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MISCIBLE POLYMER BLENDS BASED ON POLYCARBONATE AND A COPOLYESTE--ETC(U)
SEP 81 D R PAUL, J W PARLOW DAAG24-78-G-0207
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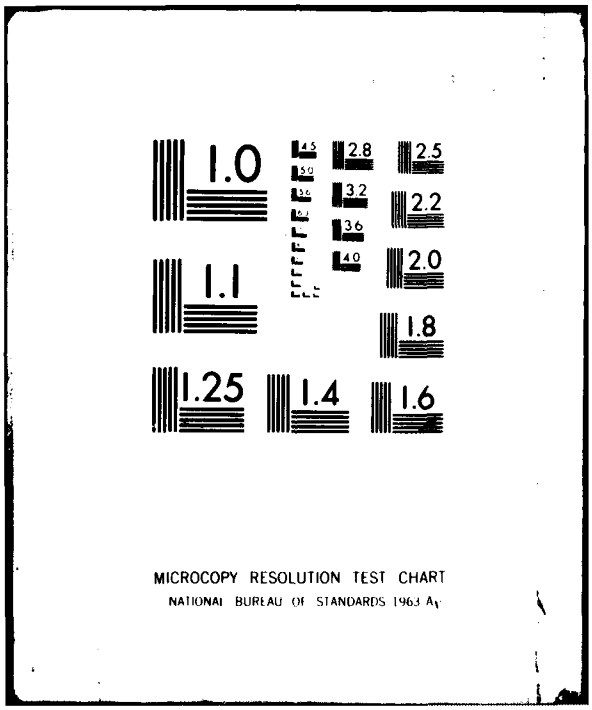

MICROCOPY RESOLUTION TEST CHART
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

POLYMER BLENDS, MISCIBLE, POLYCARBONATE, COPOLYESTER, MECHANICAL PROPERTIES, SORPTION, DIFFUSION, TRANSESTERIFICATION, CRYSTALLINE, AMORPHOUS, HUMID AGING.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A thorough study was made of the thermodynamic, melt processing, mechanical property, environmental stability, and gaseous sorption and transport behaviour of a model miscible blend system comprised of Polycarbonate, PC, and a copolyester made from 1,4-cyclohexane dimethanol and a mixture of isophthalic and terephthalic acids. Generally the mechanical properties of this blend relative to those often observed for immiscible mixtures, are —

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ABSTRACT - Block 20

quite good and data have been developed which suggest that the interactions between polymer blend components responsible for miscibility are also responsible for deviations in blend moduli, strength, density, ductility, Henry's Law portion of gas sorption, and in gas permeation rates, relative to those expected for purely additive behavior.

This miscible blend system was found to exhibit some interesting chemical phenomena. When annealed just below its melting point, Tm, the copolyester was found to undergo crystallization induced chemical rearrangements, CICR, which resulted in abnormally high levels of crystallinity and crystalline melting points. During melt processing, the blend components were found to undergo transesterification reactions, enhanced by the presence of residual titanium catalyst in the copolyester, which lead to a loss of polyester crystallinity and the development of orange coloration due to the formation of titanium phenate complexes. Arsenic oxides and phosphorous compounds were found to eliminate these reactions, thus permitting melt processing without adverse consequences. Interestingly, complexation of the titanium also greatly reduced the CICR observed during sub Tm annealing suggesting that the residual titanium catalyst is also responsible for this phenomenon.

As normally processed, the blend is amorphous. In this state it possesses a better balance of properties than when the copolyester is deliberately crystallized by annealing. Crystallization of the pure copolyester limits its use temperature to below 87^{o}C, its glass transition temperature, Tg. In blends with PC, the Tg of the mixture and therefore the use temperature is raised with increasing PC content. Humid aging studies in 100^{o}C water showed that a 50/50 blend will not embrittle by copolyester crystallization nor by hydrolysis of the PC fraction.

