# THE CORRELATION BETWEEN TEMPERATURE, LOADING RATE, AND MICROSTRUCTURE OF POLYMER BLENDS

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## ABSTRACT

The study of polymer blends is probably the most active area of polymer research. In this work, the effects of morphology on fracture performance of both uncompatibilized and compatibilized polymer blends have been investigated over a large range of loading rates and temperatures. For this purpose, blends of different concentrations were studied at various test conditions. The focus is put on the time – temperature dependence of fracture performance of these blends. The results show that the organization of the blend structure play an important role in the dependence of fracture behavior on time and temperature. For instance, the co-continuous morphology of an uncompatibilized nylon 6/ABS blend gives an optimum fracture performance at a fracture test-speed of 2.5 m/s at room temperature. However this 'optimum' property disappears when the test speed is reduced to 100 mm/min at room temperature or when the temperature is lowered to -40°C at 2.5 m/s. The addition of compatibilizers such as interfacial agents makes polymer blends more ductile. The time-temperature dependence of the brittle-ductile transition is controlled by an energy activation process. Adding the interfacial agent lowers the temperature at brittle-ductile transition and reduces the energy barriers controlling two relaxation mechanisms called a and $\beta$ , that act in parallel and affect both yielding and fracture behaviors.

## KEYWORDS

Polymer, Blend, Fracture, Yielding, Relaxation, Morphology, Brittle-Ductile Transition.

## INTRODUCTION

Blending existing polymers together has long been known to be an effective, low-cost way of developing novel materials and polymer alloys and blends represent one of the fastest growing sectors of the plastics industry. Block copolymers have been shown to be effective interfacial agents for many incompatible blends of homopolymers. They are known to reduce the interfacial tension, homogenize the morphology and improve adhesion between the phases. This effect results in an improvement in mechanical properties and fracture performance.

The emulsification curve, which relates the average minor phase particle diameter to the concentration of interfacial agent added, has been used to quantify the effect of the interfacial agents on the blend morphology [ 1, 2]. It displays some key characteristics, an initial significant drop in the size of the dispersed phase with the addition of the copolymer followed by an equilibrium diameter value at high concentrations of modifier once

interfacial saturation has been obtained. This drop in particle size is the result of reduced coalescence and interfacial tension due to the presence of the interfacial modifier [2].

The addition of an interfacial modifier to an incompatible polymer blend, though widely and successfully used in industry, can introduce certain complications into the processing, such as an additional compounding step, and increases the production costs, since modifiers are usually expensive. A clear economic advantage can result if the mechanical properties of a blend can be controlled and improved to an acceptable level without the addition of an interfacial modifier. The morphology of immiscible blends is also highly dependent on the concentration of the dispersed phase, particularly in the absence of an interfacial modifier. In recent detailed studies [3], image analysis has shown that both the size and size distribution of the dispersed phase increase rapidly with composition. At a given concentration, at the point of phase inversion, a co-continuous morphology is observed.

The influence of the above microstructures on physical properties still remains largely an unknown in the scientific literature. This paper presents the results of an investigation on the effects of morphology on fracture and yielding behaviors in compatibilized and uncompatibilized blends. The compatibilized blend consists of 80 volume % polystyrene (PS) and 20 volume % ethylene- propylene rubber (EPR) compatibilized by two triblock copolymers of styrene/ ethylene- butylene/ styrene (SEBS) of different molecular weights. The uncompatibilized blend consists of nylon 6 and ABS (Acrylonitrile-Butadiene-Styrene). The focus is put on the correlation between time, temperature and microstructure.

## EXPERIMENTAL

Blends of various compositions of nylon 6 and ABS (both polymers were supplied by Monsanto) have been prepared by extrusion. The properties and blending procedure are given in [4]. Each prepared blend is designated by $S_n$ in which n corresponds to the weight fraction of ABS. For example, $S_{10}$ contains 10% in weight of ABS, $S_{80}$ contains 80 wt% of ABS etc.

The compatibilized blend investigated consists of a polystyrene matrix (PS), supplied by Dow Chemical (Styron D685), and a minor phase of ethylene-propylene rubber (EPR), a random copolymer containing 54% ethylene, supplied by Exxon Chemical (Vistalon V-504). The interfacial agents were supplied by Shell: they consist of two styrene/ ethylene- butylene/ styrene (SEBS) triblock copolymers (Kraton 1651 and Kraton 1652, referred to as K1 and K2, respectively), containing 29% styrene. The number average molecular weights of K1 and K2 are 174,000 and 50,000 g/mol, respectively. Some properties of these materials are presented in [5]. Blends were prepared with various interfacial agent concentrations, based on the minor phase. Thus, the sample denoted as K1 10 has the following composition: 80 parts PS, 20 parts EPR, and 2 parts (10% of EPR content) Kraton 1651. Likewise, K2 20 has a composition of 80 parts PS, 20 parts EPR, and 4 parts (20% of EPR content) Kraton 1652.

