CHAPTER III

RESULTS AND DISCUSSION

In this chapter, there are two main results: mechanical properties and dynamic mechanical properties.

3.1 Dynamic Mechanical Properties

Dynamic mechanical properties were measured by DMA, using the time/temperature scan mode and the parallel plate probe. Compressive loss modulus (K'') and storage modulus (K') were measured.

Dynamic mechanical properties in this chapter are described into two parts: loss modulus and storage modulus.

3.1.1 Loss Modulus

Immiscible blend of polystyrene (PS) and polyisoprene (PI) shows two amorphous phases by the presence of two glass transition temperatures (T_g or T_α) of PS and PI. T_g of PS is between 80°C to 100°C, and T_g of PI is between -60°C to -40°C. In the region where temperature is lower than the glass transition temperature, it is called the glassy state. In the glassy state, the stiffness depends on the stored elastic energy upon deformation which is due to small displacements of the molecules. In the region in which temperature is higher than the glass transition temperature, it is called the rubbery state. In the rubbery state, the molecular chains have considerable flexibility.

In fig. 3.1, it is the loss modulus-temperature curves of PS/PI blends which have two main peaks, one for each blend component; they are called the PI peak and the PS peak. In the region where the curves have the main peaks, the loss modulus curve reaches a maximum; it is called the glass transition region.

At the glass transition region, the loss modulus is high because of the initiation of micro Brownian motion in molecular chains (Murayama, 1992). Some of the molecular chain segments are free to move, others are not. A frozen segment can store much more energy for a given deformation than a free-to-move rubbery segment. So, when frozen segments become free to move, their excess energy is dissipated as heat.

Effect of Block Copolymer on the Loss Modulus

The effects of block copolymer were studied for the PS/PI blend composition of 75/25. Percentages of block copolymer [P(S-*b*-I)] were varied from 0 %, 0.5 %, 1.0 %, 2.0 %, and 4.0 %. In fig. 3.2, it is the loss modulus-temperature curves of the blends with different % block copolymer contents.

(a) Effect of % Block Copolymer on the Transition Temperature

In fig. 3.3, the effect of block copolymer on the transition temperature is shown. The transition temperatures of the blends are nearly constant. For the transition temperature of PS-loss modulus peaks, they vary between 55.42°C and 75.64°C. For the transition temperature of PI-loss modulus peaks, they are between -52.93°C and -48.20°C.

The effect on the T_α is not evident because % block copolymer is too small to increase the miscibility of the blends. If the miscibility of the blend increases, the transition temperature of PS and PI would shift closer toward a single transition temperature.

(b) Effect of % Block Copolymer on the Loss Modulus at the Transition Temperature

In fig. 3.4, it is the effect of block copolymer on the loss modulus peak. The loss moduli of PS peaks are nearly constant with values between 10.4 MPa and 11.3 MPa. However, the loss modulus of the PI peak decreases from 6.74 MPa to 2.63 Mpa when % block copolymer from 0 to 4 % is increased. .

When the block copolymer is added, the interfacial adhesion between PS and PI is increased. PS is in the glassy state at the transition temperature of PI, and the loss modulus of PS is low. When interfacial adhesion between PS and PI increases, the loss modulus of PI is reduced.

Effect of Composition Ratio on the Loss Modulus

The effects of composition ratio were studied for blends with 1 % block copolymer and blends without the block copolymer. In fig. 3.5, the effect of % block copolymer on the loss modulus of PS/PI (83/17) blend is shown. For this blend composition, there is a particular morphology in which the block copolymer works well at the interphase and can show different loss modulus values between the blend with 1% block copolymer and the blend without block copolymer.

(a) Effect of Composition Ratio on the Transition Temperature

Figure 3.6 shows the transition temperature obtained from the PS-loss modulus peak at various blend compositions. For pure PS, the transition temperature is 86.2°C, a value close to T_g and can be considered as T_α for PS. T_α of PS increases with PI content, to values between 100°C-125°C when the blends are mostly PI or rubberlike. The effect of % block copolymer on T_α is nearly negligible and cannot be discerned from the measurements.

T_α of PS increases with PI content or when PI is added; the increase in T_α for PS on adding PI is unclear. Perhaps, plasticsisers are removed from PS and concentrated in PI which will shift T_α of PS to a higher value. Fluctuation in T_α for the blends with low PI contents comes from two sources. Most likely, because two different sets of blend were prepared. The blends which have composition ratios of PS/PI = 92/8, 75/25, and 58/42 were prepared and measured after the first set which have composition ratios of PS/PI = 100/0, 83/17, 67/33, 50/50, 33/67, 17/83, and 0/100. There are significant differences (in T_α) between the two sets of samples even though the sample preparations were controlled carefully. Thus, there may be differences in film uniformity and morphology between the two sets of blend composition.

Figure 3.7 shows the transition temperature obtained from the PI-loss modulus peak for various blend compositions. The transition temperature for pure PI is -45.4°C. There is a significant change in the PI-transition temperature for these blend compositions. The transition temperatures of the blends with 1% block copolymer and the blend without block copolymer are nearly the same.

(b) Effect of Composition Ratio on the Loss Modulus at the Transition Temperature

In fig. 3.8, the effect of composition ratio on PS-loss modulus peak is shown. For pure PS, the loss modulus peak is 3.0 MPa. The loss modulus of PS peak is high when % PI is small (between 8-25 %). For the PS/PI blend (75/25) without block copolymer, the maximum loss modulus peak is 10.9 MPa. For the PS/PI blend (83/17) with 1 % block copolymer, the maximum loss modulus peak is 12.6 MPa. The maximum loss modulus peaks between the blend with 1 % block copolymer is higher than the blend without block copolymer.

This is because when PI is dispersed in PS matrix, the blends have more ability to dissipate energy. So the PS-loss modulus peaks of the blends will increase. But when PI becomes the matrix of the blends, the PS-loss modulus peak would approach the pure PS value. For the blend with 1 % block copolymer with a particular morphology (PS/PI = 83/17), the block copolymer acts as a compatibilizer which facilitates stress transfer between the dispersed PI and the PS matrix and hence increases the PS-loss modulus of the blend.

In fig. 3.9, it is the effect of composition ratio on the PI-loss modulus peak. The PI-loss modulus peak decreases with the % PS content. For the blends without block copolymer, loss modulus increases from 0.58 MPa (% PI = 17 %) to 10.6 MPa (pure PI). For the blends with 1 % block copolymer, loss moduli are between 3.04 MPa (% PI = 33 %) and

10.6 MPa (pure PI). Loss moduli between the blend with 1% block copolymer and the blend without block copolymer are nearly the same.

The PI-loss modulus peak of the blend increases with PI content. This is because at the low temperature, it is difficult to measure the PI-loss modulus when PS is glassy. But when PI content is increased, the loss modulus of PI can be measured easier.

3.1.2 Storage Modulus

In fig. 3.10, it is the effect of composition ratio on the storage modulus. Inflection point in the blend is defined as the glass transition temperature. For each blend, PS has a peak in the storage modulus before the expected sudden decrease. The appearance of a peak may come from two factors.

The first reason is the free volume effect. The free volume effect is more dominant in the measurement of the compressive modulus. There are some differences between the compressive modulus, the extensional modulus, and the torsional modulus. When dynamic mechanical properties were measured in the time/temperature scan mode, this measurement involved the free volume of the materials. When the materials is in glassy state, the occupied volume increases uniformly with temperature. At transition temperature of the materials, the discontinuity in the expansion coefficient at T_g corresponds to a sudden onset of expansion in the free volume, which suggests that certain molecular processes which control the viscoelastic behavior commence at T_g. In the extensional and torsional measurements, free volume of the materials can expand without any limits of clamps, because there are free spaces between the top clamp and the bottom clamp. The top clamp and the bottom clamp of extensional and torsional measurements do not contact the whole surface area of the sample like those of the compressive measurements do. For the compressive measurement, at T_g, free volume of the materials can not expand freely because the materials are constrained during measurement.

The second reason is the thickness of the polymer blend film. The film thickness is quite thin (0.4-0.5 mm.), so compressional modulus measured at $T << T_g$ may not show a correct plateau due to the limitation of the DMA on the maximum force. It will show a correct plateau when some molecules of the film can move and allow the probe to compresses on the film.

Effect of Block Copolymer on the Storage Modulus

The effects of block copolymer were studied for the blend composition of PS/PI is equal to 75/25. Percentages of block copolymer [P(S-*b*-I)] were varied from 0 %, 0.5 %, 1.0 %, 2.0 %, and 4.0 %. In fig. 3.11, it is the storage modulus-temperature curves of the blends with different % block copolymer.

(a) Effect of % Block Copolymer on the Transition Temperature

In fig. 3.12, the effect of block copolymer on the transition temperature is shown. The transition temperatures of the blends are nearly the same. The transition temperature of the PS-storage modulus inflection is between -51.0°C to -42.9°C. The transition temperature of the PI-storage modulus inflection is between 63.1°C to 78.5°C.

This is because addition of block copolymer changes the structure of the phases but not their composition. The transition temperatures of PS and PI are therefore not altered.

(b) Effect of % Block Copolymer on the Storage Modulus

Figure 3.13 shows the effect of % block copolymer on the PS-storage modulus peak. This figure shows the maximum storage modulus (52.5 MPa) for the blend with 1 % block copolymer added.