Miscible Polymer Blends Based on
Polycarbonate and a Copolyester

Final Report

D.R. Paul and J.W. Barlow

September 30, 1981

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I. Statement of the Problem Studied

Miscible polymer blends, based on physical combination of two or more polymers whose chemical structures lead to complementary physical interactions, are being discoverd at a rapid rate contrary to earlier expectations. These systems offer a potentially low cost alternative to the chemical or copolymerization methods of forming new materials with improved or useful performance characteristics. In view of these facts, it is very timely to explore the physical and chemical behavior of miscible blends in order to better assess the potential applicability of this approach to new polymeric products and to understand the fundamental issues affecting property responses. Specifically, this research effort has examined selected properties of a model, miscible blend system formed from polycarbonate and a copolyester made from 1,4-cyclohexane dimethanol and a mixture of terephthalic and isophthalic acids. The work has included a thorough study of melt processing techniques and their effect on blend chemistry and physics; blend characterization by thermal analysis, volumetric behavior, and x-ray diffraction; mechanical properties and the influence of prior processing and thermal history; and the sorption and transport of gases in these blends.

The intent of this research has been to learn how various properties vary with blend composition and to interpret these responses in terms of fundamental issues affecting them. Of particular interest is whether the observed responses for blends are simply additive contributions from each component polymer or whether deviations occur that might be advantageous or a problem. While the results obtained are for a single blend system, this study represents an initiation of a systematic program that should lead to general conclusions.

II. Summary of Important Results

The details of the research findings will ultimately be published in a series of papers to appear in various polymer science and engineering journals; however, it will be useful to summarize here some of the most important results according to area of investigation.

A. Chemistry During Melt Processing

In addition to the normal processes of thermal, oxidative, and hydrolytic degradation processes experienced by most polymers during processing, blends of polycarbonate and polyesters may react with each other through interchange reactions of functional linkages or through end groups. In the present case, both possibilities were enhanced by the presence of residual titanium catalyst in the copolyester formed from 1,4-cyclohexane dimenthanol and terphthalic (80%) and isophthalic (20%) acids, but they could be suppressed or eliminated by deactivating the residual catalyst using appropriate additives including arsenic oxides and phosphorous compounds. Free phenolic groups in the polycarbonate interact with the titanium catalyst to produce an orange color in the blends, but this could be eliminated by first deactivating the catalyst. Interchange reactions between ester and carbonate linkages were followed by NMR, solubility, and crystallization techniques, but their effects could be eliminated for up to 20 minutes at melt processing temperatures (~ 275-300^{o}C) allowing blends not affected by such reactions to be mixed and fabricated. Some evidence for synergistic thermal and oxidative degradation processes of the components when blended was noted but the consequences were found to be rather minimal.

B. Thermodynamic Analysis of Blends

Volumetric measurements showed there is a decrease in volume on mixing polycarbonate and the copolyester when both components are above their glass transitions and also below the Tg when the glassy mixtures were annealed according to the same protocol. Thermal expansion coefficients above and below Tg were found to be additive functions of the composition of the component polymers. On the other hand, heat capacities for blends were found to be above the additive line for temperatures below Tg and in the melt state. It is important to note that positive excess heat capacities of this magnitude cannot be rationalized by a modern equation of state theory of mixtures such as that developed by Sanchez. Excess heat capacity determination may offer a critical experimental input to generate better thermodynamic theories for polymer mixtures - an important observation since there are so few experimental quantities which can be measured for miscible blends for use in quantifying thermodynamic behavior of these mixtures.

Melting point depression of the copolyester was examined as a means to estimate the interaction parameter for these blends. The approach included use of isothermal annealing and Hoffman-Weeks plots to extrapolate to an equilibrium melting point unaffected by crystal size; however, prolonged annealing at high temperatures was found to be accompanied by crystallization induced chemical rearrangements of the copolyester which proved interesting in that abnormally high melting points and crystallinity could be obtained but which precluded the extrapolation to infinite crystal size. An alternate thermal protocol was adopted that led to quantification of the thermodynamic interaction parameter in a way which is felt not to be seriously compromised by morphological effects. The interaction parameter is substantially negative as expected since this system does not phase separate even at very high temperatures ($>$ 325°C).

