CHAPTER II

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

2.1 Polymer blend: Classification

Polymer blend (or mixture) can be divided into two broad classes [2] and the polymer blend classification scheme is shown in figure 2.1. [3]

2.1.1 Single phase systems

Single phase systems are the systems in which the components are completely miscible or soluble in each other. In this case, the interaction between the molecules and the way they pack are important in determining the properties of the mixture(blend).

2.1.2 Two (or multi) phase systems

Two phase systems or multi-phase systems are the systems in which the components are insoluble (or only partially soluble) in each other. In this case, the factors which must be considered in the prediction of the properties are: 1. Which phases are continuous and which ones are dispersed? 2. What is the shape of the particles, and what is the morphology of the system? 3. How do the particles pack? 4. If the particles making up a phase are not spherical, how are they oriented? 5. What kind of interaction occurs at the interfaces? [2]

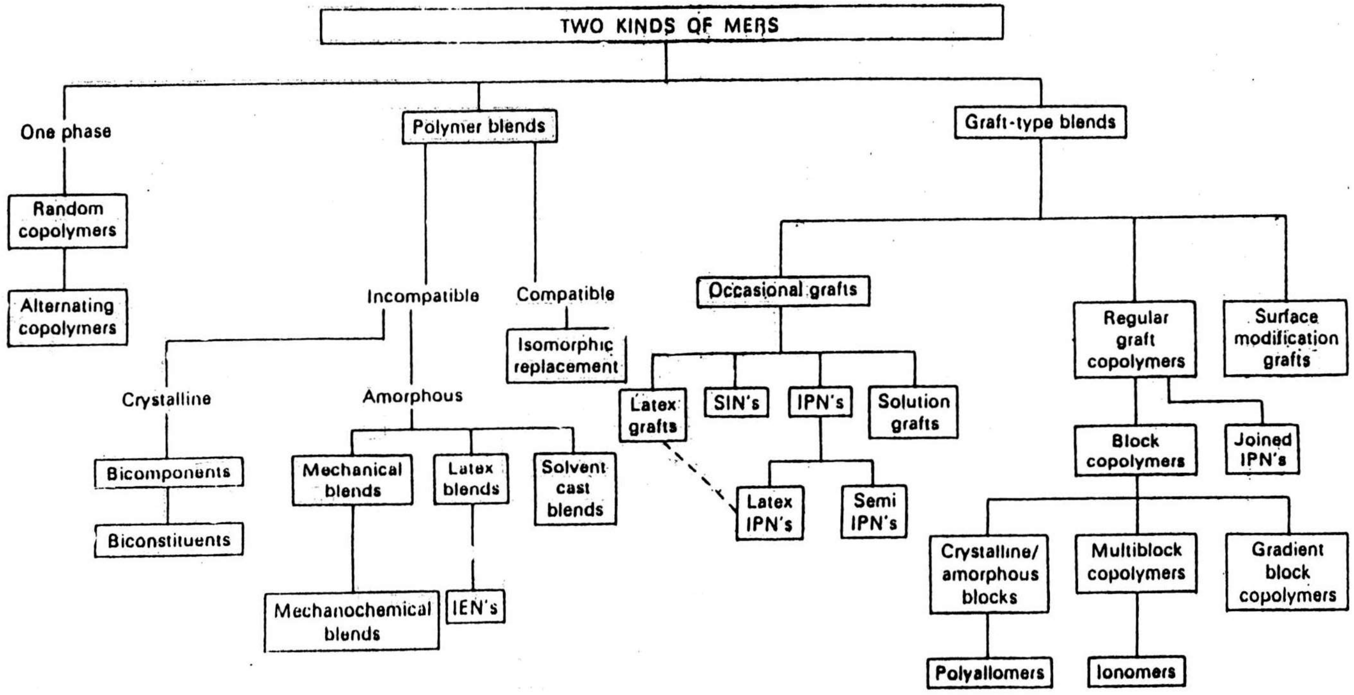

Fig. 2.1 Polymer blend classification scheme. [3]

2.2 Mechanical properties of polymer

Most plastic materials are used because they have desirable mechanical properties at economical cost. For this reason, the mechanical properties may be considered the most important of all physical and chemical properties of polymer for most applications.

