Dynamic Rheological and Mechanical Behaviours of Poly(dimethylsiloxane)/Low Density Polyethylene Immiscible Blends: Interfacial Modification via Reactive Blending

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A B S T R A C T

Dynamic rheological behaviour and mechanical properties of neat and reactive LDPE/PDMS immiscible blends were investigated, focusing on low frequency data analysis as an approach for microstructural characterization. It was observed that by analyzing low frequency data, some microstructural features such as development of continuity in the minor phase and occurrence of interfacial slip phenomenon of neat blends could be revealed. Development of continuity in the minor phase, as proved by SEM micrographs, resulted in a significant increase in low frequency values of $\eta'$ and $\eta''$ while interfacial slip phenomenon was inferred by comparing the rheological data with predictions of log-additivity and inverse mixing rules. To induce reactive blending, different amounts of DCP as curing agent was added to PDMS phase. By studying the influence of reactive blending on thermal behaviour and viscoelastic properties in low frequency region it is revealed that curing reaction during melt mixing could lead to formation of an interphase layer which acts as an efficient compatibilizer between the phases. Thus, reactively compatibilized blends exhibit desirable tensile properties.

INTRODUCTION

Melt blending of two or more polymers has been long known as an efficient and inexpensive route to develop polymeric materials possessing a combination of desired properties of both components. However, most polymers are thermodynamically immiscible and incompatible due to the low entropy of mixing and lack of specific interactions. This could result in a phase separated system with coarse unstable morphology and poor phase adhesion. Therefore, compatibilization is often required to favour a fine dispersion by lowering the interfacial tension, to stabilize the morphology by reducing...
the coalescence, and to improve interfacial adhesion between the phases. This can be achieved by addition of pre-designed block copolymers to the system [1-6] or by in-situ formation of compatibilizing copolymers via reactive blending [7-13]. From both economic and performance points of view, reactive blending is more attractive than the addition of tailored copolymers.

Considering the fact that in reactive blending, chemical reactions occur during compounding or processing, understanding the actual consequence of such reaction(s) on microstructure of the blend is of great interest. Among different methods for characterization of microstructure, analyzing low frequency dynamic rheological behaviour could be considered as an appropriate tool for extracting microstructural information, particularly about in-situ synthesized interphase [14-20]. Such morphological analysis has been carried out for two groups of most common reactive blends: dynamically vulcanized thermoplastic elastomers (TPVs) and reactively compatibilized blends (RCBs).

For both groups a significant increase in elasticity and complex viscosity at low frequency zone has been reported [14,16,21,22]. However for TPVs the increase in elasticity is more pronounced at low frequencies and the elastic behaviour is dominant in this region, $G' > G''$ while for RCBs $G''$ remains higher than $G'$ at this frequency zone. The low frequency behaviour of TPVs has been often related to the formation of a three dimensional network of cured rubber particles throughout the matrix phase [21-23]. Two possible mechanisms for network formation have been proposed [23,24]: (i) agglomeration of rubber particles through direct contact during dynamic motions and (ii) bridging between neighbouring particles via chains grafted onto their surfaces. Both of these mechanisms are highly sensitive to interparticle distance such that agglomeration is possible only if the interparticle distance is below a critical value. The characteristic feature of RCBs is formation of a relatively thick interphase due to interfacial reaction. In this case, the increased elasticity at low frequencies is attributed to the extra contribution of the in-situ formed interfacial layer [14,19]. The characteristic flow time of the grafted chains in this region is higher than that of both components, therefore the interphase remains elastic while both phases flow. This is evident from the appearance of a new relaxation process with characteristic time higher than that of the terminal relaxation of both components.

In this work dynamic rheological and mechanical behaviours of neat and reactive immiscible blends of low density polyethylene (LDPE) and poly(dimethylsiloxane) (PDMS) have been investigated. Interesting characteristics of PDMS such as maintaining elastomeric behaviour in a wide range of temperatures, good insulating properties, biocompatibility in combination with relatively good electrical and mechanical properties, and low cost of LDPE could result in a blend with unique properties. However, due to structural dissimilarities, LDPE and PDMS are incompatible and for obtaining desired combination of their properties in a blend system, it is necessary to utilize an appropriate strategy to compatibilize these two polymers. To exploit a combination of the interesting properties of these two polymers in a blend system, the feasibility of in-situ compatibilization using peroxide curing system have been also investigated.