For the binary blend system, there is an optimal amount of the compatibilizer. If the amount of compatibilizer is too high, the compatibilizer may not act as a phase linker but will change the binary blend system to a ternary blend system.

Figure 3.14, it is the effect of % block copolymer on PI-storage modulus plateau. This figure shows the maximum storage modulus for the blend with 1 % block copolymer, similar to the PS result in fig. 3.13.

For the small % block copolymer (0.5 % - 4.0 %), 1 % block copolymer is the optimum amount which effectively increases the storage moduli of the blends.

Effect of Composition Ratio on the Storage Modulus

The effects of composition ratio were studied for the blends with 1 % block copolymer and the blend without block copolymer. In fig. 3.15, the effect of % block copolymer on storage modulus of the PS/PI (83/17) blend is shown

(a) Effect of Composition Ratio on the Transition Temperature

In fig. 3.16, it is the effect of composition ratio on the PS-transition temperature of the PS-storage modulus For pure PS, the PS-transition temperature is 103.4°C. The fluctuation is in the range of 67.9°C and 118.9°C. And the effect of % block copolymer on the transition temperature is nearly negligible.

Fluctuation observed in the transition temperature-composition ratio curve will be explained by the differences between the two sets of the samples.

Figure 3.17 shows the effect of composition ratio on the PI-transition temperature of the PI-storage modulus. For pure PI, the PI-transition temperature is -43.8°C. The PI-transition temperatures of the blends are almost constant when PI increases. The PI-transtion temperatures of the blends with 1% block copolymer and the blends without block copolymer are nearly the same.

This is because at the low temperature, PS cannot affect the PI-transition temperature so much as the PS-molecular chains cannot move at very low temperature.

(b) Effect of Composition Ratio on the Storage Modulus

In fig. 3.18, the effect of composition ratio on the PS-storage modulus peak is shown. For pure PS, the storage modulus peak is 10.6 MPa. The blends with 1 % block copolymer have the highest value at the PS/PI blend composition of 75/25; it is 52.5 MPa. The PS-storage modulus peaks of the blends without block copolymer are in the range of 10.6 MPa and 25.5 MPa.

At the low % PI (% PI varied between 8 to 25 %), the interfacial area between PS and PI is small and the block copolymer can act as an effective compatibilizer. Block copolymer can increase storage modulus of the blend by stabilizing the dispersed PI in the PS matrix.

In fig. 3.19, it is the effect of composition ratio on the PI-storage modulus plateau. For pure PI, the storage modulus plateau is 41.2 MPa. For the PS/PI blends with 1 % block copolymer with % PI varied between 0 to 42 %, the PS/PI (75/25) blend has the maximum PI-storage modulus plateau of 39.9 MPa. For the PS/PI blends without block copolymer with % PI varied between 0 to 42 %, the PS/PI (75/25) blend has the maximum PI-storage modulus plateau of 23.8 MPa. But when % PI content is higher than 42 %, the PI-storage modulus of the blends will increase as % PI increases.

At very low temperature both PS and PI are in the glassy states. When PI is dispersed with a small amount in the PS matrix, it can increase storage modulus of the blend because PI will act like a reinforcement. But as % PI increases, PS and PI will separate toward a symmetrical blend state which has a low interfacial adhesion and the PI-storage modulus of the blend decreases. When PI is the matrix, the (compressive) PI-storage modulus is higher than PS, so the PI-storage modulus of the blend will increase as %PI increases.

3.2 Mechanical Properties

Mechanical properties were measured by DMA, using the creep recovery mode and the extension probe. Young's modulus was measured; stress rate and composition ratio were varied in this measurement. The Young's modulus was converted to strain rate by the following equations;

$$E = \sigma/\varepsilon = (\partial\sigma/\partial t)/(\partial\varepsilon/\partial t), \quad (3.1)$$

$$(\partial\varepsilon/\partial t) = (\partial\sigma/\partial t)/E, \quad (3.2)$$

where

E = Young's modulus (Pa)

$(\partial\sigma/\partial t)$ = stress rate (mN/min)

$(\partial\varepsilon/\partial t)$ = strain rate ($\min^{-1}$)

To convert from mN to Pa:

Pa = (mN)x(1,000)/(Area).

In this paper, mechanical properties will be explained in two parts.

3.2.1 Young's Modulus

Figure 3.20 shows the Young's moduli of the blends at various compositions and compares the blends with 1 % block copolymer and the blends without the block copolymer.

Effect of Composition Ratio on the Young' Modulus

For the blends with % PI between 25 to 50 %, the Young's modulus decreases as the blends become PI riched. For the blends with % PI between 50 to 100 %, the Young's modulus decreases slightly toward PI's value.

This is because Young's modulus of PI is lower than Young's modulus of PS.

Effect of % Block Copolymer on the Young's Modulus

For the blends with % PI between 25 to 50 %, the Young's moduli of the blends with 1 % block copolymer and the blend without block copolymer are nearly the same. For the blends with % PI between 50 to 100 %, the Young's moduli of the blends with 1 % block copolymer are higher than those of the blends without block copolymer.

This is because when % PI is lower than 50 %, PS is the matrix in the blends; extensional loading will almost influence only PS in the PS- matrix blend. When the block copolymer is added, it cannot improve the Young's modulus of the blend. But when PI is the matrix, the interfacial adhesion between the dispersed PS and the PI matrix improved by the block copolymer can increase the Young's modulus of the blends.

3.2.2 Strain Rate or Rate of Deformation

Figs 3.21-3.26 show the effects of composition ratios, % block copolymer, and stress rates on the strain rates.

Effect of Composition Ratio on the Strain Rate

In the strain rate-composition ratio curve, there is an inflection point which occurs between the strain rate values of the PS/PI (58/42) and PS/PI (50/50).

This is possibly because at that inflection point, phase inversion may occurs. The PS-matrix blend becomes the PI-matrix blends.

Effect of % Block Copolymer on the Strain Rate

For the blends with % PI higher than 50 %, the strain rates of the blends with 1 % block copolymer are smaller than those of the blends without block copolymer.

This comes from the effect of the block copolymer that acts as a phase linker between the dispersed PS and the PI matrix. PS is rigid and has a higher Young's modulus. When the adhesion at the interphase increases, it induces the strain rates of the blends with the block copolymer to lower values.

Effect of the Stress Rate on the Strain rate

For the blends with % PI higher than 50 %, the strain rate gaps between the blends with 1 % block copolymer and the blends without the block copolymer increase as the stress rates increase.

At the low stress rates (10, 100, and 200 mN/min) were applied, there is enough time for the PI-matrix blends to relax. So the block copolymer shows an effect as a phase linker at these low stress rates. But for the high stress rates (300, 400, and 500 mN/min), there is not enough time for the PI-matrix blend to relax.

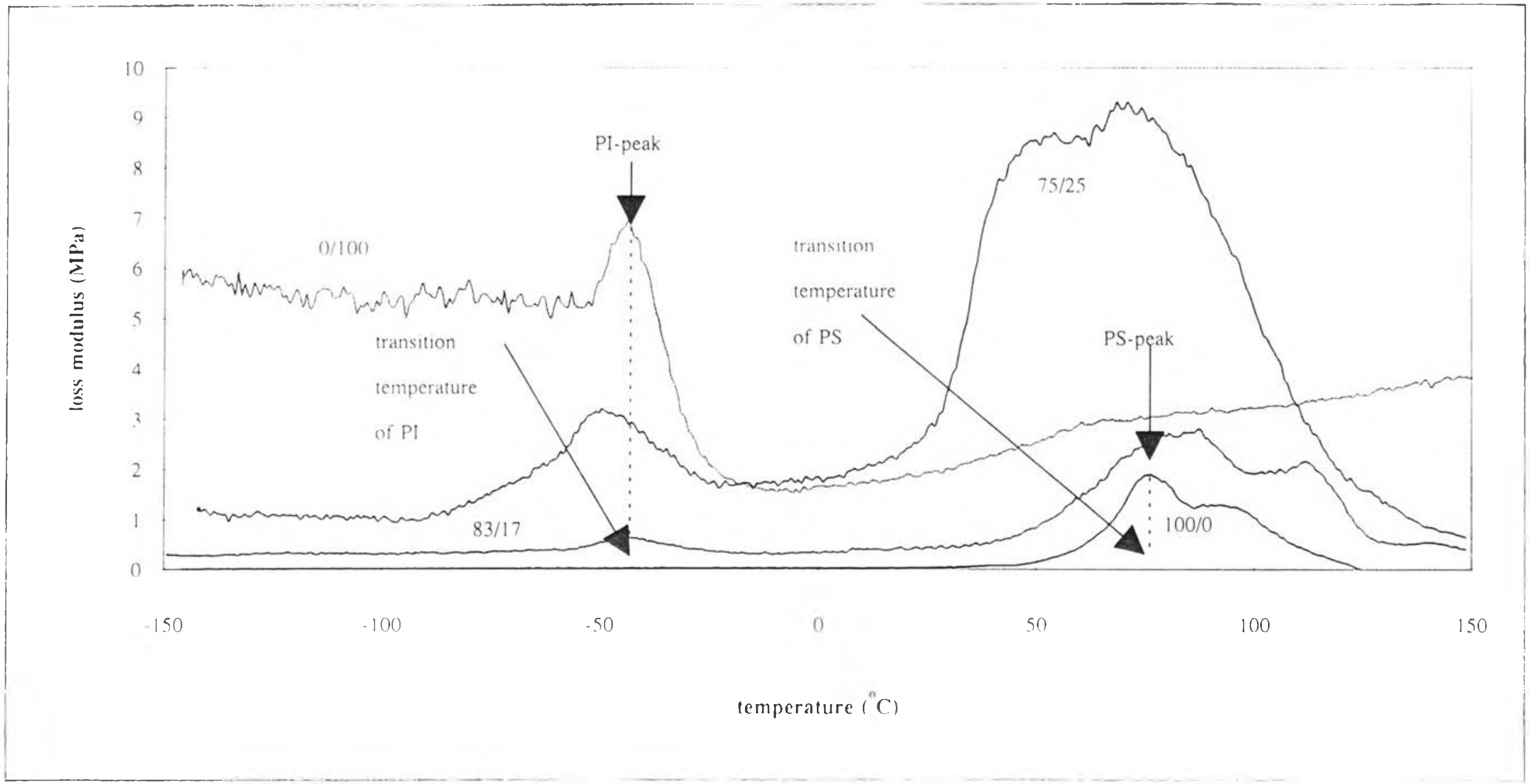

Figure 3.1 Effect of composition ratio on the loss modulus of PS/PI blends.