2.2.1 Tensile Properties

The most widely used of all mechanical tests is the stress-strain test in tensile mode. The slope of the initial straight line portion of the stress-strain curve is the elastic modulus of the material,

$$E = d\tau / d\varepsilon \tag{1}$$

The maximum in the curve denotes either the stress at break for brittle material or the stress at yield for a ductile material and correspondingly either the elongation at break or the elongation at yield. The end of the curve represents the tensile at break(or ultimate strength) and elongation at break. In tensile tests, the stress, τ, is defined by

$$\tau = \text{force / cross-section area} = F/A \tag{2}$$

The strain, ε, can be defined in several ways, but for most purposes, the engineering strain is used:

$$\varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0} \tag{3}$$

where L_0 is the original length of the specimen, while its stretch length is L .

2.2.2 Impact strength

As one might intuitively expect, the incorporation of rubber particles within the matrix of brittle plastic enormously improves their impact resistance. The degree of impact resistance obtained depends both on the quantity of rubber incorporated and the method of forming the blend.

2.3 Equation for predicting mechanical properties of polymer blends

2.3.1 Modulus of blends

In the simplest case, an upper and lower bound can be predicted for the composite elastic modulus. The maximum possible modulus for a filled system which is the result to be expected when the two materials making up the composite are connected in parallel is given by the "rule of mixtures":

$$M = \phi_1 M_1 + \phi_2 M_2 \qquad (4)$$

where the M's represent the composite and component modulus respectively, while ϕ is the volume fraction. An example would be an aligned fibrous composite with the force applied parallel to the fibers.

On the other hand, the lowest possible modulus is obtained when the two materials comprising the composite are connected in series. The equation then becomes:

$$1/M = \phi_1/M_1 + \phi_2/M_2 \qquad (5)$$

The parallel model (Voigt model) assumes uniform strain in an assembly to predict the over all modulus, while the series model (Reuss model) assumes a uniform stress in the composite assembly.

A better method which imposes much narrower limits on the moduli and which is capable of incorporating the morphology of the two-phase system in a less ambiguous manner is to use the theory of the moduli of composite materials. In practice more complicated expressions may be useful. For polymers containing nearly spherical particles of any modulus, the Kerner equation [5],

$$\frac{G}{G_m} = \frac{\{G_f\phi_f/[(7\text{-}5v)G_m + (8\text{-}10\ v)G_f] + \phi_m/15(1\text{-}V_m)\}}{\{G_f\phi_m/[(7\text{-}5v)G_m + (8\text{-}10\ v)G_f] + \phi_m/15(1\text{-}V_m)\}} \qquad (6)$$

or the equivalent equation of Hashin and Shtrikman [6] can be used to calculate the modulus of the composite if there is some adhesion between the phases.

In this particular case, G represents the shear modulus of the composite, ϕ is the volume fraction, v is the Poisson's ratio of the matrix, while subscripts m and f represent the matrix and filler respectively. In general, particle size does not appear in the Kerner equation. It is especially useful in predicting the moduli of composites of a spherical filler randomly dispersed in a glassy matrix [5].

For fillers which are more rigid than the polymer matrix, the Kerner equation up to moderate filler concentrations becomes:

$$\frac{G_b}{G_m} = 1 + \frac{15(1\text{-}V)}{8\text{-}10V}\,\frac{\phi_f}{\phi_m} \qquad (7)$$

For foams and rubber-filled rigid polymers (such as HIPS) the Kerner equation reduces to:

$$\frac{1}{G} = \frac{1}{G_m}\quad 1 + \frac{15(1\text{-}V)}{7\text{-}5V}\,\frac{\phi_f}{\phi_m} \qquad (8)$$

The theories indicate that the elastic moduli of a composite material should be independent of the size of the filler particles; however, experiments sometimes show an increase in modulus as the particle size decreases. One possible explanation has to do with the surface area of the particles. As their size decreases, the surface area increases. Now, if the polymer is changed in some manner at the interface, then the properties should change with particle size because of the change in surface area.

