. Additional structural features of the adsorbed layer, such as the distribution of skeletal carbon atoms in train, loop and tail conformations and their statistics, are also analyzed in detail and compared with the predictions of the lattice-based Scheutjens-Fleer self-consistent mean field theory in the limit of zero solvent concentration (melt case). Their atomistic simulation data demonstrated a stronger dependence of these descriptors of adsorbed layer structure on chain length than what was calculated by the mesoscopic Scheutjens-Fleer lattice model. In a second step, thoroughly equilibrated configurations of the confined model PE melt films are subjected to detailed molecular dynamics (MD) simulations in the isothermal-isobaric statistical ensemble to analyze their dynamic behaviour. The MD simulations are carried out with the rRESPA method of multiple-time-step algorithm and have allowed them to monitor segmental and chain center-of-mass mean-square displacements over time scales on the order of a few hundreds of nanoseconds. Foteinopoulou et al. [14] subjected a large number of well-equilibrated atomistic configurations of linear, strictly monodisperse polyethylene (PE) melts of molecular length ranging from C-24 up to C-1000, obtained through extensive Monte Carlo simulations based on chain connectivity altering algorithms, to a detailed topological analysis. Primitive paths are geometrically constructed connecting the two ends of a polymer chain (which in all cases are considered as fixed in space) under the constraint of no chain cross ability, such that the multiple disconnected (coarse-grained) path has minimum contour length. When applied to a given, dense polymer configuration in 3-D space, the algorithm returns the primitive path and the related number and positions of entanglements (kinks) for all chains in the simulation box, thus providing extremely useful information for the topological structure (the primitive path network) hidden in bulk PE. In particular, their analysis demonstrated that once a characteristic chain length value (around C-200) is exceeded, the entanglement molecular length for PE at $T$ 450 K reaches a plateau value, characteristic of the entangled polymeric behaviour. They further validated recent analytical predictions about the shape of the distribution for the number of strands in a chain at equilibrium. At the same time, they showed that the number of entanglements obtained by assuming random walk deviates significantly from these predictions, which they regarded as clear evidence that by directly counting the entanglements and their distribution functions, as proposed in their work, offers advantages for a quantitative analysis of the statistical nature of entanglements in polymeric systems.

### 3.2. Vital Types of Multi-Phase Polymers: Compounds and Blends

Over the years, the fact that polymer cannot mix with each other to form homogeneous mixture at segmental scale has been the driving force for a large number of studies on multiphase polymeric materials. It has been known for a long time that the physical properties of these phase-separated polymers; such as toughness, flowability, transparency and weather resistance, to men-
tion a few, are dictated by their morphology [15]. As a consequence, a variety of chemical and physical methods has been extensively exploited to control morphology of immiscible polymer mixtures. Reactive polymers are widely utilized for various practical purposes such as the modification of surface tension between different phases via which morphology and physical properties of multiphase polymeric material can be modified and controlled. These techniques are termed reactive compatibility [15].

Types of polymer blends are quite varied and comprise of many diverse combinations of polymeric materials for both academic and industrial interests. The primary differentiation of polymer blends involves their phase behaviour; specifically miscibility versus phase-separation. The primary advantage of miscible versus phase-separated polymer blends is the blend property profile (mechanical properties), which is generally intermediate between that of the unblended constituents. The technology involves in polymer blends includes a multitude of polymer alloy compositions including elastomer blends, engineering polymer blends, impact modified polymer blends, etc.

3.3. Miscible Polymer Blends

Miscible polymer blends are an expensive, easy-to-use approach for investigating and refining polymer combinations. It facilitates combinations that work and some that don’t. Miscible polymer blends behave similarly to what is expected of a single phase system. Their properties are a combination of properties of pure components. The characteristics of components affecting the properties of miscible blends are their chemical structure and molecular weight, their concentration and intermolecular interactions. While miscible blend system is of considerable scientific and practical interest, it should not be concluded that miscibility is always preferred with respect to properties.