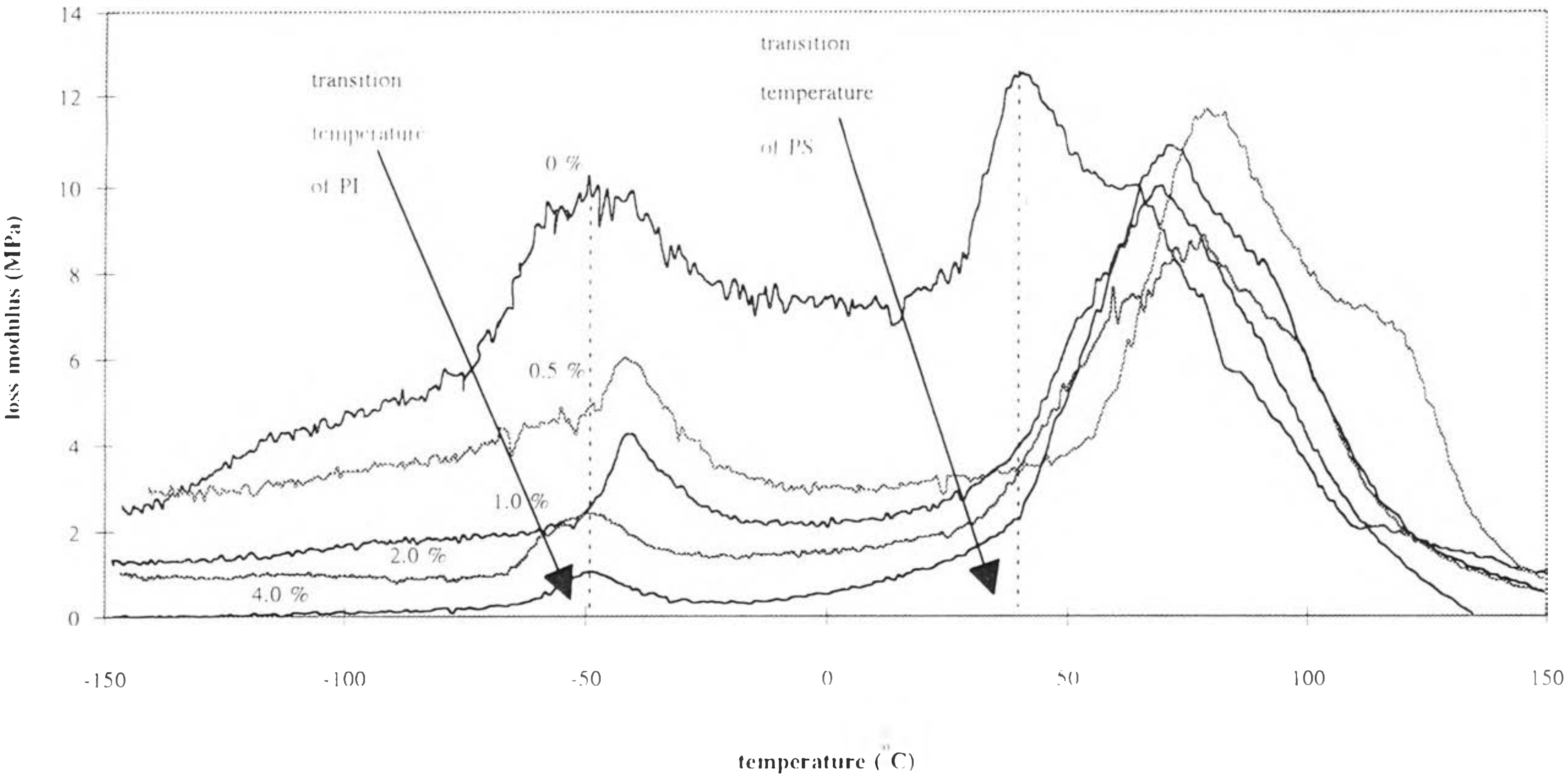

Figure 3.2 Effect of % block copolymer on the loss modulus of PS/PI (75/25) blends

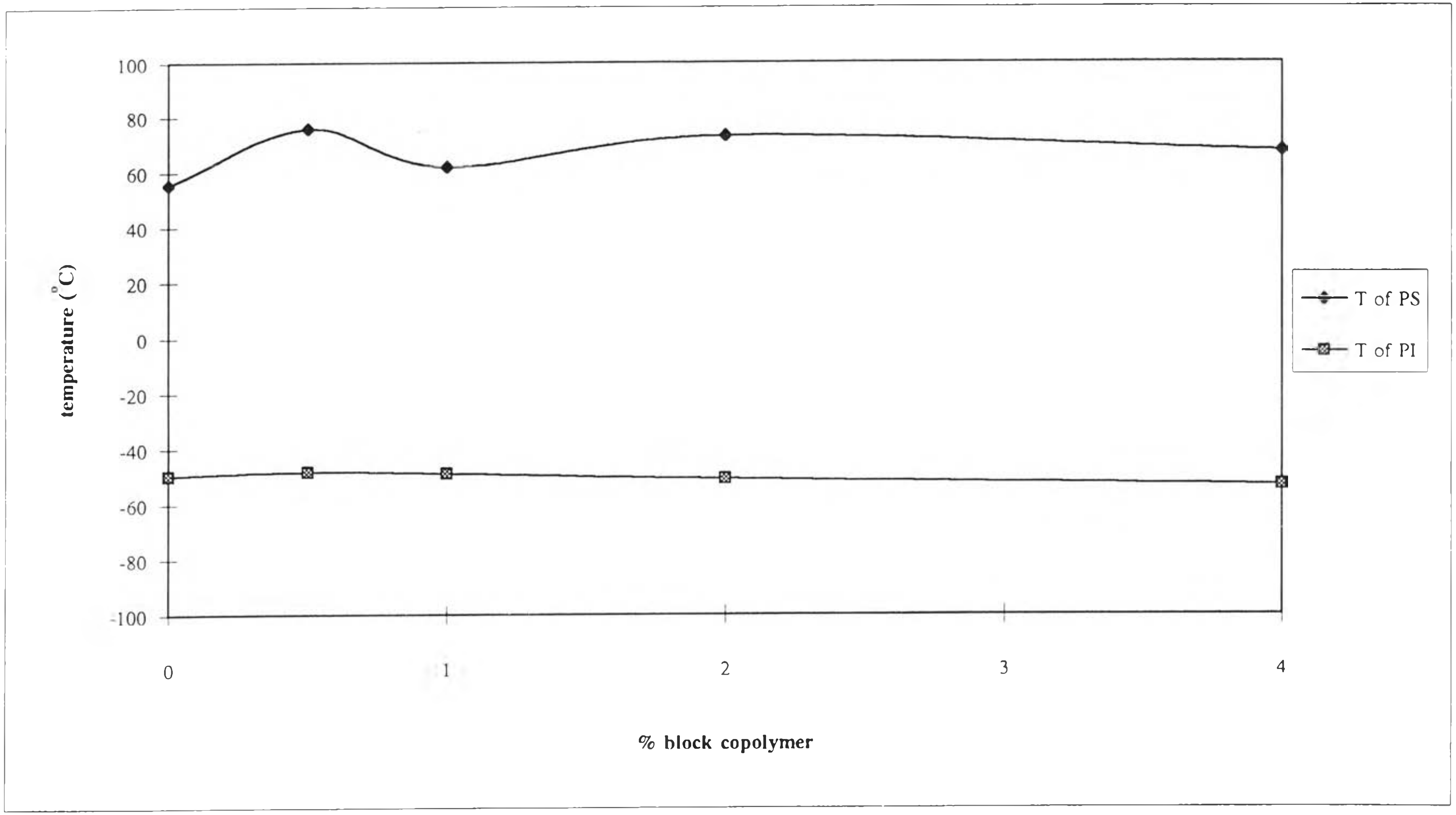

Figure 3.3 Effect of % block copolymer on the transition temperature (loss modulus peak) of PS/PI (75/25) blends.

