

CHAPTER II

LITERATURE REVIEW

Solvents have been widely used for solution casting films of polymer blends and copolymers in academic studies and in small laboratories [Walsh, 1985]. The primary purpose of the solvent is to provide the vehicle for dispersion of the multicomponent polymer systems, but in many cases the solvents have an effect on the structures and the properties of the resulting polymeric films [Semerak and Frank, 1987]. In this chapter, the literature on the influences of the solvents on the properties of the polymer blend and copolymer films are presented.

Hirschbuehler, K. and Thies, C. [1975] found that the specific casting solvents were able to affect the mechanical behavior of the resulting films of chlorinated rubber (CR) and poly(vinyl methyl ether) (PVME) blends. The cast film of 60/40 (w/w) CR/PVME from methyl isobutyl ketone (MIBK) exhibited Hookean behavior up to fracture with little strain. The same mixture cast from toluene had a distinct Hookean region at low strain but then yielded and showed a large strain at fraction. The similar stress/strain curve was also observed in blend cast from methyl ethyl ketone (MEK). The stress/strain curves of their works were shown in Figure 2.1.

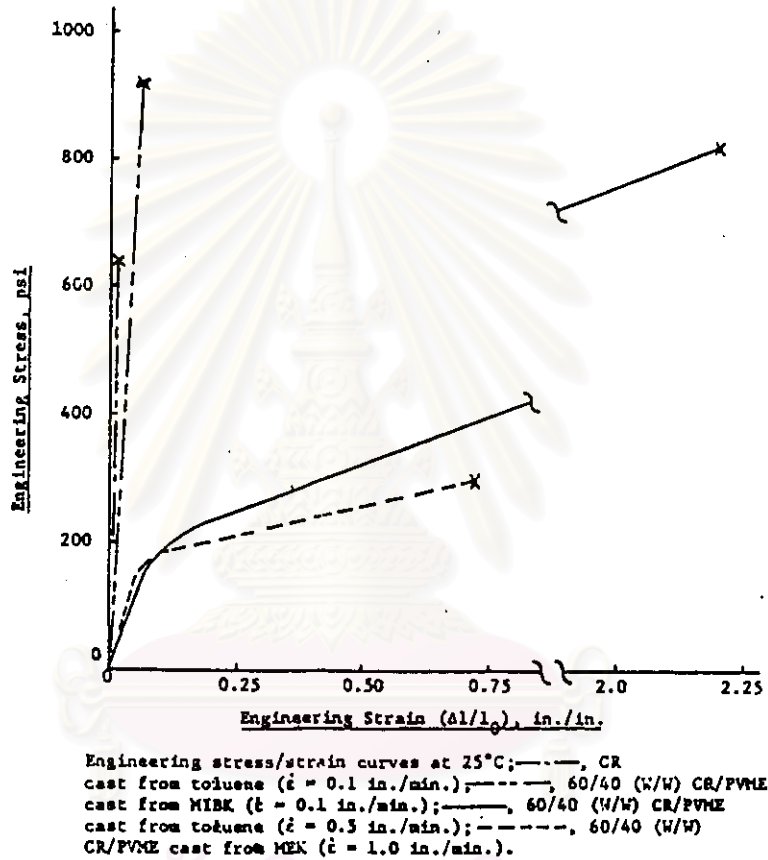


Figure 2.1 The stress/strain curves of chlorinated rubber and poly(vinyl methyl ether) blend [Hirschbuehler and Thies, 1975].

Bargodia, S. and Wilkes, G. L. [1976] studied the influence of casting solvent used for film preparation on the final mechanical properties of styrene butadiene triblock copolymers. They reported that the modulus behavior of copolymers in the range of styrene contents of 30-40 mol % were greatly affected as the solubility parameter of the casting solvent (δ) was varied. The modulus of copolymers increased as δ increased to the value of polystyrene. At lower or higher styrene content, the properties were influenced but to a lesser degree. It was also suggested in their work that the morphology of the resulting system could be changed by the selection of a suitable casting solvent.

Bajai, P. and Varshney, S. K. [1980] found that the films of poly (dimethyl siloxane-b-styrene-b-dimethyl siloxane) block copolymers cast from different solvents showed significant changes in both the phase morphology and the tensile behavior. Methyl ethyl ketone and tetrahydrofuran provided hard film. Conversely, cyclohexane, a good solvent for poly(dimethyl siloxane) segment gave softer more elastic films. Besides, they also found that films cast from cyclohexane had lower modulus and poorer tensile strength than films cast from methyl ethyl ketone, tetrahydrofuran and toluene.

Varnell, D. F., Runt, J. P., and Coleman, M. M. [1981] used Fourier transform infrared (FTIR) spectroscopy to study the variation of crystallinity of both components in the blend films of polymer blend of poly(bisphenol A carbonate) (PC) and poly(ϵ -caprolactone) (PCL) cast from different solvents

and at different evaporation rates. They found that the PC component of the blends was invariably amorphous in the methylene chloride (MC)-cast films but semicrystalline for tetrahydrofuran (THF)-cast films when both the films from MC and THF were cast at the same casting temperature. They also found that the PC component was capable of crystallization in the films prepared by slow evaporation of both MC and THF. Conversely, rapid evaporation of either THF or MC from the blend films resulted in an amorphous PC component.