C. Mechanical Properties of As Processed Blends

Amorphous blends were prepared across the entire composition spectrum using melt processing techniques to form either film or injection molded test specimens. Extensive mechanical testing showed that all properties for blends were close to the additive response with modulus and strength showing slight positive deviations while percent elongation at failure and impact strength showing slight negative deviations. The lack of any significant synergistic mechanical response was somewhat surprising since such had been observed in two other miscible systems reported in the literature. Equally surprising, the density of the fabricated blends were very near that predicted by volume additivity. Subsequent thermal annealing studies cast considerable light on these observations and demonstrated that processing history may be as important in blend property relationships as component interaction for certain systems.

D. Effect of Thermal Annealing on Blend Mechanical Properties

Injection molded specimens were subjected to sub-Tg annealing to determine what effect physical aging would have on blend properties. Blends embrittled in a manner similar to that observed for other glassy polymers and to extents expected from the behavior of the component polymers. An unexpected result was that the modulus relationship, after annealing, exhibited a pronounced maximum. This occured primarily as a result of decreases in the moduli of the pure components which is contrary to previous observations on physical aging. Subsequent detailed studies deomonstrated that these responses stemmed from simultaneous relaxations of volume, molecular orientation, and packing effects during molding that could be studied separately by first annealing the molded samples in the melt state. Strain free samples exhibited a maximum in modulus that qualitatively correlates with an observed maximum in density in plots of these properties versus blend composition. These observations illustrate the importance of prior history on glassy polymer properties and that certain processing methods can be used to enhance or to diminish property responses in glassy miscible blend systems.

E. Effect of Humid Aging on Blend Mechanical Properties

Polycarbonate embrittles in boiling water after a few days owing to chain scission via hydrolysis reactions. The copolyester used in this work also embrittles in this environment but does so because its Tg is about 87°C allowing it to crystallize after a few days at 100°C. However, certain blends can maintain their strength and ductility in boiling water for weeks owing to their higher Tg but lower content of the more hydrolysis prone polycarbonate. Parallel molecular weight analyses of blends exposed to boiling water were made to substantiate these observations.

F. Effect of Copolyester Crystallization on Blend Mechanical Properties

As mentioned earlier, the copolyester used in these studies will crystallize but this requires annealing between Tg and Tm for appropriate periods of time. As processed blends or the pure copolyester do not contain any crystallinity, and it was samples of this type employed in the studies described above. To demonstrate the influence of crystallinity on properties, samples were annealed for 30 minutes at various temperatures traversing the range where crystallization rate goes through a maximum. In every case, development of crystallinity decreased ductility but increased stiffness. The extent of either change depended on annealing temperature reflecting the influence of crystalline texture as well as extent of crystallinity. The heat treatments relaxed the molecular orientation generated by injection molding which also has its effect on properties. In general, the balance of properties in these blends is best when crystallinity is absent.

G. Gas Sorption and Transport in Amorphous Blends

Extruded film of varying proportions of the two polymers were prepared and subjected to CO_2 sorption and transport measurements a $35^{\circ}C$. The equilibrium sorption isotherms were quite non-linear and well described by the dual sorption model, a combination of Henry's Law and Langmuir's isotherm, as has been found for all other glassy polymers in recent studies. The Henry's Law coefficient exhibited a minimum versus blend composition which was successfully interpreted via an extension of the Flory-Huggins theory, and the analysis gives an interaction parameter, χ_{12}, for the blend system which is negative and in good agreement with that obtained by melting point depression. The Langmuir capacity parameter was found to be quantitatively related to the unrelaxed volume in the glassy state, relative to the equilibrium liquid state, as has been found for a variety of glassy polymers.

