



# Linear viscoelasticity of polymer blends with co-continuous morphology

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## ABSTRACT

The co-continuous morphology of polymer blends has received much attention not only because of its potential promotion of mechanical or electrical properties of polymer blends, but also due to its importance in phase separation by spinodal decomposition. Compared to the recent advances in the characterization of co-continuous structure, the rheology of co-continuous blends has not been understood clearly. In this work, a rheological model is suggested to correlate the linear viscoelasticity and the structural information of co-continuous blends. The dynamic modulus of co-continuous blends is composed of the contribution from components and the interface. The interfacial contribution, which is most important in the rheology of blends, is calculated from a simplified co-continuous structure. This model has been compared satisfactorily with available experimental results, which proves a reasonable connection between the co-continuous structure and linear viscoelasticity of blends.

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## 1. Introduction

Blending polymers with different molecular structures or different mechanical properties has become a useful route in developing new, high-performance polymeric materials nowadays. Improved mechanical properties, processability, barrier behavior and electrical properties can be achieved through such technology. Choosing suitable polymers is of course the primary task in preparation of polymer blends, however, more attention has been paid to control the morphology of blends, which has been found to have a great impact on the properties of polymer blends. Actually, most polymers used in blends are immiscible or partially miscible due to their high molecular weight and unfavorable interactions, which result in the multiphase morphology. For binary polymer blends, when the content of one component is much lower than the other component, the minor component usually forms droplet in the matrix of major component, which is usually known as the sea-island morphology. The formation of droplet morphology [1], its dependence on the mixing condition and rheological properties [2], and the relationship between the droplet morphology and rheology [2–6] have been investigated thoroughly in recent years. When the content of minor component increases, it is possible that two components both forms a continuous network, which is known as the co-continuous morphology. It is well known that one of the purposes of blending is taking advantages of the component properties, and it has been found that co-continuous morphology

sometime can supply a better combination of the component properties than the droplet morphology [7]. Besides mechanical properties, co-continuous morphology offers an opportunity to greatly decrease the conductive percolation concentration in carbon black filled composites [8]. Moreover, co-continuous morphology is often observed during phase separation of partially miscible polymer blends via spinodal decomposition [9]. Therefore, understanding the dynamics of morphology evolution and the relationship between the morphology and properties is not only a requirement to control the morphology in the development of new materials, but also the necessity to know the mechanism of polymer mixing and phase separation.

The investigations on co-continuous blends have been focused on the morphology determination [10–14], formation [15,16] and stability [17–21], mechanical properties [22–24] and rheological properties [25–31]. However, for a long time, the difficulty in the study of the co-continuous blend is the description of the morphology. The most frequently used method is the statistics on the interface due to its apparent irregularity. Theoretically, the area of interface per unit volume is used in modeling the evolution of interfacial shape [32,33], while interface per unit area of image (photos usually taken by scanning/transmission electron microscopy, SEM/TEM) is often used in experiments [11] since only two-dimensional cross section of blends can be observed in most experiments. Such description is based on the coarse grained statistics of the interface, and is useful in determination of the cocontinuity interval by image analysis [11] and modeling the dynamics of morphology evolution [32,33]. Although this description can be instructive in morphology, the detailed shape of interface can not be re-constructed due to lack of the local information of

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interface, such as the local curvatures. Until recently, some improvements have been made in describing the interface in three-dimensional spaces. Technologies used to determine the morphology include the semiautomatic serial sectioning and reconstructing [34], Transmission electron microtomography (TEM) [35], X-ray microtomography [13], X-ray phase tomography [36], three-dimensional nuclear magnetic resonance (NMR) imaging [37] and laser scanning confocal microscopy (LSCM) [14,38–40]. It is then possible to obtain the area average of the mean and Gauss curvatures of local interfaces, although incorporation such structural information in constitutive model is still a challenging work. On the other hand, the quantitative relation between the co-continuous morphology and the rheological properties is still missing. The rheological properties, especially the linear viscoelasticity, of co-continuous blend have been found to be very instructive in the determination of the phase morphology. For example, the storage modulus and complex viscosity at low frequencies will generally increase with the volume fraction of minor component, reach a maximum at certain concentration, and then decrease with the volume fraction which denotes a transition from droplet morphology to co-continuous morphology [29,30]. However, it is still difficult to predict the linear viscoelasticity of co-continuous blends. The models based on the area tensor [33] or interfacial tensor [32] are not satisfying due to lack of intrinsic length scale. Even the revisions [41,42] of these models are technically not suitable since the length scale introduced is based on droplet morphology. Moreover, lack of quantitative description on the linear viscoelasticity of co-continuous morphology also hinders our understanding on the mechanism of spinodal decomposition in phase separation. Rheology has been frequently used to determine the binodal and spinodal temperature in phase separation [9,43–45]. However, the transition point is empirically assigned to the phase separation temperature due to the lack of the interplay between the concentration fluctuation and the interface. Usually, Palierne model [46] is used to account for the interfacial contribution to rheology, but it is only applicable to droplet morphology generated during nucleation and growth in off-critical compositions and apparently not suitable for co-continuous morphology created during spinodal decomposition in near-critical blends.