The Kerner and similar equations all assume that there is good adhesion between the filler and matrix phases. Actually, good adhesion is not important as long as the frictional forces between the phases are not exceeded by the applied external forces. In most filled systems there is a mismatch in the thermal coefficients of expansion so that cooling down from the fabrication temperature imposes a squeezing force on the filler by the matrix. Thus, in most cases, even if the adhesion is poor, the theoretical equations are valid because there may not be any relative motion across the filler-polymer interface [7].

Halpin and Tsai [8] have developed equations which are general enough to cover the complete range of the moduli from the lowest lower bound (series models) to the highest bound (parallel models):

$$\frac{M}{M_m} = \frac{1 + AB\phi_f}{1 - B\phi_f} \tag{9}$$

where M is any modulus-shear, Young's, or bulk.

Additionally,

$$A = \frac{7 - 5\nu}{8 - 10\nu} \tag{10}$$

and

$$B = \frac{M_f/M_m - 1}{M_f/M_m + A} \tag{11}$$

These so-called *Halpin-Tsai* equations are actually generalized Kerner Equations and are used for both rubbery-filled systems and glassy-filled systems. When A approaches infinity, equation (6) becomes the rule of mixtures(i.e., $M = M_m\phi_m + M_f\phi_f$ and when A approaches zero, the equation becomes $1/M = M_m/\phi_m + M_f/\phi_f$).

Nielson [9] has shown that the *Kerner* or *Halpin-Tsai* equation can be generalized by taking into account the maximum packing fraction of the filler phase even further to:

$$\frac{M}{M_m} = \frac{1 + AB\phi_f}{1 - B\psi\phi_f} \tag{12}$$

where

$$\psi = 1 + \left[\frac{1 - \phi_p}{\phi_p^2}\right]\phi_f \tag{13}$$

and

$$\psi\phi_f = 1 - \exp\left[\frac{-\phi_f}{1 - \phi_f/\phi_p}\right] \tag{14}$$

The generality of Equation (9) can be further enhanced by pointing out the relation between the constant A and the generalized Einstein coefficient k. The generalized Einstein coefficient may be defined as

$$k = \frac{d(M/M_1 - 1)}{d\phi_f}\ , \tag{15}$$

as ϕ_f approaches zero and M/M_1 approaches infinity. The relation is

$$A = k - 1. \tag{16}$$

Where ψ is a function which take in account the maximum packing fraction depended upon the maximum packing fraction ϕ_p of the dispersed phase. The maximum volumetric packing fraction ϕ_p is indirectly related to morphology, and it generally has a value between 0.5 and 0.9. It has value of 1.0 in the original *Halpin-Tsai* equations. The constant *A* and *k* are strongly dependent upon the morphology of the composite.

For inverted system in which the continuous phase is more rigid one, it is convenient to rewrite equation (11), (12) and (16) as [10]

$$\frac{M_m}{M} = \frac{1 + A_i B_i \phi_f}{1 - B_i \psi \phi_f} \tag{17}$$

$$A_i = 1 / A_1 \tag{18}$$

$$B = \frac{M_m / M_f - 1}{M_m / M_f + A} \tag{19}$$

In real systems, such as polyblends and block copolymers, an inversion of the phases occurs at a volume fraction of about one half. The exact composition at which phase inversion occurs can be changed considerably by the intensity of mixing [11]. In additional, there is generally a range of compositions where both phases are partly continuous and where the modulus changes rapidly with composition.