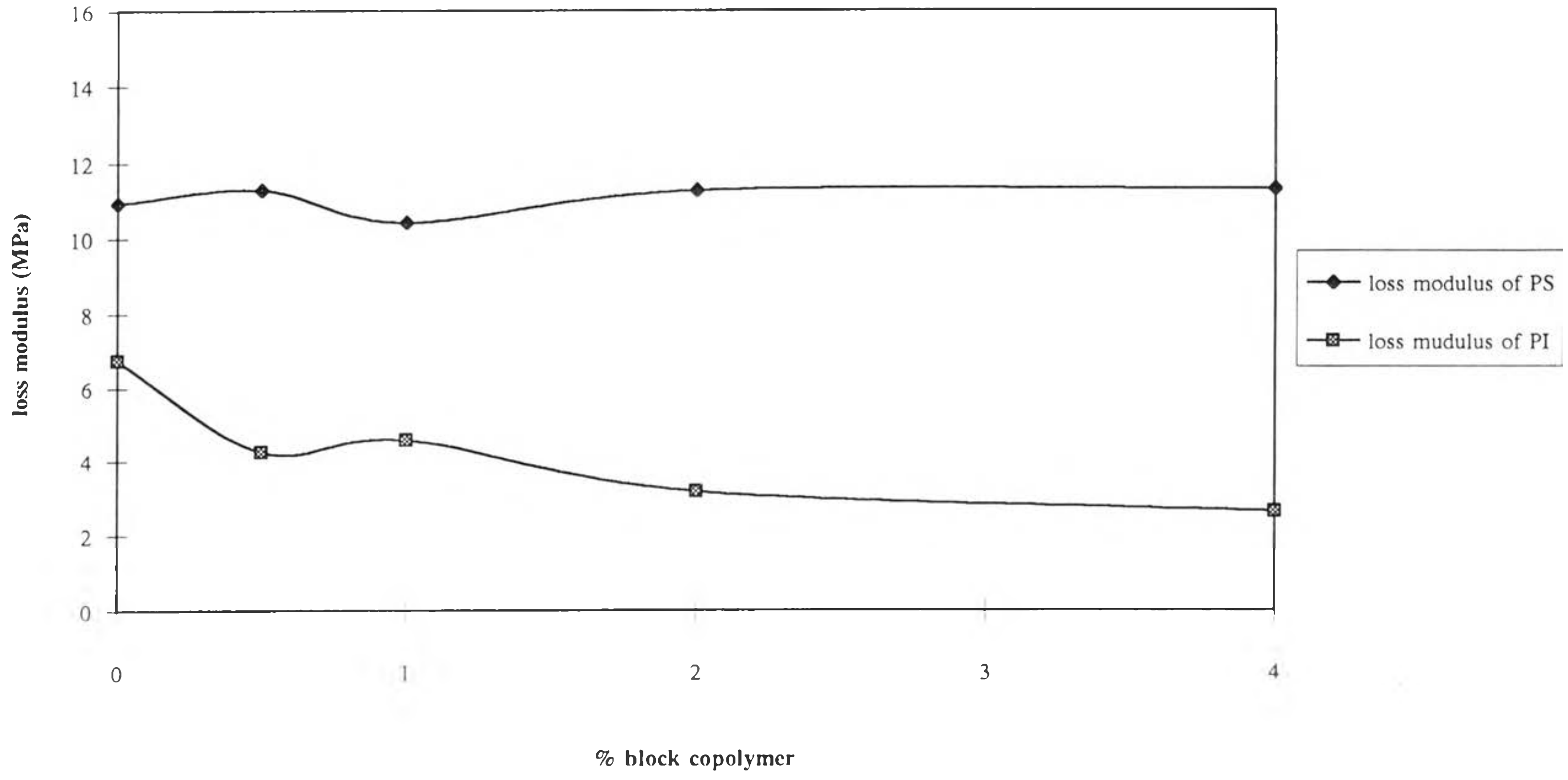

Figure 3.4 Effect of % block copolymer on the loss modulus peak of PS/PI (75/25) blends.

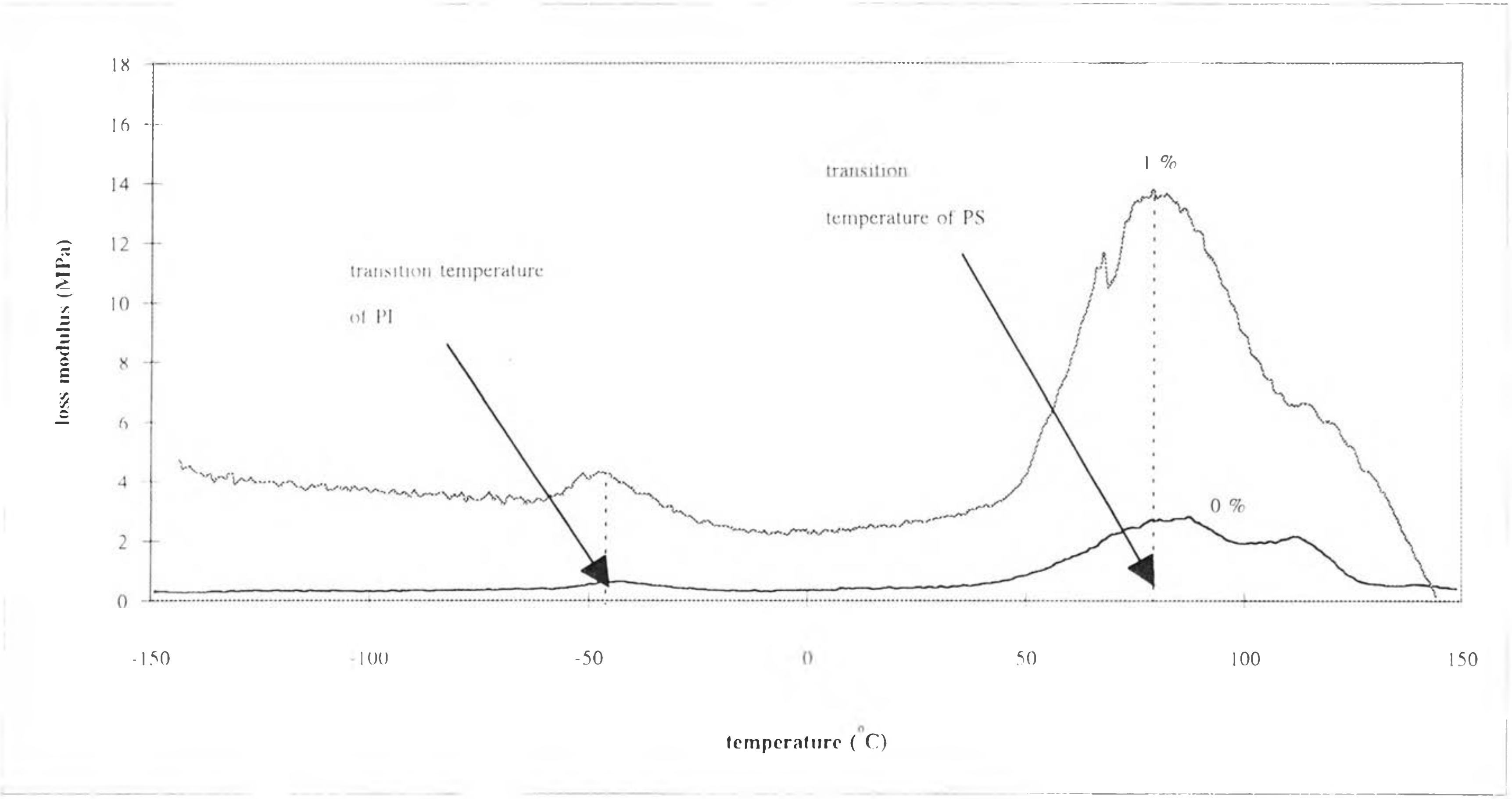

Figure 3.5 Effect of % block copolymer on the loss modulus of PS/PI (83/17) blends.