3.4. Immiscible Polymer Blends

Mixing immiscible polymers in the liquid state can result in various phase morphologies. These depend on the nature and the relative amounts of the polymers used and on the flow history of the sample. Immiscible polymers behave as different materials at different flow fields. The phase morphology is an important factor in the rheology of immiscible polymer blends. Most binary polymer blends are immiscible. To a large extent, the characteristics of these immiscible polymer blends are determined by the state of the interface between the components. The interaction of two melts at the interface is primarily represented by a quantity $k$, called the interfacial tension. “Interfacial tension is the excess free energy caused by the existence of an interface, arising from the unbalanced molecular forces [16]. Generally, chemically different polymers are immiscible and their blending leads to materials with weak interfacial adhesion and thus poor mechanical integrity. The conversion of immiscible blend to useful polymeric products with the desired properties requires some manipulations of the interface. One of the classical methods to ensure adhesion between the phases (reduction of the interfacial tension) is the use of a third component, a compatibilizer, which is miscible in both cases. According to Elias et al. [17], in recent years, new concept of compatibilization using rigid nano-materials like silica nano-particles has been proposed.

3.5. Compatibilization

Compatibilization is the process of modification of interfacial properties in immiscible polymer blends. This results in the reduction of the interfacial tension, stabilization of the desired morphology and improved interaction between phases of solid state. In order words, compatibilization results in the formation of polymer alloys. Compatibilization is accomplished by physical or chemical means. In the former case, the desired level of dispersion is generated by physical means, then physically stabilised (e.g., by quenching, retardation, cross-linking or co-crystallization). In the later case, the morphology does not only depend on the level of mechanical mixing, but to a great extent, it is controlled by the compatibilizer [18].

Table 1 below, shows the different type of polymer blends [3].

4. Experimental Results on Polymer Blends

Young and Kim [6] investigated the effect of the amount of in-situ prepared graft copolymers on the blend mor-

Table 1. Types of polymer blends.

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<th>TYPES OF POLYMER BLENDS</th>
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<tr>
<td>1. Engineering polymer blends</td>
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<td>2. Impact modified polymer blends</td>
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<td>3. Emulsion blends</td>
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<td>4. Crystalline-crystalline polymer blends</td>
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<td>5. Crystalline-amorphous polymer blends</td>
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<td>6. Thermosetting polymer blends</td>
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<td>7. Impact modified polymer blends</td>
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<td>8. Molecular composites</td>
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<td>9. Biodegradable polymer blends</td>
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<td>10. Reactive compatibilized blends</td>
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<td>11. Liquid-crystalline polymer blends</td>
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<td>12. Polyolefin blends</td>
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<td>13. Interpenetrating polymer networks</td>
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<td>14. Polyelectrolyte complexes</td>
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<td>15. Recycled polymer blends</td>
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<td>16. Water soluble polymer blends</td>
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<td>17. Polymer blend composites</td>
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<td>18. Black copolymer-homopolymers blends</td>
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<tr>
<td>19. Core-polymer blends</td>
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<tr>
<td>20. Elastomer blends</td>
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1.3-2 PBT chains grafted onto a PS-GMA chain. From the FTIR analysis and the morphology of the blend investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), they found that the interfacial area density of the in-situ formed PS-g-PBT is ~0.1, chains/\text{nm}^2, for the blends prepared by SOM, regardless of the amounts of PS-GMA added initially in the blend.

Block copolymers may be added as surface-active compatibilizers in order to control the morphology of blends of immiscible polymers. Velankar et al. [19] investigated the effects of such added compatibilizers on the rheological properties of droplet-matrix blends are experimentally. They studied the model blends composed of polyisobutylene (PIB) droplets in a polydimethylsiloxane (PDMS) matrix, compatibilized with a diblock copolymer of PIB and PDMS. The viscosity and the first normal stress difference under steady shear conditions, and complex moduli after cessation of shear are measured. They found that addition of the compatibilizer slightly raises the magnitude of the terminal complex viscosity of blends at all ratios of viscosity. With addition of the compatibilizer, the terminal relaxation time was found to increase sharply at high viscosity ratio, whereas the steady shear was found to increase at low viscosity ratios. Lu and Isacsson [20] studied the rheological properties of styrene-butadiene-styrene copolymer (SBS) modified bitumen. The modified binders were prepared using a laboratory mixer. Two different blending methods to prepare the blends: A melt blending (MB) and a solution blending followed by an oscillatory shearing in the molten state (SOM). The molecular weight of the in-situ PS-g-PBT copolymers formed from the reaction between PS-GMA and PBT in the blend was determined using high temperature gel permeation chromatography (GPC). The concentration of the in-situ formed graft copolymers of PS-g-PBT in the blends [copolymer blend] prepared either by MB or SOM was determined by solvent extraction and followed by Fourier Transform Infrared Spectroscopy (FTIR) analysis. On the basis of the GPC and FTIR results, they concluded that the PS-g-PBT in the blend has between 1.3-2 PBT chains grafted onto a PS-GMA chain. From the FTIR analysis and the morphology of the blend investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), they found that the interfacial area density of the in-situ formed PS-g-PBT is ~0.1, chains/\text{nm}^2, for the blends prepared by SOM, regardless of the amounts of PS-GMA added initially in the blend.