There is often a discrepancy between theoretical predictions and experimental results for the modulus of particulate filled polymers due to the present limitation of understanding of these materials. It is for this reason that the simple parallel and series models which present the upper and lower bounds to the composite moduli, respectively, are so useful [12]. However, the Kerner or Halpin-Tsai equations seem to agree with experiment as well as any other equations that been proposed [7].

Other than the most widely used Kerner equation, there are, of course, many other equations describing the modulus of composite. These will be discussed briefly now.

One of the most first fundamental studies illustrating the effects of fillers on the modulus was described by Nielson et al [13], who showed that the shear modulus of PS was increased by the incorporation of mica, calcium carbonate, or asbestos. The proposed equation was of the form:

$$G = G_m\phi_m + AG_f\phi_f \qquad (20)$$

where A is an empirical term to give a measure of the filler-matrix adhesion. It allows for the fact that upper bound modulus values are not found consistently in practice with such systems.

Equation (20) is very similar to that used for fiber-filled polymers. If fibers are long and oriented in the direction of applied stress, the rule of mixtures is found to hold:

$$E_{11} = E_f\phi_f + E_m\phi_m \qquad (21)$$

which again represents an upper bound(or maximum obtainable modulus). In general, long oriented fibers in a matrix tend to yield upper bound values of modulus, while particulate fill system tend to yield lower bound values(as predicted by relationships such as Kerner's). Another similar equation commonly used for fiber-resin composites is the Kelly-Tyson equation [14] which presents the composite longitudinal modulus:

$$M_L = K\,M_f\phi_f + M_m\phi_m \qquad (22)$$

The value for K is unity for parallel continuous filaments and is less for randomly arranged filaments. Degree of adhesion has little effect on modulus, but a great effect on strength and ultimate elongation.

It should be remembered that most fiber-filled composites are highly anisotropic, so that the equation relating the elastic moduli to composition depends upon the orientation of the test. The rule of mixtures only holds in the case of very long fibers oriented parallel to the stretching deformation. For truly randomly oriented three dimensional composites, Nielson [10] has proposed a logarithmic rule of mixtures:

$$\log E = \phi_m \log E_m + \phi_f \log E_f \qquad (23)$$

This equation has no theoretical basis.

The logarithmic rule of mixtures has also been applied to semicrystalline polymers [15]. The equation then has the following form:

$$\log_{10} G = W_a \log G_m + W_c \log G_c \qquad (24)$$

In this equation W_a is the fraction of amorphous phase and W_c the fraction of crystalline phase. The logarithmic rule of mixture has also been found empirical useful for predicting the modulus of block copolymers and polyblends when both polymerics phases are continuous.

Davies [16] has theoretically derived equations which are applicable when both phases are continuous in contrast to the usual theories in which one phase is assumed to be dispersed. His equations are specific examples of the general mixing equation:

$$G^n = \phi_1 G_1^n + \phi_2 G_2^n \quad ; -1 \leq n \leq 1 \qquad (25)$$

where ϕ_1 and ϕ_2 are volume fractions of phase 1 and 2, respectively. As a special case, Davies' equation for the shear modulus of systems containing two continuous phases is:

$$G^{1/5} = W_a G_a^{1/5} + W_c G_c^{1/5} \tag{26}$$

Equation (26) fits many experimental data on crystalline polymers over a wide rang of crystallinities [16]. It works well also for interpenetrating networks(IPN's) [17]. IPN's, one can say, exhibit dual phase continuity.