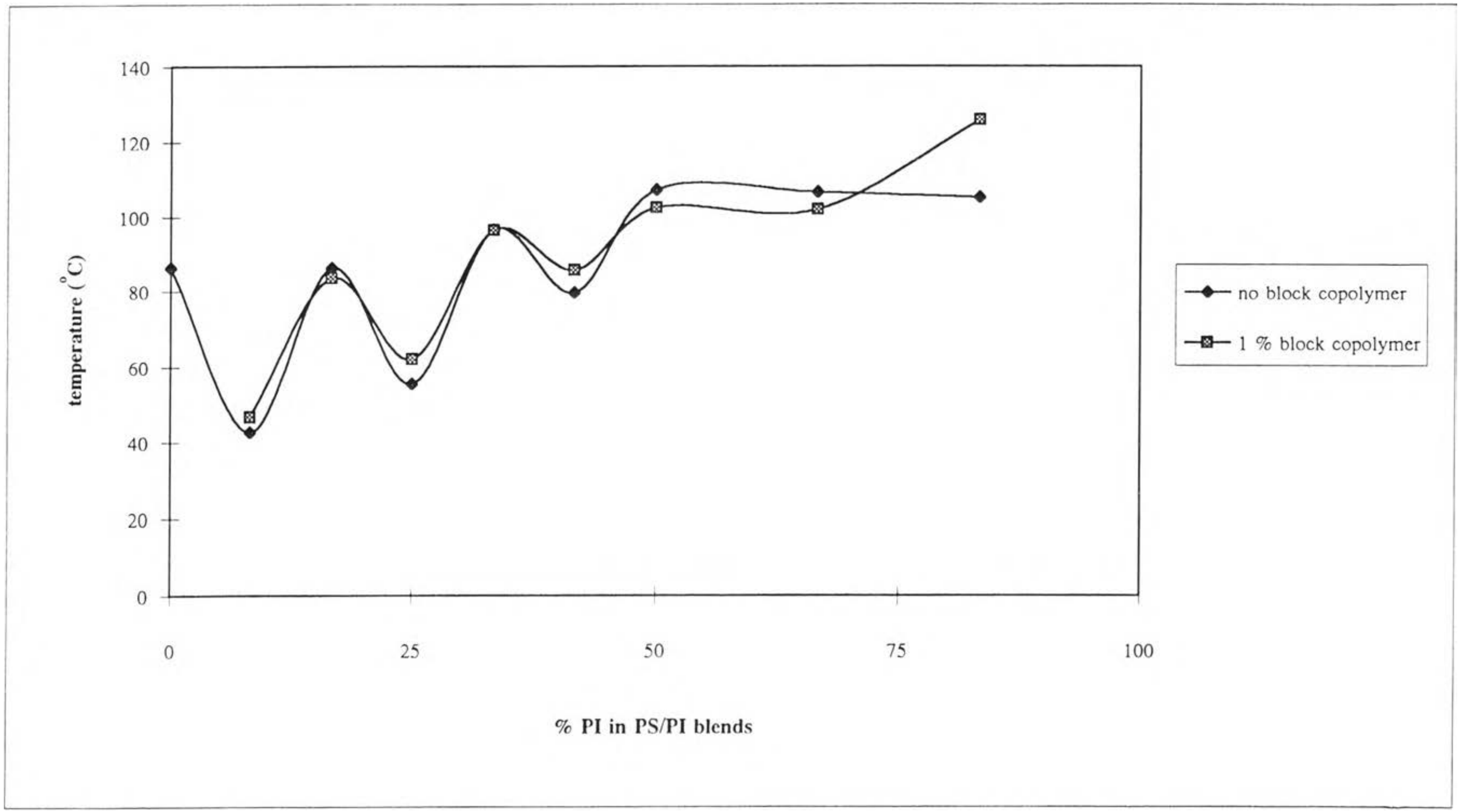

Figure 3.6 The transition temperature of PS-loss modulus peak as a function of % PI with and without the diblock copolymer.

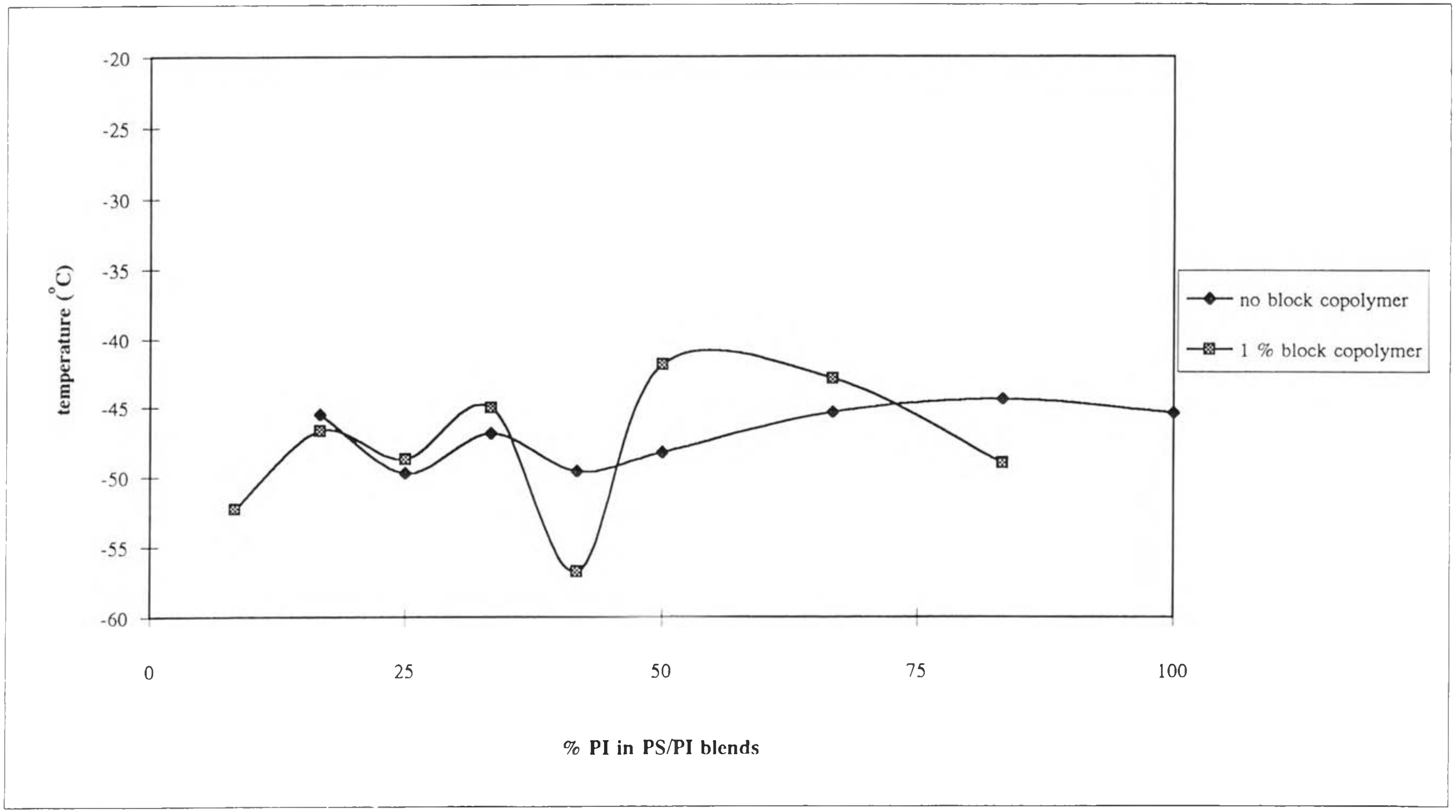

Figure 3.7 The transition temperature of PI-loss modulus peak as a function of % PI with and without the diblock copolymer.

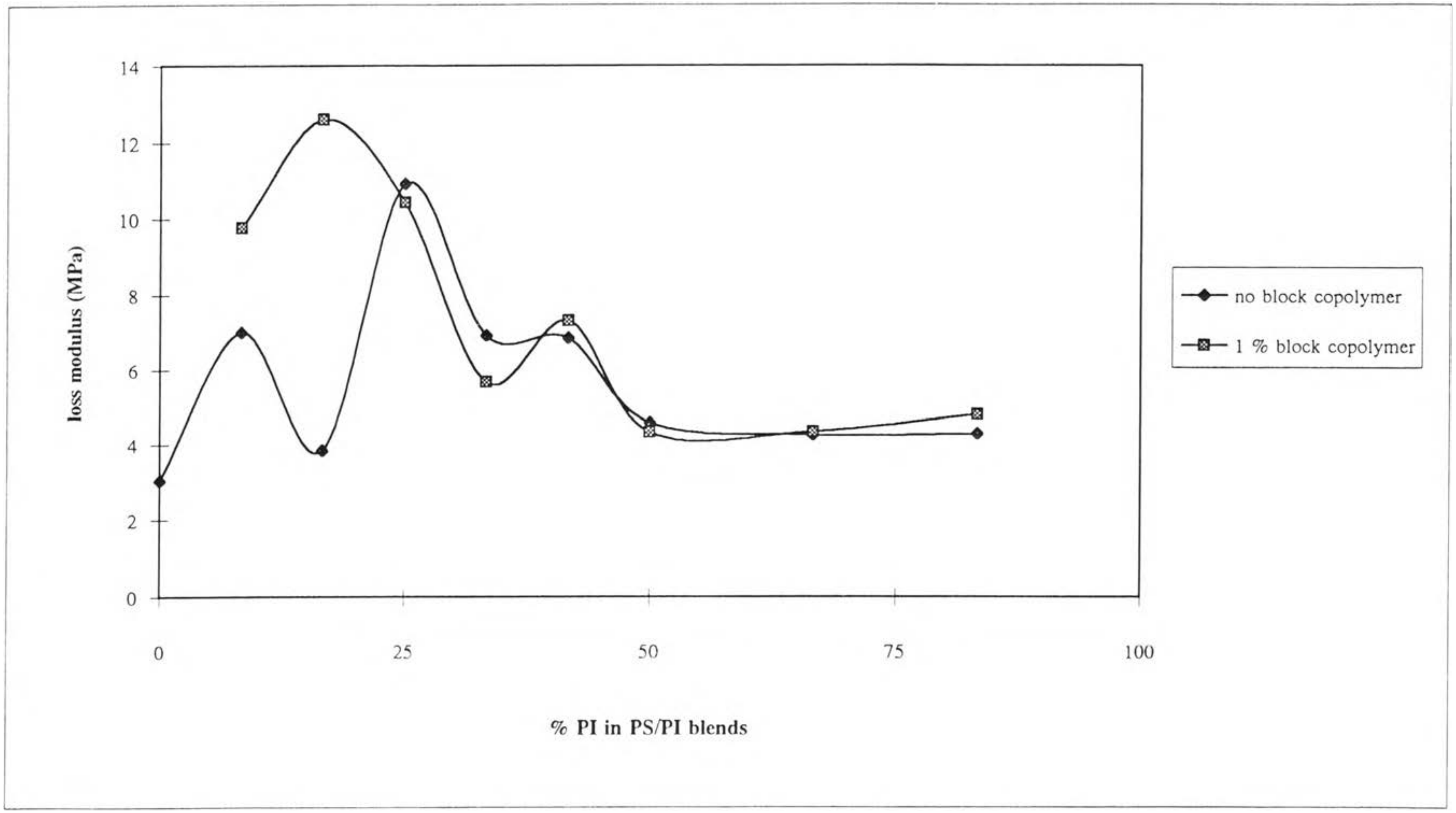

Figure 3.8 The PS-loss modulus peak as a function of % PI with and without the diblock copolymer.