William and Wagner [21] demonstrated a new method that applies the Porod limit of small angle neutron scattering to measure the interface morphology in concentrated, immiscible blends under simple shear. The effect of viscoelasticity contrast on rheology and blend microstructure was probed for a model dispersion of liquid crystalline polymer dispersed in a linear polymer matrix. In comparison to the theories demonstrated by the complex morphological evolution, is a consequence of the unique rheology of liquid crystalline polymers. The results at low shear rates were used to predict the onset of stable micro-fibrillation at higher shear rates through consideration of the contrast in the first normal stress differences. Kuo and Chang [22] prepared polymer blends of poly (vinylphenol) (PVPh) with poly (vinylpyrrolidone) (PVP) by solution casting from the N, N-dimethylformamide (DMF) solution. Differential scanning calorimeter (DSC), Fourier transforms infrared spectroscopy (FTIR) and solid state Nuclear Magnetic Resonance (NMR) were used to investigate the hydrogen bonding and miscibility behaviour of the blend. The PVPh/PVP blend system has a single glass transition temperature over the entire composition range, indicating that this blend is able to form a miscible phase due to the formation of inter-hydrogen bonding between the hydroxyl of PVPh and the carbonyl of PVP. FTIR and solid-state NMR were further employed to study the hydrogen-bonding interaction between the PVPh hydroxyl group and the PVP carbonyl group at various compositions. According to the Painter-Coleman association model (PCAM), the inter-association constant for the PVPh/PVP blend is significantly higher than the self-association constant of PVPh, revealing that the tendency towards hydrogen bonding of the PVPh and PVP dominates the intra-hydrogen bonding of the PVPh in the mixture. Kim et al. [23] examined block copolymers of PC-b-PMMA (polycarbonate-b-polymethylmethacrylate) and PC-b-SAN (polycarbonate-b-(styrene-c-acrylonitrile)), as compatibilizers for blends of PC with SAN copolymer. The average diameter of the dispersed particles was measured with an image analyzer, and the interfacial properties of the blends were analyzed with an imbedded fiber retraction (IFR) technique. The average diameter of dispersed particles and interfacial tension of the PC/SAN blends reached a minimum value when the SAN copolymer contained about 24 wt\% AN. Interfacial tension


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and particle size were further reduced by adding compatibilizer to the PC/SAN blends. In reducing the average diameter of the dispersed particles and interfacial tension of PC/SAN blend, PC-b-PMMA was more effective than PC-b-SAN as a compatibilizer. A direct proportionality between the particle diameter and interfacial tension was also observed. The interfacial properties of the PC/SAN blends were optimized by adding a block copolymer and using an SAN copolymer that had minimum interaction energy with PC.

