

Reactive Melt Modification of Polypropylene/ Unsaturated Polyester Blends

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Abstract

The general objectives of this work are the formation of polypropylene (PP) based compositions with modified structural and rheological characteristics by reactive processing. Such compounds are considered as suitable compatibilizers of PP/thermoplastic polyester blends and as materials for low density extrusion foaming. In the experiments reported in this presentation, PP was melt blended with a low molecular weight unsaturated polyester (UP) in a batch mixer and a twin-screw extruder with or without organic peroxide as free radical initiator. Competing degradation and crosslinking reactions of the peroxide with the blend components were studied and controlled during the blending process. Rheological studies show that the reacted PP/UP blends have a more pronounced suspension behavior due to the presence of the dispersed polyester gel particles. It is evident from SEM microphotographs that the reacted blends have a more uniform and finer morphology than the unreacted ones. The blends are also characterized by other tests in order to examine the possibility of the formation of "block" or "graft" PP-UP structures which would enhance phase interaction and promote compatibility. Work is under way to optimize reaction conditions and characterize in detail reacted products in terms of viscoelastic properties including melt strength and their ability to act as interfacial agents.

Introduction

Polypropylene blends have been the subject of considerable research and development efforts prompted by a combination of desirable properties and potentially low materials cost [1]. However, the absence of polar functional groups and lack of reactive sites on the PP backbone are major issues in blends with polar polymers such as polyamides and polyesters, since blend immiscibility is accompanied by considerable technological incompatibility [2]. Chemical modification of the blend by incorporating a reactive or non-reactive compatibilizing agent offers an effective means to obtain compositions with unique properties that are generally not attainable by simple mechanical melt blending. In this short article, we report preliminary results on melt blending PP with a non-conventional low molecular weight polyester containing unsaturation (UP) at a 5:3 PP/UP weight ratio in the presence of organic peroxides by reactive processing. The objectives are to obtain PP based compositions with modified structure and rheological characteristics that could be used as compatibilizers of PP/ thermoplastic polyester blends and as rheology modifiers in extrusion foaming. More data on a variety of compositions involving different PP resins processed at different component ratios and different peroxide concentrations will be included in the oral presentation.

Experimental

The materials used as blend components include polypropylene (Achieve 3825), unsaturated polyester (COR 75-187-686, Interplastic) and peroxide (Luperco 101XL). The unsaturated polyester was pre-dried under vacuum for about 20hrs at room temperature. The PP-UP blends were melt compounded in a batch mixer (Brabender Model PL2000) at 160°C for various time periods and in a 30mm, co-rotating intermeshing twin-screw extruder, TSE (modified ZSK-30, Coperion) by using a 170-190-210°C temperature profile. Dynamic properties of the processed samples were determined in a Rheometrics Mechanical Spectrometer (RMS-800) with 25-mm diameter parallel plates at 180°C. The morphology of the samples was observed by SEM at 1keV of working voltage. The samples were microtomed at -120°C, and the surfaces were chemically etched in THF to reveal subsurface detail. Relative reactivities of the blend components towards peroxide and extent and type of reactions in

blends of different compositions were determined by a variety of rheological, FTIR and wet chemistry techniques and will be presented in the oral presentation.

Results and Discussions

The PP and UP respond in opposite ways to peroxide: PP degrades due to β -chain scission while UP crosslinks due to macroradical recombination [3-6]. Figs. 1a and 1b show these different tendencies as a function of time, measured as steady shear viscosity in RMS-800 and torque in the batch mixer, respectively. Peroxide was either premixed in the RMS experiments or added in the melt in the batch mixer. The competing degradation and crosslinking reactions of the peroxide with the PP and UP components are expected to also occur during formation of the blend by melt mixing, hence affecting miscibility, morphology and, consequently, properties.