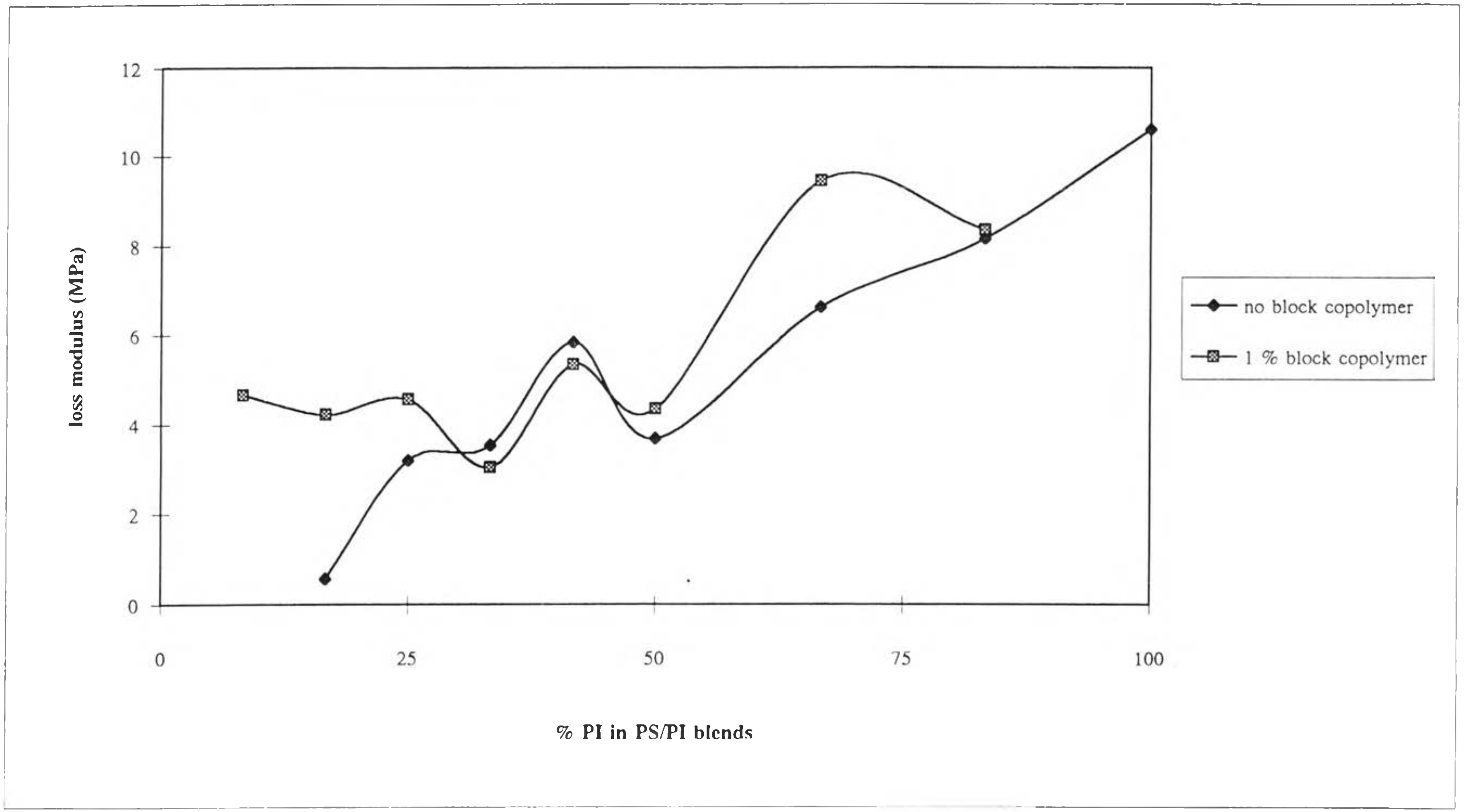

Figure 3.9 The PI-loss modulus peak as a function of % PI with and without the diblock copolymer.

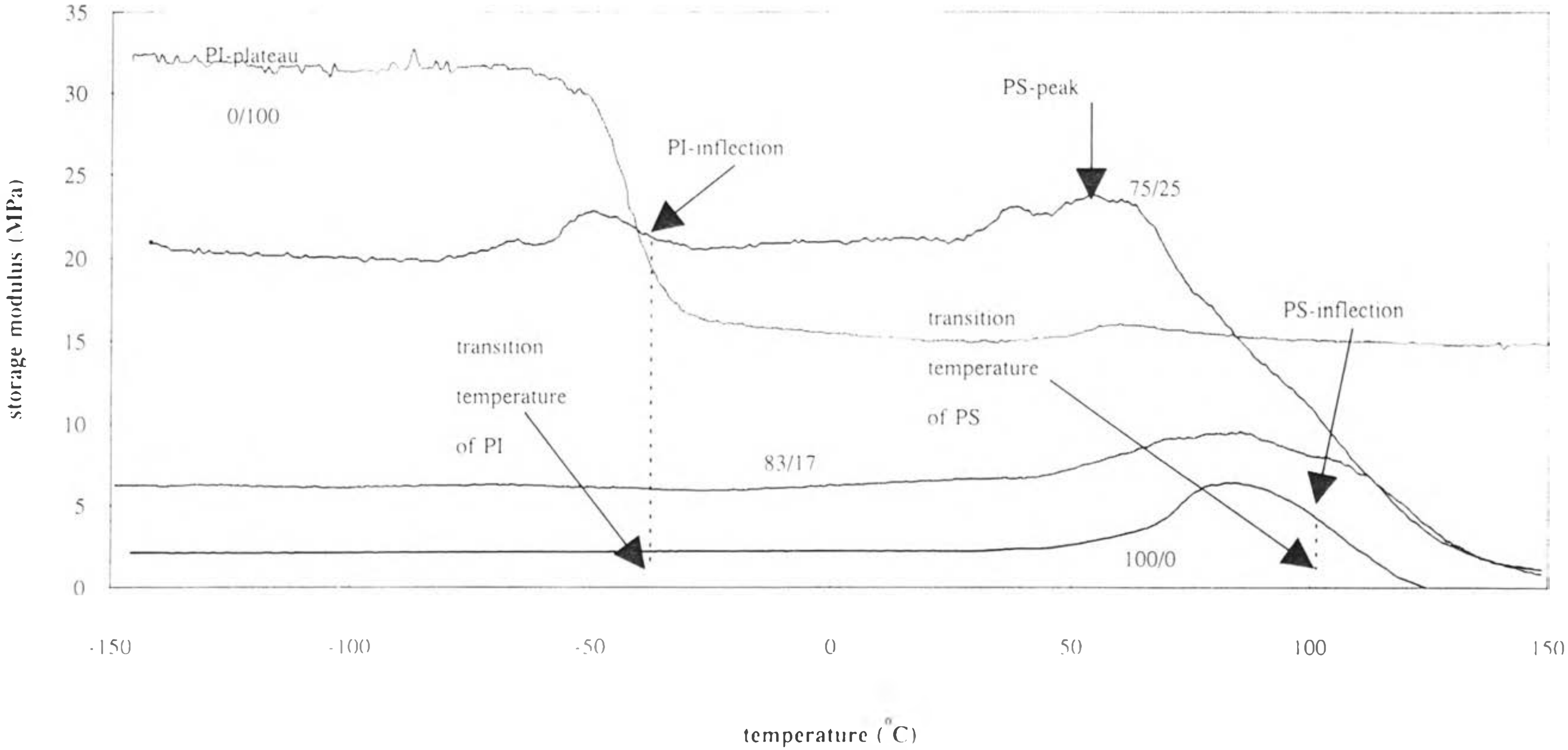

Figure 3.10 Effect of composition ratio on the storage modulus of PS/PI blends.