## RESULTS AND DISCUSSIONS

Figure 1a shows the variation of the measured fracture energies at crack initiation as a function of ABS concentration. It can be seen that, with increasing ABS content, fracture is brittle up to about 70wt% and then becomes ductile with a significant jump in fracture energy. The morphological analysis of the blends [4] revealed that phase inversion occurs around 70wt% ABS, where a co-continuous morphology is observed. The change in mechanical performance of the blend and the peak in fracture energy at this composition were therefore attributed to this co-continuous morphology. However, further fracture tests at low loading rates have shown that the peak in fracture energy does not always occur around 70wt% ABS but its location varies with the loading rate of the fracture test. Figure 1b shows an example of variation of fracture energy with ABS content at a cross-head speed of 100 mm/min. In this case, the peak in fracture energy occurs at about 10wt% ABS, with the same change in fracture type from brittle to ductile. In polymer blends, it has long been shown that the morphology strongly controls fracture performance and optimum microstructure has always been researched for good performance. Figure 2 shows the variation of the ABS content at the peak of fracture energy, as a function of the loading speed of fracture test. It clearly indicates that optimum morphology depends on loading rate. The rate dependence of physical and mechanical properties of polymer

has always been attributed to an energy activation process. It can therefore be expected that the optimum morphology also depend on temperature. To confirm this effect, fracture tests were then carried out at lower temperatures. Measurement of the impact fracture energy at $-40°C$ for the two constituent polymers and three selected blends $S_{10}$, $S_{40}$, and $S_{70}$ revealed that the above peaks in fracture energy disappear, suggesting a strong dependence of these peaks with temperature.
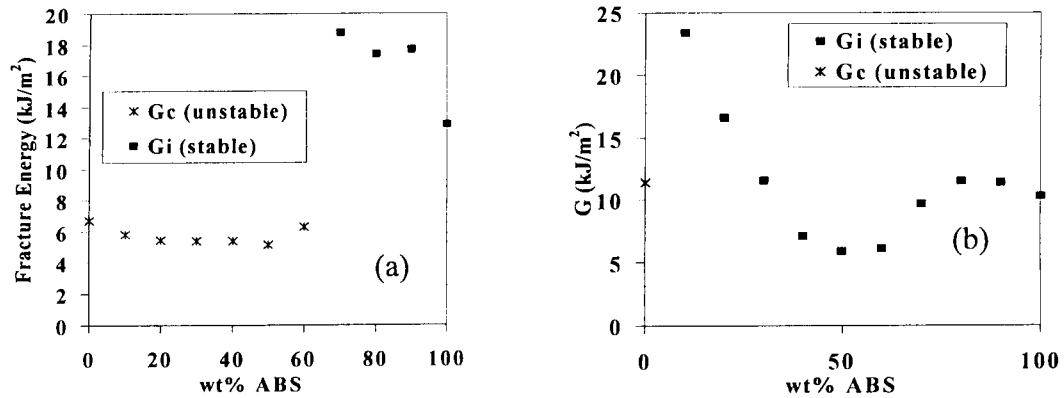


Figure 1: Fracture energies versus ABS content at impact speed of 2 m/s (a) and 100 mm/min (b).
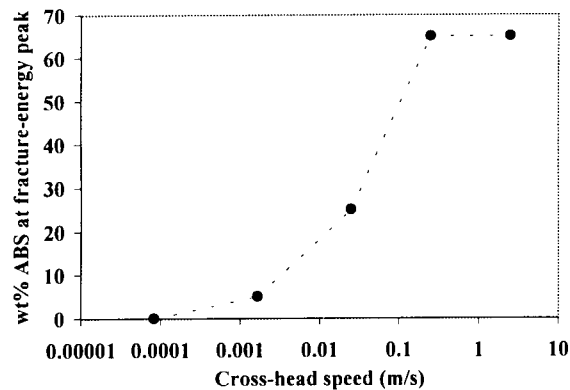


Figure 2: ABS content at the peak of fracture-energy, as a function of loading speed.