5. Importance of Rheological Properties in the Development of the Phase Structure

Rheological properties of a two-phase system depend, not only on the rheological behaviour of the components, but also the size and size distribution and the shape of discrete phase droplets dispersed in a continuous matrix phase. Rheological properties of multiphase systems are strongly influenced by the morphology, which depends on the thermodynamic interactions between the constituent polymers and flow history. Therefore, rheological properties are essential in order to relate the morphology of the phase-separated state to the processing of multiphase systems [24]. Most models of the morphological changes of polymer blends assume that an average response (e.g. an average size drop is being broken or average size drop coalescence) provides good representation of the whole system. This assumption should be reasonably correct for blends with narrow distribution of drop size. However, there are reports, for instance, that during the initial stage of blending in the twin screw extruder, the domain sizes may differ by three orders of magnitude. Here, the average size may not be valid. According to Utracki [18], a recent kinetic theory of the structure development in the moderately concentrated polymer blends, was proposed. The break-up coalescence in a steady state shearing was considered, assuming a temporal population balance model. Kroger and Hess [25] studied a certain critical molecular weight that controls rheological properties of the multi-bead finitely extensible nonlinear elastic (FENE) chain model of polymeric melt. The rheological crossover (where $G' = G''$) manifested itself in a change of power law behaviour for the viscous properties at a critical number of beads per chain, $N_c = 100 \pm 10$. Their finding confirmed a newly proposed relationship between dimensionless critical weight, characteristic length and the flexibility which they obtained as a side result. Sivashinsky et al. [26] studied shear stress growth and relaxation behaviour of two well-characterized SBS block copolymers using a melt elasticity tester. Effects of casting solvents on the transient rheological properties and structure variation during flow were determined via samples cast from THF/MEK and cyclohexane. The temperature-dependence of the shear stress observed at the yield point and the steady-state viscosities provide an insight into the mechanism of structure breakdown, induced by the applied flow. Shear stress relaxation, upon cessation of flow, reveals complex behaviour, depending on temperature, casting solvents and duration of previous flow. Strain recovery data have also been obtained, indicating strong dependence on the composition of the copolymers. Dispersed phase morphology development has been mainly studied in capillary flow. To explain the fibrillation processes, not only the viscosities ratio, but also the elasticity effects and the interfacial properties had to be considered. In agreement with the microrheology of Newtonian systems, an upper bound for the viscosity ratio, $\lambda$ has also been reported for polymer blends-above certain value of $\lambda$, which can significantly be larger than the Newtonian value of 3.8, during which time, the dispersed phase could not be deformed. By contrast, lower bounds of $\lambda$ were not established for polymer blends [18].

6. The Importance of Considering the Stress or Strain History of a Material Sample in a Rheological Investigation

In order to measure a material’s rheology, five criteria must be met: geometric boundary conditions, stress, strain, strain rate and mode of deformation. For a good comprehension of the rheological properties of materials, it is essential to either measure the deformation resulting from a given force or measure the force required to produce a given deformation. As a measure of force, one can use the stress which is defined as the ratio of applied force to the cross sectional area on which the force acts. Deformation can be described in term of strain or rate of strain. There are two basic flows used to characterize polymer: shear and shear-free flows. For these two types of flow, the component of the stress and the rate of deformation tensor take on a distinct form. Owing to its sensitive response to changes of microstructures for heterogeneous polymers, rheological measurement has been a preferred approach in the characterization of the formation and evolution of microstructures for multi-component or multi-phase polymeric material systems. According to Qiang et al. [27], some of the recent progresses made in the studies on the correlations between the micro-structural change and rheological response have been introduced as two aspects, viz: relationships between viscoelastic behaviour and microstructure of nano-composites and relationships between rheological behaviour and liquid-solid transition in isothermal crystallization of polyolefins. By means of rheological measurements, not only are some valuable and pertinent information responsible for the evolution of morphology and structure development, dealing with
these polymer systems can be obtained, but also the corresponding results are in favor of designing and preparing novel polymer-based composites and functional materials.

Kohli et al. [28] assessed the effect of deformation history on the morphology and properties of liquid crystalline polymers (LCP) blended with polycarbonate resin. The addition of an immiscible LCP phase was found to improve the melt processability of the host thermoplastic polymer. In addition, by employing a suitable deformation history, the LCP phase may be elongated and oriented such that microfibrillar morphology can be retained in the solid state. This has important ramifications for the development of self-reinforcing polymer blends to compete with conventional inorganic fiber reinforced polymers. Shear flows are generally ineffective in developing these morphologies, but flows that incorporate an extensional region, such as the converging flow found at the entrance to a capillary or die can produce an elongated LCP phase. Bousmina et al. [29] assessed the phase segregation in the poly(styrene-co-acrylonitrile)/poly (methyl methacrylate) (SAN/PMMA) blend with lower critical solution temperature (LCST) by linear viscoelastic rheology, optical microscopy and inverse gas chromatography (IGC) techniques for various blend compositions. At low temperatures, the blends showed a classical behaviour of homogeneous polymer melts, whereas in the vicinity of phase segregation, a shoulder in the storage modulus and in the linear relaxation modulus, $G(t)$ was observed. The width of such a low-frequency/longer-time plateau and the terminal relaxation time were found to increase with temperature. Such behaviour was attributed to variable morphologies appearing at different temperatures. The development of the morphology was found to take place within a given interval of temperature rather than at a single critical temperature. Optical microscopy and IGC analyses supported the peculiar behaviour observed, of such a blend. Time-temperature superposition, origin of elasticity, and the Fredrickson and Larson theory were discussed in light of the results obtained.