**EXPERIMENTAL**

**Materials**

Commercial grades of PDMS (Elastosil R401; Wacker Chemie, Germany) and LDPE (0200; National Petrochemical Company, Iran) have been used without any further treatment. Dicumyl peroxide (DCP 98%; Di-Cup, Hercules Inc.) has also been used as cross-linking agent.

**Blends Preparation**

All blends were prepared by melt-mixing of the components in an internal mixer (Haake Rheomix; HBI SYS90) with rotor speed of 50 rpm and at 150°C or 10 min of mixing time. Neat blends of LDPE/PDMS were prepared in the range of composition from 20/80 to 90/10 wt%. To induce reactive blending, DCP was first mixed with PDMS at 50°C for 5 min inside the same internal mixer. No sign of curing reaction was observed in this step. Next, PDMS containing reactive agent was melt-mixed with LDPE mixing torque reached a constant value. In all cases the blends were compression moulded into sheets immediately after mixing was finished. Specification of prepared blends

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Thermal analysis was performed on LP82 and LPR821 blends using PL-DSC (Polymer Laboratories) differential scanning calorimeter. To minimize the possible influence of inhomogeneity of blends, 5 samples from each blend were tested. Each sample was first kept at 200°C for 15 min and then the temperature was reduced to room temperature with 10°C/min cooling rate. After making thermal history of both samples the same, the main experiment was done from room temperature to 150°C with 10°C/min heating rate.

Rheological Analysis
Frequency sweep experiment in the range of 0.01-100 Hz was carried out on neat components and all the prepared blends at 150°C using PaarPhysica MCR300 rheometer with parallel plate geometry. For neat components and LPR821 blend, the test was also performed at 180°C. Before the measurements, the limit of linear viscoelasticity was determined for each sample and the amplitude of oscillation was selected within this limit.

Morphological Analysis
The morphology of the cryogenically fractured surface of blends, after coating with a thin layer of gold was investigated with a Cambridge S-360 scanning electron microscope (SEM, Cambridge Instruments, MA). For LP8020 and LP5050 fractured surfaces where etched in toluene for 48 h at room temperature.

Mechanical Testing
Dumb-bell shaped specimens having dimensions in accordance with ASTM D638 were cut out from moulded sheets of neat polymers and the prepared blends. Tensile measurements were performed on these dumb-bells using MTS tensile testing machine with crosshead speed of 50 mm/min at 23±1°C. The elastic modulus is determined from initial slope of the stress-strain curve.

RESULTS AND DISCUSSION
Neat Blends
Viscoelastic behaviour of components at T=150°C and T=180°C are presented in Figures 1 and 2.
respectively. As it is evident in these Figures that, PDMS possesses much higher complex viscosity and storage modulus than LDPE and shows rather rubber-like behaviour in the applied testing conditions. A noticeable point in Figure 1 is that with increasing temperature from 150°C to 180°C, a change in the slope of $G'$ vs $\omega$ curve could be observed at lower frequencies. This change of slope probably arises from a molecular relaxation process which is rather slower than terminal relaxation of LDPE (it appears at lower frequencies) and reduces melt elasticity.

Storage modulus and complex viscosity data of neat blends at 150°C are shown in Figures 3 and 4. As the composition changes, the extent of contribution of each phase in blend properties varies, along with morphological variation. Figure 5 shows the effect of blend ratio on the morphology of neat blends. It is clear in the Figure 5 that one of the most remarkable aspects of morphological variation with composition is the development of continuity in the minor phase. At 20 wt% of both components, a rather complete dispersion of the minor phase could be observed. With increasing minor phase concentration, the fraction of elongated domains of this phase increases noticeably which leads to evolution of partially continuous (Figure 5b) and then fully co-continuous phase structure (Figure 5d) as a consequence of inter-particle interactions.

Variations of $\eta'$ and $\eta''$ parameters at $\omega = 0.01$ Hz have been plotted as a function of composition in Figure 6. Data at $\omega = 0.01$ Hz were selected to minimize the effect of dynamic flow on the morphology.
of samples. Analyzing these data could reveal some microstructural features of blends. As it is evident in both curves, up to 20 wt% of PDMS (17 vol%), there is slight change in blend properties comparing to neat LDPE. But with further increase of PDMS concentration from 20 to 30 wt% a significant increase in both

**Figure 5.** SEM micrographs of neat blends: (a) LP2080; (b) LP3070; (c) LP5050; (d) LP8020 (magnification ×2000).

**Figure 6.** Variation of $\eta'$ and $\eta''$ parameters at $\omega = 0.01$ Hz and $T=150^\circ$C as functions of composition.