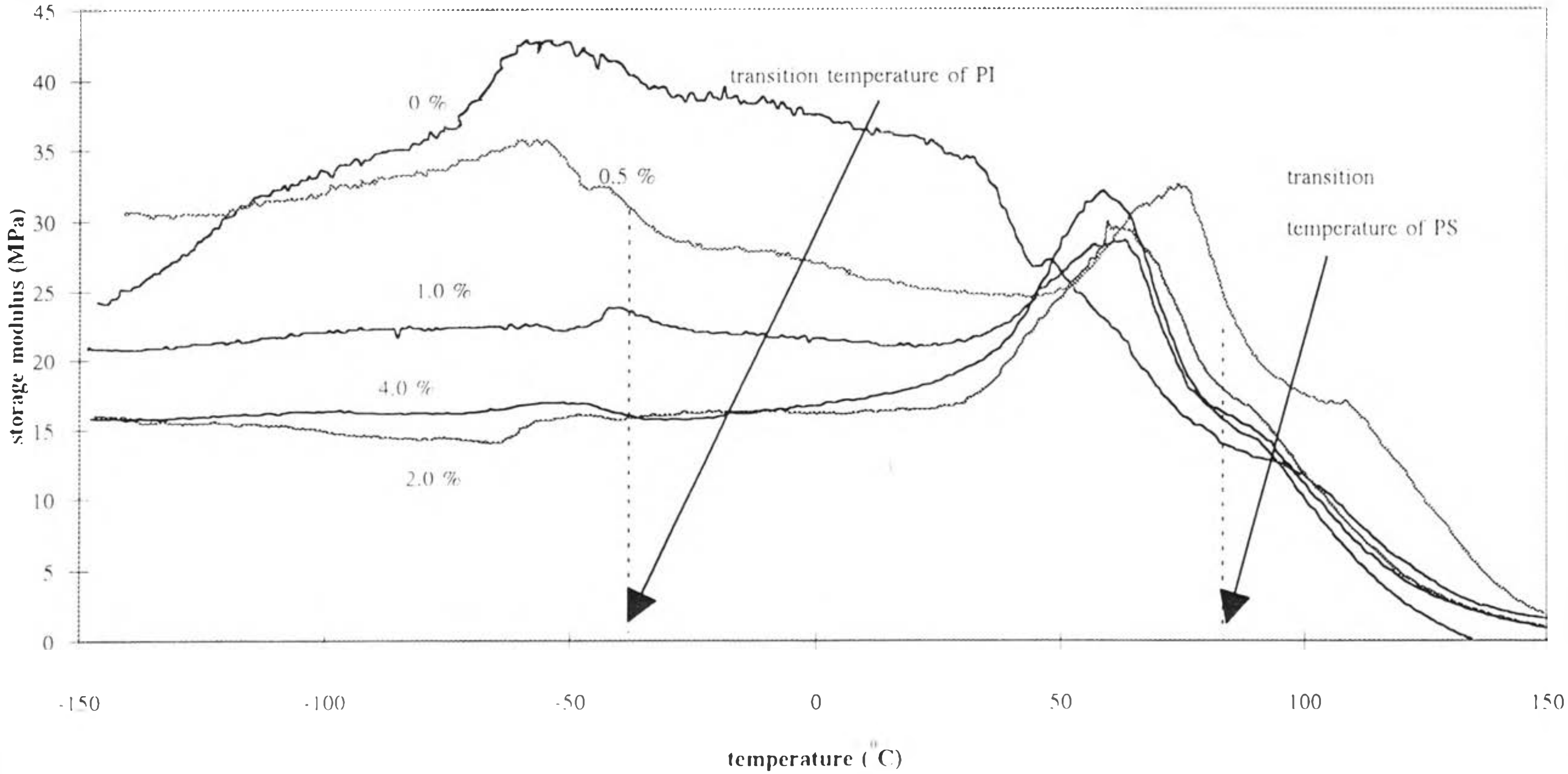

Figure 3.11 Effect of % block copolymer on the storage modulus of PS/PI (75/25) blends.

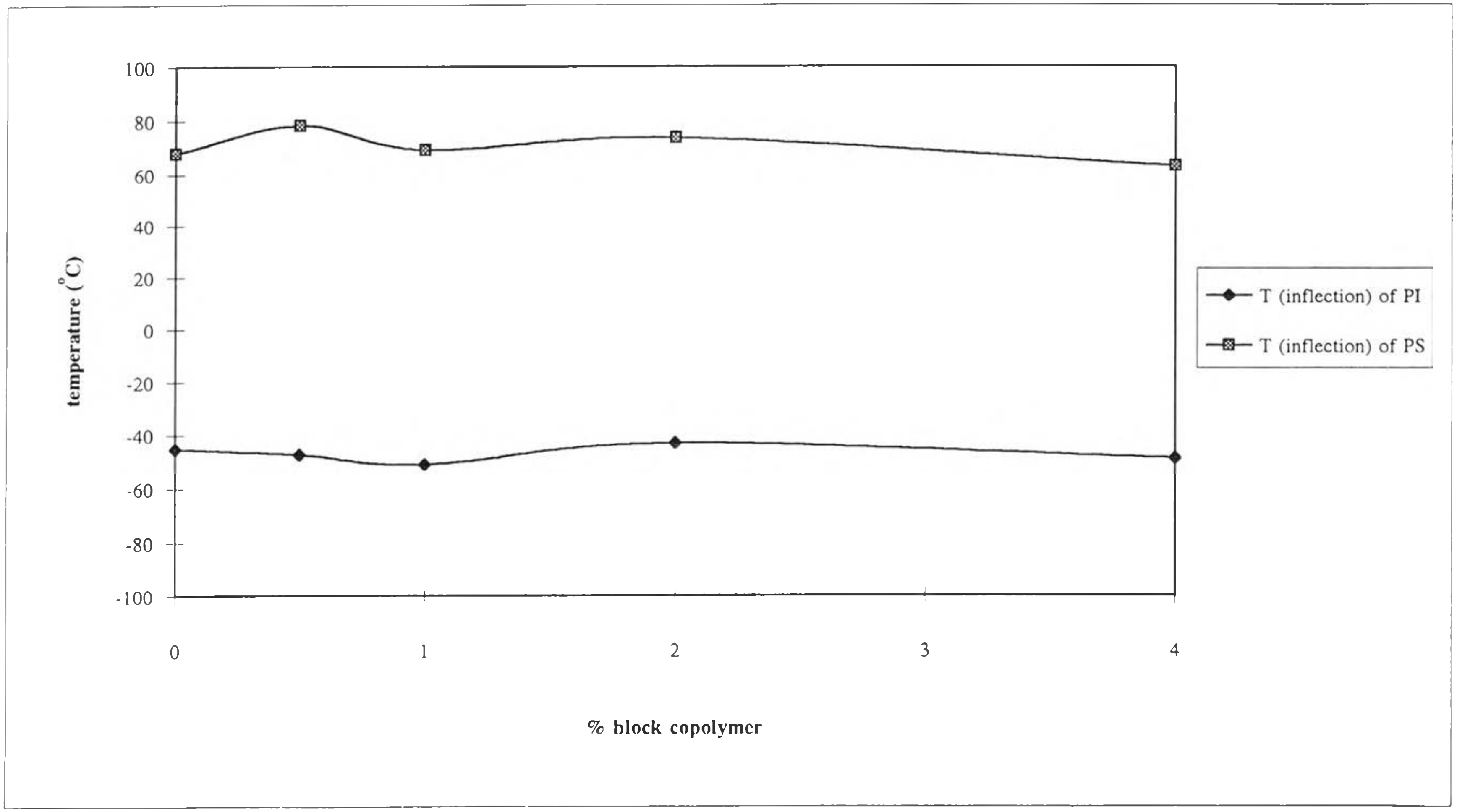

Figure 3.12 Effect of % block copolymer on the transition temperature (storage modulus inflection) of PS/PI (75/25) blends.