7. Developments in the Field of Polymer Blend Rheology

7.1. Past, Present and Future Developments in the Field of Polymer Blend Rheology

The technology of polymer blends has been one of the major areas of research and development in polymer science in the past three decades. The advantages of polymer blends versus developing new polymeric structures have been well documented. The ability to combine exiting polymers into new compositions with commercializable properties offer the advantage of reduced research and development expenses compared with the development of new monomers and polymers to yield similar property profile. Another specific advantage of polymer blends versus new monomers/polymers composition is that the blends can often offer property profile combination not easily obtained with new polymeric structures. In rapidly emerging technological landscape, polymer blend technology can quickly respond to developing needs much faster than the time consuming research and development involved with new monomer/polymer development. The technical response to emerging needs is now primarily directed to polymer blend technology in order to determine if such needs can be met compared to the development of wholly new polymeric compositions [3]. The understanding of polymer blend technology to design the specific compositions to meet application requirements is of primary importance. A number of useful analytical and characterization methods have been developed for polymer blends, allowing for an improved understanding of the nature of their miscibility and phase behaviours.

While miscible polymer blends have attracted considerable interest due to the thermodynamic implications and commercial relevance, phase-separated blends have had a prominent role in polymer blend technology. While mechanical compatibility is assured in miscible blends, phase-separated blends can often achieve property advantages not capable with single phase blends [29]. Mechanical compatibility refers to an average property of the blend constituents in the final blend mechanical properties. Impact modification is a well known property of phase-separated blends but other properties; including rheology, environmental stress, rupture resistance, opacity, flammability, cost reduction, specific film properties, adhesion and performance of coating can be achieved via specific combination of immiscible blends. In order to achieve mechanical compatibility in phase-separated polymer blends, different approaches have been proposed, demonstrated and in many cases commercialized. These methods include: addition of graft or block copolymer, interpenetrating polymer network, reactive extrusion, addition of polymeric interfacial agents and minor addition of acid and base compatibilized units. Reactive extrusion is an area that has attracted considerable interest as a facile means of compatibilizing polymer blends, which offers limited performance as simple blends. This technology initially, emerged with “super tough” polyamides, where maleic anhydride grafted onto an ethylene propylene rubber allowed for graft formation with terminal $\text{NH}_2$ groups of polyamide. The resultant grafted structure stabilized the interface between the ungrafted constituents and allowed for the desire impact modifications.
In engineering polymer blends, a number of advances in the technology and the commercial areas have been realized in the past decades. New commercial polymers have been manufactured by various combination of pre-existing polymers. One of the major areas has been the polyester and polycarbonate (polybutyleneetherephthalate/polycarbonate; polylarylate/polycarbonate; cyclohexane dimentional-based polyesters/polycarbonate and polyethyleneetherephthalate/polycarbonate). The emergence of polymeric material for the future auto panels resulted in a large number of potential candidates, based almost exclusively on engineering polymer blends [30]. The most recent addition to the engineering polymer field is the ethylene carbon monoxide alternating copolymers, initially introduced by Shell. The commercial polymer is highly crystalline and believed to contain small amount of propylene to reduce the crystalline melting point in order to allow a broad window of process ability. There are several areas involving extensive research endeavours, presently been investigated that are relevant to polymer blends of the future: These areas include, but not limited to: molecular composites, liquid crystalline polymer blends, blends that involve electrically conductive polymers, blends containing biodegradable polymers and theoretical studies that involve the prediction of polymer phase behaviour. Another interesting area involves the computation model predictions of polymer miscibility.