The time and temperature dependence of the properties of polymers is known to be due to the molecular relaxation. In immiscible polymer blends, the phase separation usually results in clear and distinct molecular relaxation corresponding to each constituent of the polymers present. The relaxation time or temperature has been found to be an intrinsic property of the polymer. The organization of the blend structure at a larger scale does not affect the relaxation processes. Multiple impact peaks have been reported for several polymers [6-8] and, although it is still a controversial subject, attempts have been made to relate the observed impact peaks to the molecular relaxation peaks of the polymer. A peak in the fracture energy is always observed at the brittle-ductile transition temperature. For toughened polymers, the cause of ductile-brittle transition has often been attributed to the glass transition of the rubbery phase [9]. The brittle-ductile transition in a rubber-toughened nylon 66 (Zytel ST-801) and a High Impact Polystyrene (HIPS) have been analyzed as a function of the molecular relaxation mechanisms of the rubbery and matrix phases in these materials [7]. It has been found that the type of molecular relaxation with lower activation energy seems to be related to the brittle-ductile transition phenomenon. In the case of HIPS, the relaxation process involved seems to be the glass-rubber transition of the polystyrene matrix. In the case of Zytel ST-801, the β transition of the Nylon 66 seems to be related to the brittle-ductile transition of fracture [7].

Unlike these effects, the results on the nylon-6/ABS blend suggest that the organization of the blend structure plays an important role in the dependence of fracture behavior on time and temperature. The co-continuous morphology at about 70wt% ABS gives an optimum fracture performance at a fracture test-speed of 2.5 m/s at room temperature. However this 'optimum' property disappears when the test speed is reduced to 100 mm/min (at the same room temperature) or when the temperature is lowered to $-40°C$ (at the same loading

speed of 2.5 m/s). It is worth mentioning that other mechanical properties such as Young modulus, yielding or strength do not show any peak when the ABS concentration increases. The yield stress of the blend continuously decreases with increasing ABS content. A reduction in the loading rate also results in a continuous decrease in the yield stress of the blend as expected.

In the PS/EPR blends, fracture also exhibits a brittle, semi-ductile, or ductile behavior, depending on the temperature and loading speed. Figures 3 shows the variation of various fracture energies as a function of temperature at 100 mm/min and 2.5 m/s, for the K1 30 sample. The transition from brittle to ductile behavior occurs with a peak in the measured value of fracture energy. As the temperature increases, a semi-ductile behavior is generally observed at the region of the peak, before the onset of ductile fracture. In the semi-ductile behavior, a certain amount of stable crack propagation occurs in the sample before the onset of unstable fracture. The reported value corresponds to the fracture energy at instability. It should be noted [8, 10] that one cannot base only on the initiation value of fracture energy to determine the fracture performance but the type of crack propagation should also be considered. With the same value of fracture at crack initiation the material exhibiting a stable crack propagation performs better in terms of impact resistance since after initiation, fracture can only continue with further supply of energy by external loads. However, in the case of brittle fracture, the crack accelerates without any additional supply of energy from the external forces.
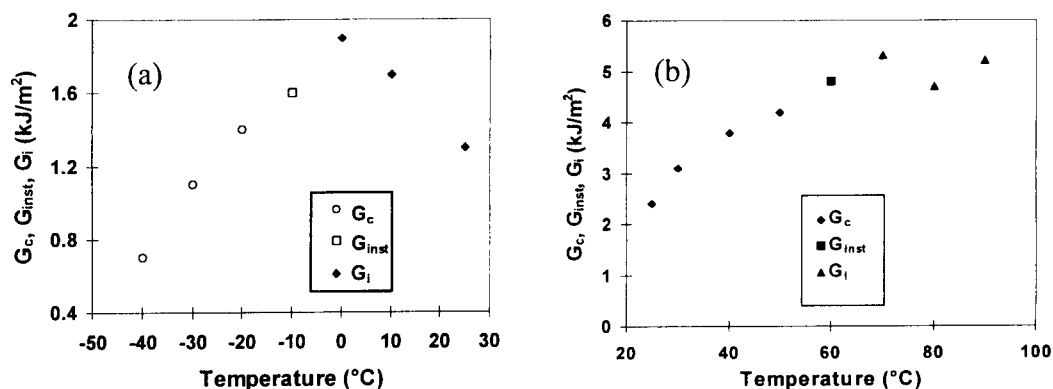