The Hashin-Shtrinkman theory of the elastic properties of a hard matrix with randomly dispersed soft inclusions appears to work quite well also for semi-crystalline polymers [6,18]. The equation has the following form:

$$\frac{B - B_c}{B_c} = \frac{1 - \phi_c}{(B_a/B_c - 1)^{-1} + \phi_c f(\nu)} \tag{27}$$

where ϕ_c is the volume fraction crystallinity, a and c represent the amorphous and crystalline regions respectively, and $f(\nu)$ is a slowly varying function of the Poisson's ratio of the crystalline phase. For example, when $\nu = 0.33$, $f(\nu) = 0.5$ so that equation (27) becomes:

$$\frac{B - B_c}{B_c} = \frac{1 - \phi_c}{(B_a/B_c - 1)^{-1} + 0.5\phi_c} \tag{28}$$

In the crystallinity range, $\phi_c > 0.5$, experimental evidence strongly suggests that the crystalline regions form the load-bearing phase. The elastic moduli of such a structure can be estimated by the method of Hashin and Shtrikman [6], who assume the discontinuous phase to be present as randomly distributed spheres obtain as the representative equation:

$$\frac{G - G_c}{G_c} = \frac{1 - \phi_c}{G_c / G_a - G_c + \phi_c f(\nu)} \tag{29}$$

where $f(\nu)$ is a slowly varying function of the Poisson's ratio $f(\nu) = 0.467$ when $\nu = 0.33$).

Because the elastic properties depended very strongly on packing density and to some extent on the proximity of the melting point, these properties should be known before any correlation of elastic moduli can be attempted. When both these properties are known, the correlation of the bulk modulus has succeeded quite well, while those of the Young's and shear modulus are only suggestive, but far from quantitative [17].

2.3.2 Strength of blends

Neilsen [19] and Leidner et. al.[20] proposed that the tensile strength of composite materials, consisting of a matrix with spherical inclusions, can be related to the area fraction of the dispersed phase, with a general equation of this form:

$$\sigma_b = K\sigma_1 (1-K \phi_2^n) \tag{30}$$

The parameter K reflects the possible modification in the strength of the matrix due to the presence of the second phase, but normally K=1 if the two are immiscible. Leidner concluded that if there is no cohesion between the inclusions and the matrix, then the yield strength of the blend should be decreasing as the volume fraction to the first power, in which case $n = 1$ in equation (30) . However, further considerations by Nicolais and Narkis [21] result in a modified

$$\sigma_b = \sigma_1 (1-1.21 \phi_2^{2/3}) \tag{31}$$

The value of the constrain in front of ϕ_2 is chosen so that $\sigma_b = 0$ when $\phi_2 = 0.75$ (maximum packing by filler). Another approach was taken by Neilsen [22] and Geil [23], who suggested that in a blend, where the two components display considerable decohesion, the particles do not contribute to strength and can be thought of as voids. In this case the following equation should describe the tensile strength:

$$\sigma_b = \sigma_1 \exp(-\alpha \phi_2) \tag{32}$$

where α is an empirical constant.

2.2.3 Elongation at yield and break

Generally, fillers in a composite system cause a dramatic decrease in elongation at yield and break. The decrease in elongation to break, ε_B, (rigid fillers) arises from the fact that the actual elongation experienced by the polymer matrix is much greater than the measured elongation by the specimen. Although the specimen is part filler and part matrix, practically all of the elongation comes from the polymer, if the filler is rigid. The theory is still incomplete and at best gives semi-quantitative understanding of experimental results. For good adhesion, the following equation is expected: [24]

$$\varepsilon_b = \varepsilon_m(1-\phi_f^{1/3}) \tag{33}$$

2.4 Modeling the properties of mixtures-simplex lattice design [4]

To a first approximation linear additivity is usually employed for the prediction of thermodynamic properties of multicomponent systems. Higher precision calculation is often unattainable because the excess property cannot be predicted. As a generalization during mixing, the deviation of property from linearity is unattainable or difficult to predict.

Nevertheless, the empirical data resulting from a mixing or blending experiment can usually be modeled. Often, semi-empirical significance can be attached to the coefficients of the model equation. One convenient modeling technique arises from a statistical method for investigating properties of multi-component system as a function of composition. The method was originally devised by *Sceff'e* [25] for designing experiment of multi-component systems. The fraction of components making up any mixture must add to unity and hence factor space may be represented by a regular simplex (an element or figure contained within a Euclidean space of a specified number of dimensions having one more boundary point than number of dimensions).