In this paper, the linear viscoelasticity of polymer blends with co-continuous morphology will be modeled. The purpose is to establish a quantitative connection between the structural information of co-continuous morphology and the corresponding linear viscoelasticity.

## 2. Theoretical model

The dynamic modulus under small amplitude oscillatory shear flow will be considered here. It is assumed the co-continuous morphology will not change under sinusoidal shear strain with sufficient small strain amplitude. Although some experiments have shown the possibility of coarsening [13] during annealing, the change of morphology will be ignored in the present work. This has been verified by almost collapsed dynamic modulus in repeated frequency sweep on the same sample. The complex modulus of co-continuous blends can be assumed to be a sum of components contribution and interface contribution, i.e.,

$$G_{\text{blend}}^* = G_{\text{components}}^* + G_{\text{interface}}^* \quad (1)$$

This is similar to the model of blends with droplet morphology [47], where the additivity comes from the separate contributions from the polymer components and the interface to the total free energy of the blends.

In modeling the rheological properties, the definition of co-continuous morphology in polymer blends is of critical importance. Generally, two main views have been reported in literature [16]. The classical one defines an ideal co-continuous morphology where at least two continuous structures exist in the same volume. The other one is based on the percolation threshold theory, and defines a co-continuous morphology as one in which at least a part of each phase forms a continuous structure that permeates the whole volume, which allows the existence of discrete domains that are not part of the network structure. When the concentration of one component increases, the morphology will gradually change from the droplet structure into a co-continuous structure of the second definition, i.e., a mixture of discrete droplet structure and a continuous network structure. An ideal co-continuous structure can be obtained when the concentration of minor component is sufficient high. These two definitions can be differentiated by the portion of a fully co-continuous structure, i.e., the continuity index [48]. The ideal continuous structure corresponds to the continuity index of 1, while the second definition of co-continuous structure generally covers a wider range of concentrations. Although the classical definition is a special case of the second definition, only the ideal co-continuous structure will be modeled here.

### 2.1. Components contribution

The most frequently used model for linear viscoelasticity of polymer blends is the Palierne model [46], from which the contribution of components can also be obtained under zero interfacial tension condition,

$$G_{\text{components}}^* = G_2^* \frac{1 + 3\phi_1 H}{1 - 2\phi_1 H} \quad (2)$$

where  $H = (G_1^* - G_2^*) / (2G_1^* + 3G_2^*)$ .  $G_1^*$  and  $G_2^*$  are the complex modulus of fluid I and II, respectively.  $\phi_1$  is the volume fraction of fluid I. Palierne model has been used to predict the dynamic modulus of blends with droplet morphology. It is clear that exchanging two fluids in Eq. (3) will certainly cause a different complex modulus of blends. This suggests that Palierne model might be unsuitable for co-continuous blends.

The other model for the contribution from components in oscillatory shear has been suggested by Veenstra et al. [23] more recently. The original model was put forward to predict the mechanical properties of polymer blends with co-continuous morphology. A parallel model with series-linked parts and a series model with parallel-linked parts were derived for co-continuous blends. The parallel model was then extended to predict the complex modulus of co-continuous blends [28], where the Young's modulus in the original model was replaced by the dynamic complex modulus of components. It is assumed that the co-continuous morphology can be schematically shown in Fig. 1 a. The only important parameter is the volume fraction, and the length of the cell is normalized to 1. Therefore, no characteristic length is considered here. The complex modulus from the components of co-continuous blends can be expressed as [23,28]

$$G_{\text{components}}^* = \frac{a^2 b' G_1^{*2} + (a^3 + 2a'b' + b'^3) G_1^* G_2^* + a'b'^2 G_2^{*2}}{b'G_1^* + a'G_2^*} \quad (3)$$

where  $\phi_1 = 3a^2 - 2a^3$  is the volume fraction of fluid I and  $b' = 1 - a'$ . It is noticed that Eq. (3) is symmetric for fluid I and II, which suggests that exchanging fluid I and fluid II will not change the complex modulus of blends. It should be stressed that the original Veenstra et al. model is sufficient for mechanical properties

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