**Figure 7.** Variation of elastic modulus as a function of composition in neat blends.
Figure 8. Comparison of composition dependence of dynamic viscosity data measured at $\omega = 0.01$ Hz and $T=150^\circ$C with predictions of log-additivity rule.

$\eta'$ and $\eta''$ can be observed. A similar trend exists in the variations of mechanical properties with composition. Increasing LDPE concentration from 20 to 30 wt% makes noticeable improvement in tensile properties (Figure 7). According to SEM images, this behaviour could be attributed to development of partial continuity in the minor phase.

The comparison of dynamic viscosity data at different compositions with predictions of log-additivity and inverse mixing rules are shown in Figures 8 and 9, respectively. At low concentrations of PDMS, experimental values show negative deviation from log-additivity rule. The negative deviating behaviour, which is contrary to the prediction of the classical theory of emulsion rheology is usually attributed to the occurrence of the interfacial slip phenomenon [24-27]. Interfacial slip originates from weak interactions between components at interface. Such weak interfacial interactions can result in a thin interphase with low density of entanglements and therefore lower viscosity than the bulk viscosity of both phases. It is believed that if the interfacial slip phenomenon persists in a blend system, the inverse mixing rule can be used to predict viscosity of the system [24,26,27]. This is exactly the case for LP8020 blend as is evident in Figure 9.

Reactive Blends

In the studied blend systems, both components are capable of undergoing chemical reaction with free radicals from decomposition of DCP to give cross-linked networks. However it should be noted that in the applied processing condition there is a remarkable difference in the rate of curing reaction between components. Considering the direct addition of DCP to PDMS, the elastomeric phase could easily undergo cross-linking reaction. However as the reaction proceeds in one phase during melt mixing, it might be transferred to the other phase via the interface through the possible presence of free radicals in this region. These could be free radicals from decomposition of DCP or free radical sites located on PDMS chains. To investigate the possible influence of curing agent on
LDPE phase, the melting peak of this component is compared in DSC thermograms of reactive and neat blends (Figure 10). It is clear that, although the crosslinking agent was directly added to PDMS, the reaction could also affect the LDPE phase thus, the melting peak in the reactive blend differs from that in the neat blend.

Reaction transfer via the interface may alter the state of this region. To investigate this, the low frequency dynamic rheological behaviour of reactive blends was analyzed. Low frequency zone was selected to minimize the effect of dynamic flow on initial morphological aspects and more importantly because the contribution of interface in viscoelastic behaviour is perceivable in this zone. Dynamic rheological behaviour of 80/20 (LDPE/PDMS) blends with different amounts of added DCP at T=150°C is shown in Figures 11 and 12. With increasing the amount of added DCP, the relative increase in melt elasticity is more pronounced at lower frequencies. Nevertheless there is no tendency in $G'$ vs $\omega$ curves towards a low frequency plateau region even for the highest concentration of DCP. A noticeable influence of reactive blending on dynamic rheological behaviour is that for blends containing 0.75 and 1 wt% of DCP, the low frequency plateau of complex viscosity has been replaced with a region of increasing slope (Figure 13). Comparing to uncured blend, at frequencies lower than approximately 0.02 Hz, the plateau region is replaced by region of viscosity upturn with an increasing slope for LPR821 sample. None of the neat blends show such behaviour, but as mentioned before, increased viscosity at low frequencies has been reported for thermoplastic vulcanizates (TPVs) and reactivity compatibilized blends (RCBs) by several authors.

In our reactive blend systems, because the reaction is transferred via the interface, there is a great probability for the occurrence of the chemical reaction between LDPE and PDMS chains which are located at the interface. In this way, an interphase layer consisting of in-situ formed graft copolymers and crosslinked LDPE chains could be formed around the elastomeric dispersed particles. Graft copolymer formation during reactive blending has been reported in the
Considering that the presence of this shell-like interphase layer around PDMS particles would reduce the interparticle distance and also regarding the fact that the reactive blending procedure in this work is somewhat similar to the preparation procedure of TPVs. At first sight, agglomeration of dispersed phase particles to give three dimensional network throughout the melt seems to be probable in reactive LDPE/PDMS blends by the mechanism of the interparticle bridging through the interactions between chains grafted to their surfaces. However there are significant differences in rheological behaviours of reactive blends studied here with TPVs in which cured elastomeric particles agglomerate into a network. In these blends, contrary to TPVs, no plateau region in $G'$ vs $\omega$ curves could be distinguished in low frequencies. Also, in this range of frequencies, loss modulus is higher than the storage modulus for reactive LDPE/PDMS blends, indicating that the viscous behaviour is dominant. Both the above mentioned facts may imply that even if interparticle bridging is possible, it is only limited to a small number of particles and cannot result in the formation of the elastomeric particles network throughout the melt.