**Figure 3**: Fracture energy versus temperature for K1 30 sample at: a) 0.0067 m/s; and b) 2.5 m/s.

Table 1 summarizes the temperature at brittle-ductile transition at loading speeds (v) of 100 mm/min and 2.5 m/s for the non compatibilized (NC), K1 30 and K2 30 samples. Ductile behavior of fracture is observed at higher temperatures for the non compatibilized sample. Adding an interfacial agent results in a lower temperature at brittle-ductile transition. This effect is also much more pronounced with the K2 interfacial agent. With an impact loading of 2.5 m/s, the brittle-ductile transition occurs at around 0°C for the K2 30, 65°C for the K1 30, and 80°C for the NC samples. Furthermore, the dependence of fracture behavior on loading rate and temperature also depends on the molecular weight of the interfacial agent. When loading speed increases from 100 mm/min to 2.5 m/s, the shift in the transition temperature, $\Delta T$, is less significant in the K2 30 sample. The result is rather surprising since it has been generally recognized that the effects of loading rate and temperature on the mechanical properties of polymers are mainly controlled by molecular relaxation.

TABLE 1
APPROXIMATE TEMPERATURE AT BRITTLE-DUCTILE TRANSITION

| Blend | NC | K1 30 | K2 30 |
|---|---|---|---|
| v = 100 mm/min (0.00167 m/s) | 0°C | -10°C | -20°C |
| v = 100 mm/min (0.00167 m/s) | 80°C | 65°C | 0°C |

The above results indicate that morphology and interfacial strength also have a significant effect on the time-temperature dependence of fracture behavior. The differences in morphology and interface of these samples have been presented in [5]. It has been shown that adding these interfacial agents results in a continuous decrease in the diameter of the minor phase, and the lower molecular weight interfacial agent K2 results in a

more important reduction in this diameter. In this case, the volume average particle size is reduced from 2.72 to around 0.55 μm, a decrease of nearly 80%, whereas the K1 copolymer only decreased it to about 1.1 μm.

In terms of fracture performance, secondary transitions have often been found to play an important role and the energy barrier controlling the time temperature dependence of the fracture process can be estimated using the Arrhenius equation [7, 8]. The energy barrier $\Delta H$ controlling the time temperature dependence of the brittle-ductile transition in the fracture process can been estimated using a set of data of the temperatures and the average times to fracture measured at this transition. Table 2 summarises the effect of K1 and K2 on the activation energy ($\Delta H$) controlling the brittle-ductile transition in the fracture process. Increasing the amount of interfacial agent decreases the diameter of the minor phase and the value of $\Delta H$. Smaller diameters of the minor phase associated with K2 also results in a lower value of the activation energy.

TABLE 2
ACTIVATION ENERGY OF BRITTLE-DUCTILE TRANSITION

| Blend | NC | K1 2.5 | K1 10 | K1 20 | K1 30 | K2 2.5 | K2 15 | K2 30 |
|---|---|---|---|---|---|---|---|---|
| $\Delta H$ (kJ/mol) | 42.3 | 71.87 | 52.08 | 50.56 | 39.6 | 45.21 | 38.37 | 32.10 |

The yielding process of a polymer is usually regarded as a momentary condition of pure viscous flow because it denotes the point at which the change of stress with strain is zero for a given strain rate. It has been thus considered to be a thermally activated process involving inter-and intramolecular motion and has been described by Eyring's viscosity theory. Ree and Eyring [11] have suggested later that the yielding behavior of polymers could be controlled by two relaxation processes (α and β) acting in parallel. The equation governing the yield stress and the two molecular relaxation processes has been expressed by:

$$\frac{|\sigma_y|}{T} = \frac{|\sigma_{y\alpha}|}{T} + \frac{|\sigma_{y\beta}|}{T} = \frac{R}{V_\alpha^*}\left[\frac{\Delta H_\alpha}{RT} + 2.303\log\left(\frac{2\dot{\varepsilon}}{\dot{\varepsilon}_{o_\alpha}}\right)\right] + \frac{R}{V_\beta^*}\sinh^{-1}\left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{o_\beta}}\exp\left(\frac{\Delta H_\beta}{RT}\right)\right]$$