The permeability of CO_2 through these blends was pressure dependent and well described by the recently developed dual mobility model. The trend of permeability with blend composition was quite interesting. The experimental values fall far below the additive prediction demonstrating that miscible blends may offer a useful means to achieve good barrier properties.

H. Extension to other Systems

In one brief part of this study, the copolyester was replaced in blends with polycarbonate by poly(ethylene terephthalate). In contrast to the polycarbonate - copolyester system, blends of PET and polycarbonate are not miscible over the entire spectrum of compositions. As a result of this difference in miscibility, the mechanical property relationships are more complex. Interestingly, the elongation at break appears to go through a maximum at the composition which divides miscible from two phase blends. Partially miscible systems represent another important category of blends needing further study.

Summary

The work done as part of this grant was very successful and has made some important contributions to the emerging technology of miscible blends. The study has been realistic and addressed the potential chemistry which occur during processing and has examined the large effect processing can have on blend property responses. In general, the properties of a miscible blend are found to be quite good compared to what is often observed for immiscible mixtures of polymers. There is a strong suggestion that the thermodynamic interactions responsible for miscibility play an important role in the nature of the property responses. These points are described in detail in forthcoming publications.

III. Publications Completed to Date

A. Theses and Dissertations

Name	Title	Date
M.D. Lorenz (M.S.)	"A Study of the Mechanical Properties of Blends of Polycarbonate and Kodar A150"	May 1980
P. Masi (M.S.)	"Sorption and Transport Properties of Compatible Polymer Blends"	July 1980
E.A. Joseph (M.S.)	"Mechanical Properties of Blends of Polycarbonate and Kodar A150 Copolyester"	May 1981
W.A. Smith (M.S.)	"Degradation and Interchange Reactions in Blends of Polycarbonate and a Copolyester"	May 1981
R.S. Barnum (Ph.D.)	"Thermodynamic Characterization of Miscible Polymer Blends"	May 1981

(Copies of the above are in the library of the University of Texas at Austin)

B. Papers in Print

1. P. Masi, D.R. Paul, and J.W. Barlow, "Properties of Compatible Blends of Polycarbonate and a Copolyester", RHEOLOGY, Vol.3: Applications (1980). Edited by G. Astarita, G. Marrucci, and L. Nicolais, Plenum Press, p.315.
2. D.R. Paul and J.W. Barlow, "Properties of Polymer Blends", Plasticon 81 - Polymer Blends, Plastics and Rubber Institute, England, Preprint 7.

(Reprints of the above have been sent to ARO)

C. Papers Submitted and Accepted for Publication

1. P. Masi, D.R. Paul, and J.W. Barlow, "Gas Sorption and Transport in a Copolyester and Its Blends with Polycarbonate", J. Polym. Sci.: Polym. Phys. Ed.
2. E.A. Joseph, M.D. Lorenz, J.W. Barlow, and D.R. Paul, "Mechanical Properties of Miscible Polycarbonate - Copolyester Blends", Polymer.
3. W.A. Smith, J.W. Barlow, and D.R. Paul, "Chemistry of Miscible Polycarbonate - Copolyester Blends", J. Appl. Polym. Sci.

(Manuscripts of each of the above have been sent to ARO)

Other papers are in preparation and will be submitted for publication at a later date.

IV. Participating Scientific Personnel

The following individuals received financial support from this grant:

Name	Status	Comment
J.W. Barlow	Faculty	Summer support
R.S. Barnum	Ph.D. Student	Degree granted May 1981
J.E. Harris	Ph.D. Student	Degree to be granted Dec. 1981. Mr. Harris was supported briefly by project.
E.A. Joseph	M.S. Student	Degree granted May 1981
M.D. Lorenz	M.S. Student	Degree granted May 1980
S.R. Murff	M.S. Student	Continuing
W.E. Preston	M.S. Student	Continuing
W.A. Smith	M.S. Student	Degree granted May 1981

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