Viscous ($\eta'$) and elastic ($\eta''$) components of complex viscosity for LPR821 blend at $T=150^\circ C$ and $T=180^\circ C$ are presented in Figure 14. At $T=150^\circ C$ both parameters follow an increasing trend by lowering the frequency. However, by increasing temperature to $180^\circ C$, it becomes evident that the complex viscosity upturn which is more pronounced at this temperature mainly originate from the contribution of the viscous component rather than the elastic component.

The observed low frequency behaviour could be justified considering the influence of reactive blending on the state of the interface. As described before, during the reactive blending process, an interphase layer which is chemically associated with PDMS particles could be formed as a result of an interfacial reaction. On the other hand, the nature of this layer is such that it could have strong physical interactions with the matrix (LDPE) phase. This would profoundly increase compatibility and interfacial adhesion but suppresses the interfacial slip phenomenon. Therefore the improved interaction between the matrix phase and the cured dispersed particles, with much more limited deformability is the underlying reason for dynamic viscosity upturn at low frequencies.

At this point it should be noted that in the studied reactive blends, although the interfacial reaction improves the compatibility between phases, unlike the common behaviour of RCBs, there is not any noticeable change in the slope of $G'$ vs $\omega$ curves in low frequency zone (Figure 15). This behaviour of RCBs is usually attributed to the extra contribution of modified interface to melt elasticity and corresponds to a new relaxation process which appears as a new peak in low frequency zone of relaxation time spectrum [14-19]. The characteristic time of this relaxation is longer than terminal relaxation of both components [28] therefore, this process would occur only if the dispersed phase undergoes terminal relaxation.
However in LDPE/PDMS reactive blends, both the dispersed phase and the interphase layer are cross-linked and do not undergo terminal relaxation.

**Tensile Properties**

The addition of curing agent to one or both components could have strong effects on factors determining tensile behaviour of the blend, such as morphology, mechanical properties of components, and the nature of interface. Tensile properties of reactive blends in comparison with those of the neat blends are exhibited in Figure 16. As it is expected the most dominant influence of the curing agent is the alteration of mechanical properties of components which is more noticeable for PDMS because of its very low properties in uncured state. It has been reported that introducing a small amount of DCP (lower than 1 wt%) increases the stress- and strain-at-break values and decreases the elastic modulus of LDPE [29]. Furthermore, as mentioned earlier, formation of graft copolymers at the interface can improve interfacial adhesion and stress transfer across the interface in blends containing DCP. Therefore, the observed increase in tensile properties of cured blends is aroused from two contributions: modified mechanical properties of the components and improved interfacial adhesion.

**CONCLUSION**

Dynamic rheological behaviour of the neat and reactive LDPE/PDMS immiscible blends was investigated, focusing on low frequency data analysis as an approach for microstructural characterization. For neat blends, it was observed that development of continuity in the PDMS phase, which has much higher viscosity and elasticity than the LDPE phase, is clearly reflected in the trend of variation of the low frequency rheological parameters with composition. This also results in the positive deviation of the experimental data from prediction of the log-additivity rule at higher concentrations of PDMS. At lower concentration of this component, negative deviation from log-additivity rule was observed which was attributed to the interfacial slip phenomenon.

For the case of reactive blends, low frequency dynamic rheological data and results of thermal analysis was used to investigate the influence of the reactive blending on the state of the interface. The obtained results indicate that in the applied processing condition, an interfacial reaction may occur that leads to the formation of an interphase layer associated chemically with rubber particles. The nature of the interphase is such that it could effectively increase compatibility and interfacial adhesion which is evident in the low frequency dynamic rheological behaviour of the reactive LDPE/PDMS immiscible blends. The improved mechanical properties of the reactive blends may be attributed to the combined effects of the curing agent on the component properties and the interfacial adhesion.

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