where $\Delta H$ denotes the activation energy of the yielding process, $T$ the absolute temperature, $\dot{\varepsilon}$ the strain rate (proportional to the cross-head speed ). $V^*$ is known as the activation volume, $\dot{\varepsilon}_o$ is the pre-exponential factor and R is the universal gas constant. The symbols $\alpha$ and $\beta$ refer to $\alpha$ and $\beta$ relaxation process respectively. In order to verify the Ree-Eyring model, compression tests have been carried out over a wide range of temperatures. The yield stress in uniaxial compression was measured at different temperatures from -75°C to 100°C and over nearly four decades of loading rate from 0.1 to 200 mm/min. An example for the time-temperature dependence of the yielding behavior of the K1 2.5 blend is shown in Figure 4.
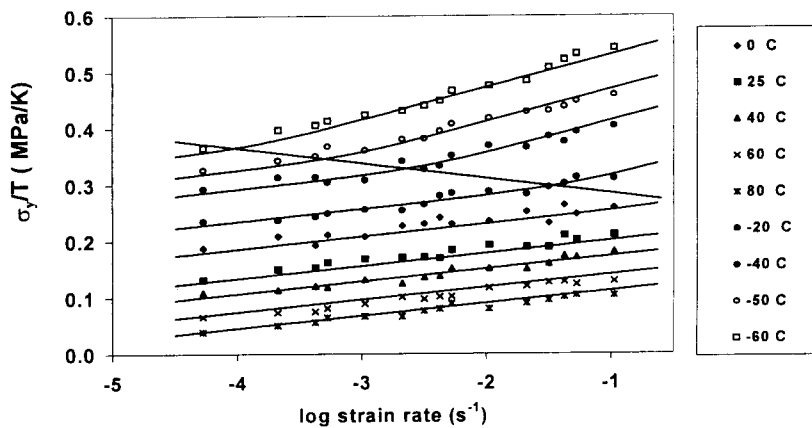


Figure 4: Time - temperature dependence of yield stress for K1 25 sample.

It can be seen that the diagram of $\sigma_y/T$ versus logarithm strain rate can be separated into two regions: region I at high temperature and low loading rate where the process $\alpha$ dominates; and the region II at low temperature and high loading rate where the process $\beta$ is activated. Between the regions $\alpha$ and $\beta$, the curve of $\sigma_y/T$ as a function of logarithm strain rate shows a noticeable variation in slope. This variation can be used to find the transition boundary between these two regions by standard mathematics or using the procedure proposed in [12]. In Table 3, the values of the parameters ($V_\alpha^*$, $\Delta H_\alpha$, $\dot{\varepsilon}_{0_\alpha}$, $V_\beta^*$, $\Delta H_\beta$, $\dot{\varepsilon}_{0_\beta}$) characterizing the yielding behavior of the blend with three compositions; K1 2.5, K1 10 and K1 20, are presented. It can be seen that the addition of interfacial agent results in an increase in the activation volume $V^*$ and a reduction of the activation energy $\Delta H$ for both $\alpha$ and $\beta$ processes. The results also show that the values of energy barrier controlling the $\beta$ process are close to those presented in Table 2, measured by the brittle-ductile transition of the fracture tests. This suggests that the brittle-ductile transition in fracture behavior is controlled by a secondary relaxation of the polymer molecules. Furthermore, the plasticizing effect of the interfacial agent also reduces the energy barrier of the secondary motions that occur at low temperatures and high loading rates. The correlation between the activation energy of the $\beta$ process and the energy barrier controlling the brittle-ductile transition suggests therefore that there is an implicit correlation between yielding and the fracture behavior.

TABLE 3
PARAMETERS CONTROLLING THE $\alpha$ AND $\beta$ PROCESSES IN YIELDING

| Blend | $\Delta H_\alpha$ (kJ/mol) | $V_\alpha^*$ (nm$^3$/segment) | $\Delta H_\beta$ (kJ/mol) | $V_\beta^*$ (nm$^3$/segment) |
|---|---|---|---|---|
| K1 2.5 | 145 | 1.43 | 66 | 0.89 |
| K1 10 | 138.3 | 1.46 | 61.1 | 0.91 |
| K1 20 | 133.5 | 1.58 | 58 | 1.13 |

## CONCLUSION

The organization of polymer blend structure plays an important role in the dependence of fracture behavior on time and temperature. The time-temperature dependence of the brittle-ductile transition in fracture performance of the blend is controlled by an energy activation process and can be predicted by the Arrhenius equation. The yielding behavior of the blend is controlled by two processes ($\alpha$ and $\beta$) acting in parallel and can be predicted by the Ree-Eyring model. It has also been found the value of energy barrier controlling the $\beta$ process in yielding is close to the energy barrier controlling the brittle-ductile transition in fracture. The results suggest an implicit correlation between yielding and fracture behavior.

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