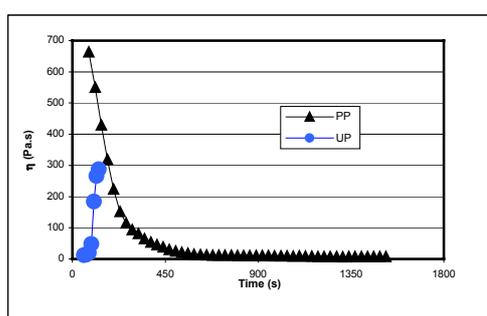


Fig. 1a. Changes in torque of PP and UP with peroxide (1phr) in RMS-800, respectively.

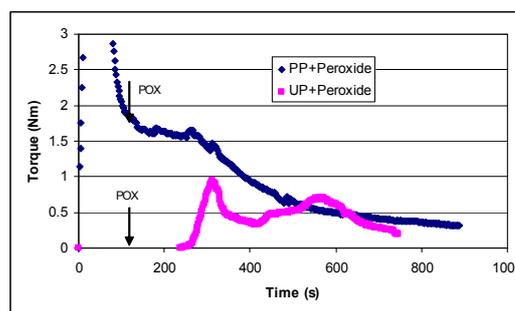


Fig. 1b. Changes in torque of PP and UP with peroxide (1phr) in the batch mixer, respectively.

The storage modulus (G') and the complex viscosity (η^*) vs. frequency of 5:3 PP-UP blends produced in the batch mixer and the TSE with or without peroxide (referred to as “reacted” or “unreacted” PP-UP blends) were determined at 180°C and are shown in Figs. 2 and 3. Overall differences in the properties of unreacted materials produced by the two different processing methods may be attributed to differences in process conditions including mixing efficiency and residence times (15 minutes in batch mixer vs. about 3 minutes in the TSE). In general, reacted blends have overall lower η^* and G' values than their unreacted counterparts reflecting the higher concentration of the degradable PP matrix. Viscosity curves of the TSE blends suggest a more pronounced suspension behavior, which is apparently related to morphological changes and the presence of more dispersed polyester gel particles. Differences in feeding protocols and better mixing offered by the TSE may also contribute to the observed differences.

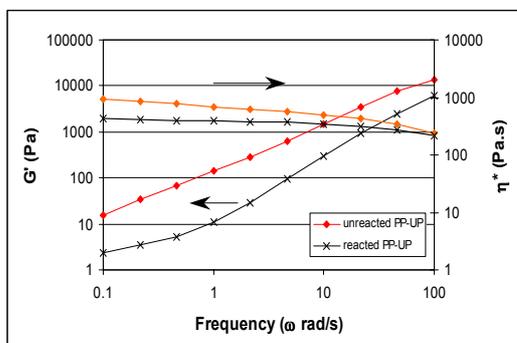


Fig. 2. Storage modulus (G') and complex viscosity (η^*) vs. frequency (ω) of 5:3 PP-UP blends, (batch mixer)

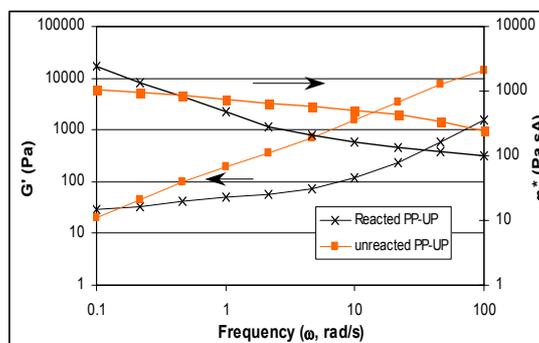


Fig. 3. Storage modulus (G') and complex viscosity (η^*) vs. frequency (ω) of 5:3 PP-UP blends (TSE).

The morphologies of selected reacted and unreacted 5:3 PP-UP blends, prepared in the batch mixer and the twin-screw extruder are compared in Figs. 4-7. It is evident that the reacted blends have a more uniform and finer morphology than the unreacted ones. The domain size in the reacted blend is about 2 μm while a domain size of about 20 μm is shown for the unreacted blend. This may be the result of reduction of viscosity mismatch between the blend components as a result of the competing reactions, leading to conditions favoring dispersive mixing. There are also possibilities of coupling PP and UP macroradicals to form a graft copolymer, which promotes the compatibility of the two phases. It is of interest to note that extraction of the UP phase in the TSE blends is considerably more difficult, presumably the result of higher degree of UP crosslinking and/or stronger attachment onto the PP matrix.