Due to the two-phase or multiphase nature and from the macroscopic point of view, the rheological behaviour of incompatible (or heterogeneous in general) polymer blends must be dealt with from phenomenological (i.e. fluid mechanics) consideration. Conversely, the rheological behaviour of miscible polymer blends can be dealt with (or interpreted) using the molecular approach. While there are few miscible polymer blends that have met with commercial success, numerous investigators have reported on the rheological behaviour of miscible polymer blends [31]. Multi-phase polymer blend systems examine the current state-of-the-art, challenges and future prospects in the field of polymer blends. The hand-picked selection of topics and expert contributors, make this survey of phase morphology in polymer blends accessible to both industrial and academic laboratories around the world. It is obvious that research and development on polymer rheology is purely fundamental and serves long-term objectives.

### 7.2. Current Research Status

The developments of melt rheology of polymer blends depend largely on the understanding of the structure-properties relationship of the materials which requires multiscale model to predict the material properties. The current research in the modeling and simulation of polymer blends are largely limited to length and time scale. However it should be noted that some efforts have been made to develop multiscale strategies for the prediction of multiscale level structure, properties and processing performance of polymer blends. Some of these works will be mentioned. Bouhlel et al. [32] recently used Biot’s model to describe the quasi-static deformation of a continuous porous medium, saturated by incompressible Newtonian fluid at a microscopic scale. The microscopic description involves four effective properties, i.e. the effective elasticity tensor, Biot’s effective tensor, the coefficient $\beta$ and the permeability tensor. The numerical results obtained from their work were compared with bounds, self-consistent estimation, exact expansion and experimental result available in the literature on ceramic and metals. Balazs and co-workers [33] recently combined DFT with SCF to calculate phase behaviour of clay-based polymer nanocomposites and other polymer nanoparticles mixtures. In this model, the thermodynamic behaviour and interaction information among various components are obtained from the SCF model which served as input to a DFT to calculate the phase behaviour. Chu et al. [34] proposed a modified model of Chen’s for the calculation of the relative viscosity of BR-SBS blends of different compositions. The agreement between the theoretical prediction and experimental results was satisfactory. Edwards et al. [35] isothermally studied the dynamic and creep behaviour of 80ln15Pb5Ag and 50Sn50Pb over nine decades of time and frequency. 80ln15Pb5Ag was examined at $-6, 21, and 50^\circ C$, while 50Sn50Pb was examined at $21^\circ C$. Viscoelastic behaviour as a function of temperature and time/frequency was observed at strain less than $10^{-5}$. At the small strain level employed in the study, the alloys exhibit linear viscoelasticity rather than the viscoplasticity observed at larger strain. Viscoelasticity was subject to constitutive modeling. The creep followed a superposition of a stretched exponential and power law, in time and an Arrhenius form, in temperature. Behaviour was thermorheologically simple over at least nine decades of true time and frequency.
7.3. Opportunities and Challenges

An overview of technological developments involving rheological properties of polymer, structure and morphology of molten polymer blends clearly indicates that the field expands at unprecedented rates. The guiding principles behind this progress are efficiency, functionality and precision of these materials. However, effective implementation of morphology of molten polymer blend, structure and its effects on rheology directly depends on the degree of understanding of their behaviour and properties. In this regard, challenges arise due to the sensitivity of the polymers to variations in their fabrication, time- and temperature-dependent effects and the non-linearity of their coupled mechanical, physical and chemical properties. A problem of immediate significance stems from the fact that polymer blend materials are often dependent on the morphology and control of the materials. In fact, these materials are considered as primary candidates for distributed control of compliant structures. The inherent properties of polymers combined with their control functions tend to produce new and unexplored effects that should be fully understood. It is also of importance that polymers perform their functions in dynamic environments over a wide range of temperatures and frequencies. Such conditions tend to accelerate their degradation and, consequently, alter their functional response through electromechanical couplings. Besides the experimental investigations required in addressing the outlined problem areas, there is a need to advance the computational rheology of polymers. In this regard, it is important that modeling and simulation are treated as an integral part of design and manufacturing processes.