The method is particularly useful when several properties are of interest. The regression equations used for the modeling of mixtures are polynomials. In principle any mixture response can be represented by polynomical, if enough terms are included. In practice, polynomial models are limited to low order models. For the sake of simplicity, the cubic model for the three-component systems will initially be presented, although equations could easily be generated for any order model for any number of components. So, the representation for a three-component system (using a polynomial model of third order to express the response of a property, P, as a function of composition χ) is:

$$\begin{aligned} P = {} & \beta_1\chi_1 + \beta_2\chi_2 + \beta_3\chi_3 + \beta_{12}\chi_1\chi_2 + \beta_{13}\chi_1\chi_3 + \beta_{23}\chi_2\chi_3 + \gamma_{12}\chi_1\chi_2(\chi_1-\chi_2) \\ & + \gamma_{13}\chi_1\chi_3(\chi_1-\chi_3) + \gamma_{23}\chi_2\chi_3(\chi_2-\chi_3) + \beta_{123}\chi_1\chi_2\chi_3 \end{aligned} \tag{34}$$

or more compactly

$$P = \sum_{1 \leq i \leq q} \beta_i\chi_i + \sum_{1 \leq i \leq j \leq q} \beta_{ij}\chi_i\chi_j + \sum_{1 \leq i \leq j \leq q} \gamma_{ij}\chi_i\chi_j(\chi_i-\chi_j) + \sum_{1 \leq i \leq j \leq k \leq q} \beta_{ijk}\chi_i\chi_j\chi_k \tag{35}$$

The β's and γ's are the coefficients of the compositions of the composition and q is equal to the number of components. In this work we will be interested primarily in a quadratic two model. Hence, we can reduce equation (34) to

$$P = \beta_1\chi_1 + \beta_2\chi_2 + \beta_{12}\chi_1\chi_2 \tag{36}$$

The first two terms of equation (36) correspond to the linear rule of mixtures for which all higher order coefficients are zero. The magnitude of β_{12} expresses the extent of deviation from non-linearity. A positive β_{12} represents a nonlinear synergism while a negative β_{12} expresses an antagonism effect.

The quadratic model for binary systems describes a response curve with no more than one minimum, but not both, and with no point of inflection. The deviation from linearity is symmetrical and a maximum at the 50:50 mixture. Of course, all equations are subject to constrain $\sum \chi_i = 1$.

One can readily solve for the coefficients of equation (36) which for the sake of convenience will be represented in the following form:

$$P = \sum_{1 \leq i \leq 2} \beta_i\chi_i + \sum_{1 \leq i \leq j \leq 2} \beta_{ij}\chi_i\chi_j \tag{37}$$

The solution is

$$\beta_i = P_i \tag{38}$$

and

$$\beta_{ij} = 4P_{ij} - 2P_i - 2P_j \tag{39}$$

P_i and P_j represent the responds of the pure components and P_{ij} represents the response of the 50:50 mixture. More explicitly, the solution can be written:

$$\beta_1 = P_1 \quad (40)$$

$$\beta_2 = P_2 \quad (41)$$

and $$\beta_{12} = 4P_{12} + 2P_1 + 2P_2 \quad (42)$$

Here the excess properties would be equal to $\beta_{12}\chi_1\chi_2$ and one can think of β_{12} as a type of interaction term. Of course similar expressions could be written for many properties. In this work , the primary interest will be in excess modulus, strength and elongation at break represented by the following equations, respectively:

$$E = E_1\chi_1 + E_2\chi_2 + \beta^E{}_{12}\chi_1\chi_2 \quad (43)$$

$$\tau = \tau_1\chi_1 + \tau_2\chi_2 + \beta^\tau{}_{12}\chi_1\chi_2 \quad (44)$$

$$\varepsilon = \varepsilon_1\chi_1 + \varepsilon_2\chi_2 + \beta^\varepsilon{}_{12}\chi_1\chi_2 \quad (45)$$

A superscript has been placed on each interaction term, β_{12}, to emphasize that β_{12} will have different values for different properties.