Runt, J. and Rim, P. B. [1982] studied a polymer blend between poly(ϵ -caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN) at the 20 weight percent of PCL. The development of PCL crystallinity in blend was studied for samples prepared under a variety of conditions. Solvent casting was observed to be a method capable of inducing considerable PCL crystallinity, whereas melt mixing yielded amorphous samples. The degree of crystallinity of samples prepared from solvent casting was found to be sensitive to a variety of factors: film thickness, blend preparation temperature, solvent evaporation rate and the type of solvent.

Eastmond, G. C. and Haraguchi, K. [1983] investigated the effects of casting solvents on the dynamical mechanical properties of three polycarbonates (PC), of polystyrene (PS) and of a blend and copolymer of polystyrene with one polycarbonate. The properties of the blend were found to be a simple combination of those of the constituent homopolymer. Besides, the modified α -relaxation behavior of the polystyrene chains in the

copolymer was dependent on the casting solvent and thermal treatment used in the sample preparation.

Hashimoto, T., Itakura, M. and Shimidzu, N. [1986] found that the kinetics of phase separation of the poly(vinyl methyl ether) (PVME) and polystyrene (PS) blend were affected by the moisture taken in the samples after exposure to atmosphere at various times. The longer the time that the samples were exposed to the atmosphere with a relative humidity of about 30%, the faster the phase separation rate.

Chiou, J. S., Barlow, J. W. and Paul, D. R. [1987] studied the miscibility of bisphenol-A polycarbonate (PC) with poly(methyl methacrylate) (PMMA) by differential scanning calorimetry (DSC) and optical indications by looking at the phase separation on heating, i.e., lower critical solution temperature (LCST) behavior. Various methods were used to prepare the blend including solvent casting from methylene chloride (CH_2Cl_2) and tetrahydrofuran (THF), melt mixing, and precipitation of PC and PMMA simultaneously from THF solution by the nonsolvents methanol and heptane. It was shown that the resulting phase behavior for PC/PMMA blend was strongly affected by the blend preparation method. The blends were found to be miscible over the whole blend composition range when prepared by precipitation from solution using heptane as the nonsolvent, whereas methanol precipitation did not lead to fully mixed blends. To the contrary, solvent casting and melt mixing PC/PMMA blends were all phase separated.

Saldanha, J. M. and Kyu, T. [1987] studied the effects of solvent casting on the structure evolution of bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) mixtures as a function of solvent evaporation rate, casting temperature, and the kind of solvent used. The casting conditions exerted profound effects on the final blend morphology. PC/PMMA blends cast from tetrahydrofuran (THF) at low temperatures (20 °C or below) exhibited phase separation behavior as well as solvent-induced crystallization in the PC phase. The solvent casting at ambient (23 °C) showed the development of a modulated biphasic structure with high level of interconnectivity characteristic of spinodal decomposition. However, the casting at an elevated temperature (47 °C) yielded transparent amorphous film. Solvent casting of PC/PMMA blends from cyclohexanone (CHN) resulted in phase separation. The casting from methylene chloride (MC) showed no indication of solvent-induced crystallization, but the system phase separated during solvent evaporation.

Semerak, S. N. and Frank, C. W. [1987] used the excimer fluorescence technique to study the solvent casting films of poly(2-vinylnaphthalene) (P2VN) and polystyrene (PS) blends. The opalescence of the resulting blends depended on the kinds of solvent used for preparation of the blends. P2VN/PS blends cast from toluene, ethylbenzene, and n-propylbenzene were cloudy for PV2N concentrations of 6 and 10 wt%, whereas blends cast from 1,2-dichloroethane, tetrahydrofuran, and chlorobenzene were transparent for all PV2N concentrations (1, 3, 6 and 10 wt%). Blends cast from

dichloromethane were also transparent at all PV2N concentrations except at 10 wt% of PV2N.

Tsitsilianis, C. and Staikos, G. [1992] used the enthalpy relaxation method to investigate the miscibility in polymer blends and block copolymers between polystyrene (PS) and poly(methyl methacrylate) (PMMA) prepared from solvent casting and precipitation. It was shown that a partial phase mixing behaviour observed in PS-b-PMMA copolymer was strongly dependent on the choice of solvents and/or the precipitant. On the contrary, the respective polymer blend showed complete immiscibility irrespective of the solvent and/or the precipitant used.

Thongyai, S. [1994] used small angle light scattering technique to study the phase separation behavior of tetramethyl-bisphenol-A polycarbonate (TMPC) and polystyrene (PS) blend. He found that the phase separation of the blend cast from toluene took place at higher temperature than the blend prepared from melt mixing. Nevertheless, the comparison of phase separation of TMPC/PS blends from solvent casting and melt mixing was only studied on the blend at 50 wt% of PS.

Lu, S., Pearce, E. M., and Kwei, T. K. [1995] found that the miscibility window of the poly(styrene-co-4-vinylphenyl-dimethylsilanol) (ST-VPDMS) and poly(n-butyl methacrylate) (PBMA) blend at the 50 wt% of PBMA depended on the kind of solvents used for blend preparation. The blends cast from toluene were miscible when VPDMS in copolymers was in the

composition range of 4 to 18 mole %. Whereas, the miscibility of the blends cast from methyl ethyl ketone was found when VPDMS in copolymers was in the composition range of 9 to 34 mole %.

From the above literature, it could be demonstrated that many properties such as the mechanical properties, crystallinity, etc. of the films of polymer blend and copolymer were affected to some degree by the solvent used for casting the films.



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