The prediction of the end-use properties of polymeric products is faced with some daunting challenges. The current process simulation approach, which is based on the continuum mechanics of non-Newtonian fluids, must be combined with models describing macromolecular conformations, relaxation and polycrystalline morphologies. The various types of constitutive models, whether continuum [36] or reptation [37], have had very limited successes in predicting the unusual rheological phenomena exhibited by polymeric liquids, even under isothermal conditions. Determination of heat transfer coefficients and modeling of flow-induced crystallization [38], are necessary for the eventual prediction of properties of films and other extruded products. Numerous other problems remain unresolved in other polymer processes, such as the prediction of shrinkage, warpage and stress cracking in injection molding. The goal of precise property prediction is likely to remain a challenge for a considerable length of time. However, new technologies, even without detailed scientific understanding, are likely to play a significant role in the field of polymers. These include: nanocomposites with exceptional properties, conductive plastics for electronics, self-assembly processes for the creation of special polymeric structures and fabrication of biomaterials and polymer-based tissue engineering. In the immediate future, continuing progress in the field of smart polymers will depend on the intensity of research efforts directed towards the development of polymer rheology systems with enhanced adaptive capabilities. Concurrently, it is critical to develop formulation of advanced theoretical models for the simulations of the rheological behaviour of polymer. On this basis, the unprecedented opportunities offered by generating mathematical models for simulating rheological characteristics of polymers, will continue to stimulate further technological inquisition.

8. Conclusion Remarks

This review provides the collection of knowledge based on what is published in the scientific literature. Developments involving rheological properties of polymer, structure and morphology of molten polymer blends vividly show that the field of polymer technology rapidly expands at higher rates. Different polymer blends may represent a feasible method for exploiting some of these developments. Some modeling techniques used for the prediction of mechanical properties of polymer blends have been reviewed in this paper. Future research is expected to be focused on the generation of advanced mathematical models for simulating rheological properties of polymers, in order to stimulate further technological progress.

REFERENCES


Rheological Properties of Polymers: Structure and Morphology of Melted Polymer Blends


Rheological Properties of Polymers: Structure and Morphology of Molten Polymer Blends


Glossary of Some Rheological Terms [39]

- Rheology—The science of deformation and flow of matter.
- Rheometer—An instrument for measuring rheological properties.
- Flow—A deformation of which at least part is non-recoverable.
- Elasticity—Reversible stress/strain behaviour.
- Modulus—In rheology, this is the ratio of a component of stress to the component of strain. Pa.
- Model—An idealized relationship of rheological behaviour in mathematical, electrical or mechanical terms.
- Relaxation time—The time taken for the strain in a material that obeys the Kelvin model to reduce to 1/e (0.368) of its original equilibrium value after the removal of stress. Generally, it is the time required for an exponential variable to decrease to 1/e of its original value.
- Yield stress—The stress corresponding to the transition from elastic plastic deformation. \( \sigma_y \), Pa.
- Stress—A force per unit area, Pa

Abbreviations

- PPE Polyphenylene Ether
- PS Polystyrene
- PE Polyethylene
- PP Polypropylene
- PA6 Polyamide 6
- SMA2 Styrene-maleic anhydride
- PVP Poly (vinylpyrrolidone)
- PVPh Poly (vinylphenol)
- DSC Differential scanning calorimeter
- FTIR Fourier transforms infrared spectroscopy
- NMR Nuclear magnetic resonance
- PS GMA-poly (styrene-\text{-}ran\text{-}glycidy methacrylate)
- MB Melt blending
- SOM Solution blending followed by an oscillatory shearing at a molten state
- GPC Gel permeation chromatography
- SEM Scanning electron microscopy
- TEM Transmission electron microscopy
- PIB Polys(isobutylene)
- SBS Styrene-butadiene-styrene
- PDMS Polymethylsiloxane
- DBM Dimethylformamide
- PCAM Painter-coleman association model
- PMMA Poly methyl methacrylate
- SAN24 Styrene-co-\text{-}acrylonitrile
- EVA Ethylene-vinyl acetate
- FENE Finitely extensible nonlinear elastic
- LCP Liquid crystalline polymer
- LCST Lower critical solution temperature
- IGC Inverse gas chromatography
- SC Self consistence function
- DFT Density function theory
- MC Monte Carlo
- MD Molecular Dynamic
- \( G' \) Storage modulus
- \( G'' \) Loss modulus

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