2.5 Literature Reviews

The simplex equation was original devised by Sceff'e [26]. The theory is developed for experiments with mixtures of q components. Its propose is the empirical prediction of the response to any mixture of the components, when the response depends only on the proportion of the components and not on the total amount.

For the polymer blend application, Kleiner et. al. [1] proposed an empirical equation of second order called Simplex equation that can describe a synergistic effect of blending on modulus in term of interaction parameter because the modulus at each blend composition of PS-PPO is higher than that would be calculated by the simple "rule of mixture". Clearly, no composite equation such as Kerner equation, logarithmic rule of mixture, and Davies equation is able to model the modulus of glassy compatible polyblend. Although composite equations fail to model the modulus of blends, Simplex equation can be generated which agrees with the empirical data over the entire composition range. The interaction term, β_{12} , expresses the magnitude of the deviation from nonlinearity. A positive β_{12} represents a nonlinear synergism(criterion for compatibility?), while a negative β_{12} expresses a nonlinear antagonism(criterion for incompatibility?).

Mondragon, I. and Nazabal, J.[26] studied polymer blend of polyacrylate(PA)-a copolyster of bisphenol A with a mixture of terepthalic acids. The processing produces transreacted mixtures that exhibited a modulus and yield stress with a maximum that is above the linear. The moduli of the blend as a function of composition give the results similar to PPO/PS compatible blend. The results are compared with the simple rule of mixture and modified rule of mixture(Simplex equation). Simplex equation can predict the moduli of this blend.

Ueda, H. et. al. [27] studied the tensile properties of the mixture of Linear Polyethylene with ultrahigh and moderate molecular weights. An enhancement of both crystallinity and density and an obvious synergism in tensile properties were observed for quenched film made from the mixture in which both components had been co-dissolved. The Simplex equation is chosen to predict the strain at break and strength at break of mixture.

Ahn, O. T. et. al. [28] prepared binary blend of ethylene vinyl alcohol copolymers with nylon by melt mixing in twin screw compounding. Positive deviations viscosity and flexural modulus were generally observed. The positive deviation is probably due to increased intermolecular interaction of nylon-6 due to the addition of EVOH . Modulus as function of composition, both in the form of positive and negative deviation from simple rule of mixture, can be expressed by Simplex equation .

Lee, K. Y. et. al. [29] blended two types of ultralow-density polyethylene(ULDPE) of difference melt viscosity with polypropylene(PP). Morphological observation from SEM showed a clean phase separation of PP/ULDPE blends. The melting temperature of PP and ULDPE were respectively increased and decreased in the blend. Their mechanical properties were closely relatable to the morphology. The impact strength of PP is significantly improved by ULDPE addition. The modulus of polymer blends can be expressed by Simplex equation. The modulus of the blends shows a negative deviation from the additive rule of mixture.

Flaris, V. and Stachurski, H. Z.[30] studied the improvement of polypropylene's poor impact strength at low temperature by blending with polyethylene. The addition of an ethylene-propylene block copolymer to the blend alleviates the problem of poor adhesion at the interface. The modulus and yield strength of blends can be expressed by Simplex equation.

Pal, N. S. et. al. [31] studied the mechanical properties of ternary blends of plastizied poly(vinyl chloride) (PPVC1), acrylonitrile-butadiene rubber (NBR1), and graft polymer of vinyl chloride and ethylene-vinyl acetate copolymer (EVAPVC). A simple generalized equation (similar to Simplex equation for ternary mixture) is proposed for mechanical properties namely, UTS, elongation at break, modulus at 100% elongation, and TEB. Values calculated are generally quite close to the experimental ones for the blend system studied.