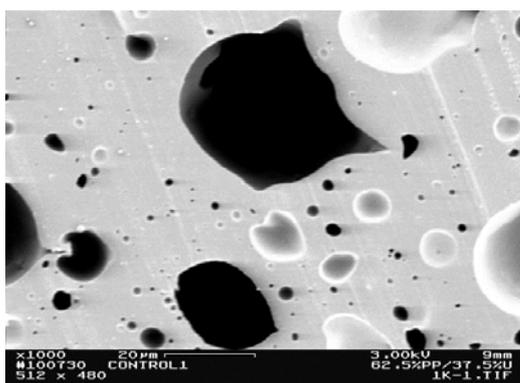


Fig. 4. SEM of the unreacted PP-UP Blend (batch mixer, 15 mins Res.T.)

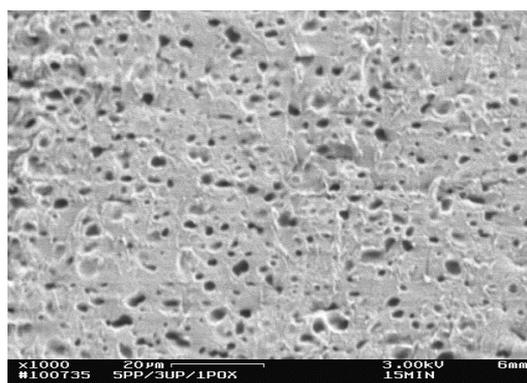


Fig. 5. SEM of the reacted PP-UP Blend (batch mixer, 15 mins Res.T.)

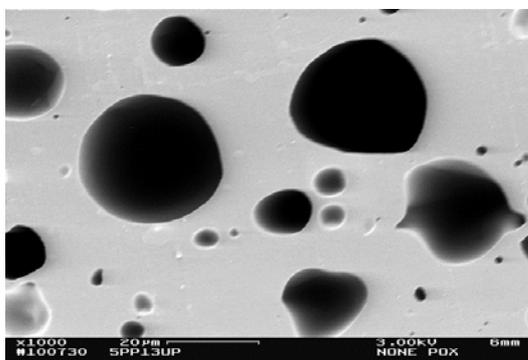


Fig. 6. SEM of the unreacted PP-UP Blend (TSE, 3 mins Res.Time)

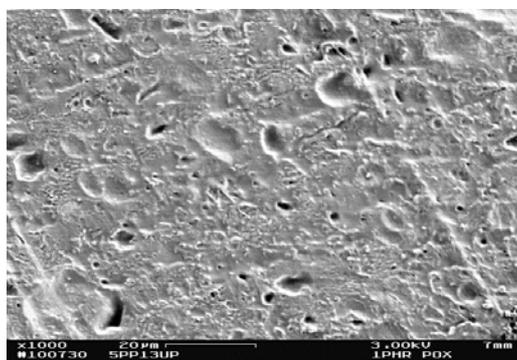


Fig. 7. SEM of the reacted PP-UP Blend (TSE, 3 mins Res.Time)

Conclusions

Polypropylene and unsaturated polyester react in opposite ways with peroxide. Their vastly different rheological properties may be adjusted by peroxide initiated reaction during reactive melt blending to produce a finer and more uniform morphology in the reacted PP-UP blends and different properties. This may be due not only to the change of viscosity ratio of PP and UP but also the possibility of the formation of “block” and/or “graft” PP-UP compatibilizing copolymers. Research is under way to investigate the effect of processing conditions and peroxide concentration on rheology, morphology and other properties and evaluate the blends as coupling agents and rheology modifiers.

References

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