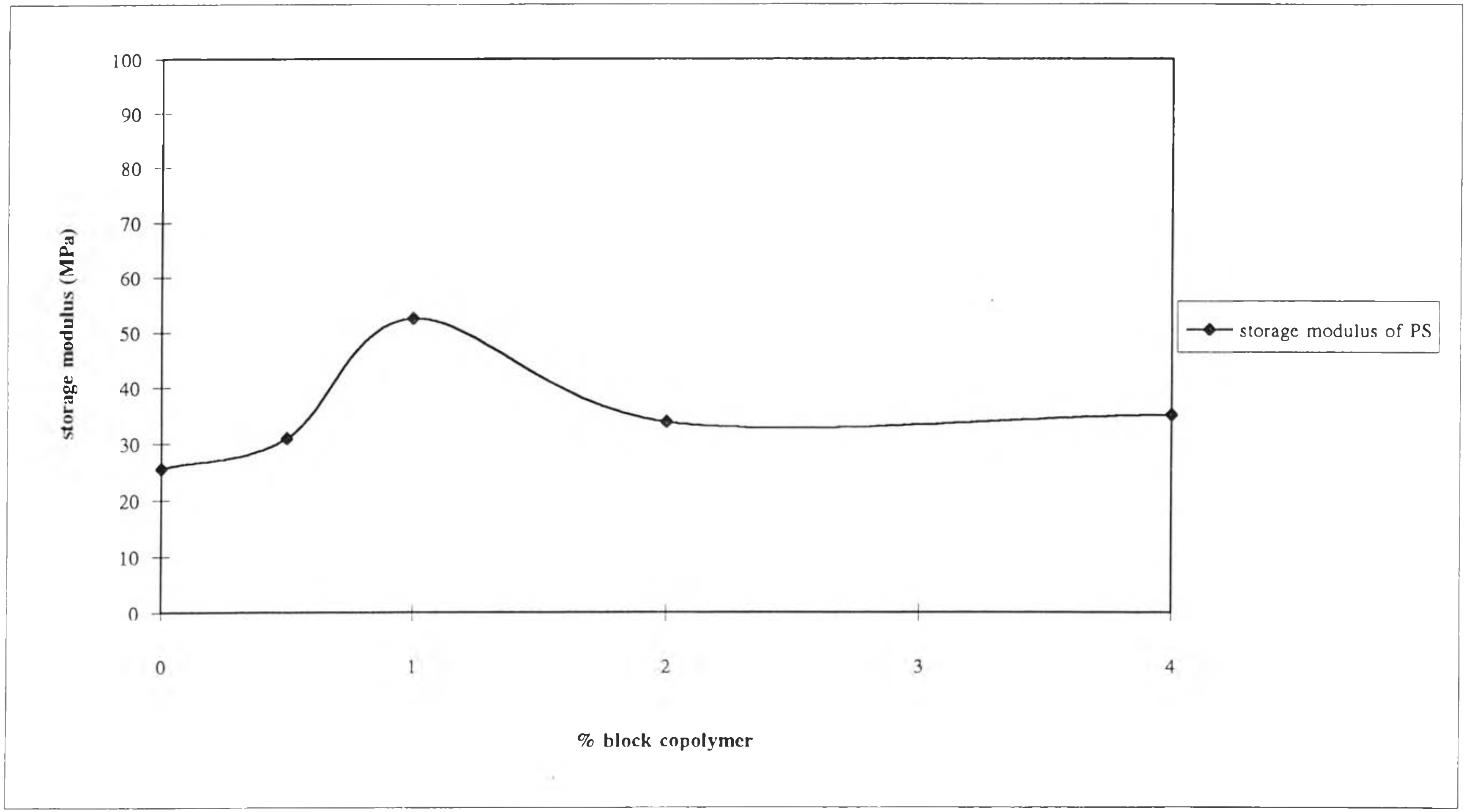

Figure 3.13 Effect of % block copolymer on the PS-storage modulus peak of PS/PI (75/25) blends.

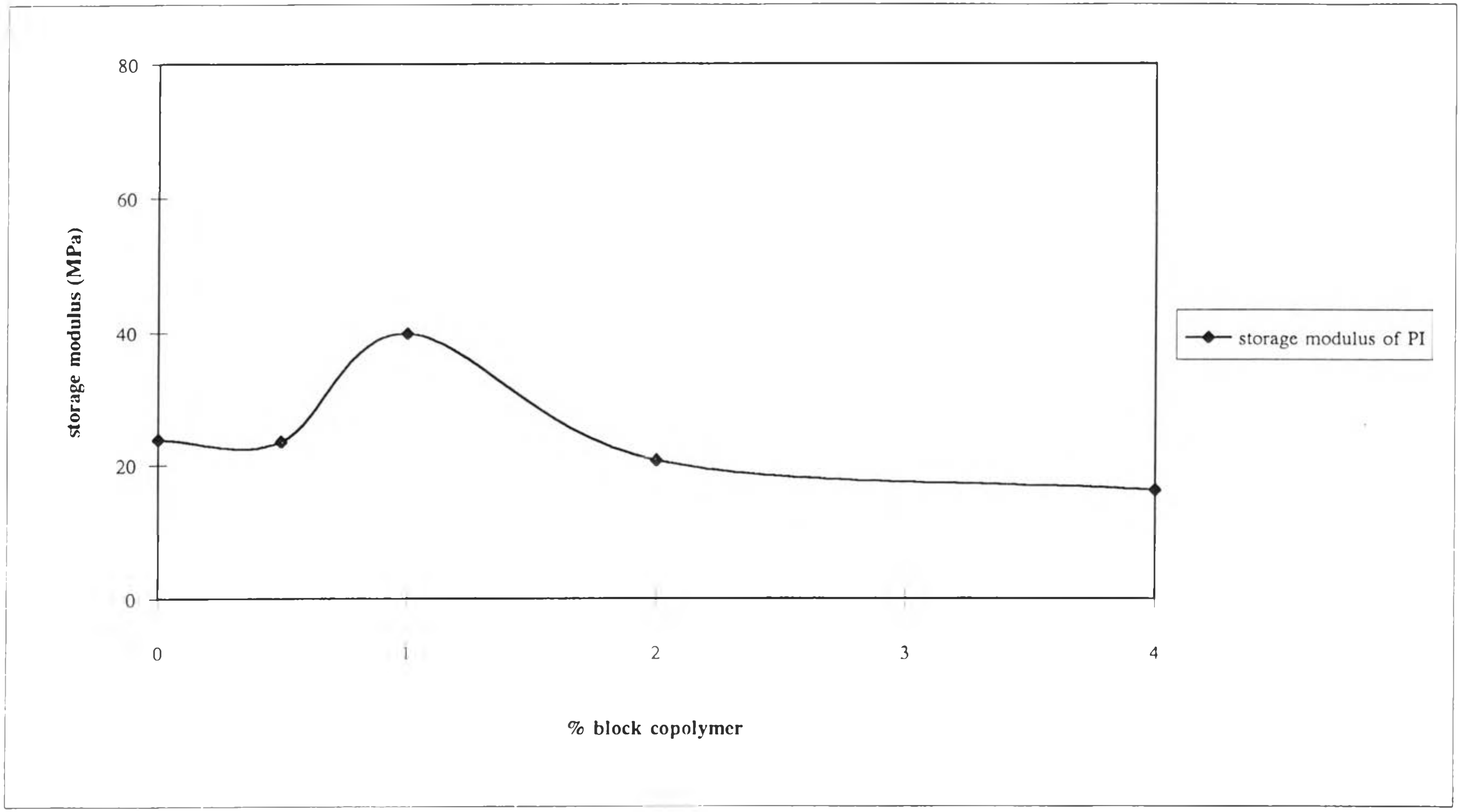

Figure 3.14 Effect of % block copolymer on the PI-storage modulus plateau of PS/PI (75/25) blends.

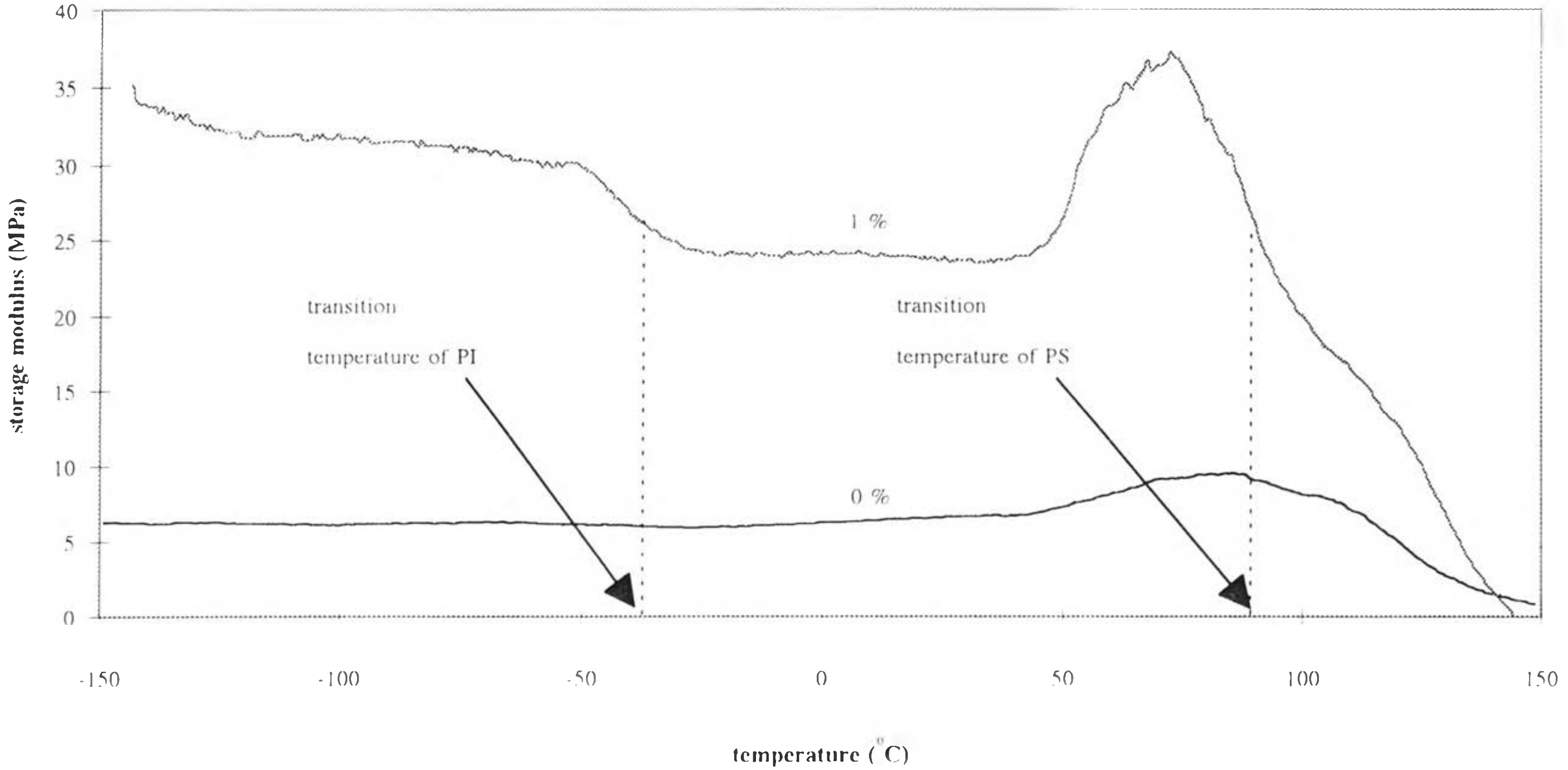

Figure 3.15 Effect of % block copolymer on the storage modulus of PS/PI (83/17) blends.

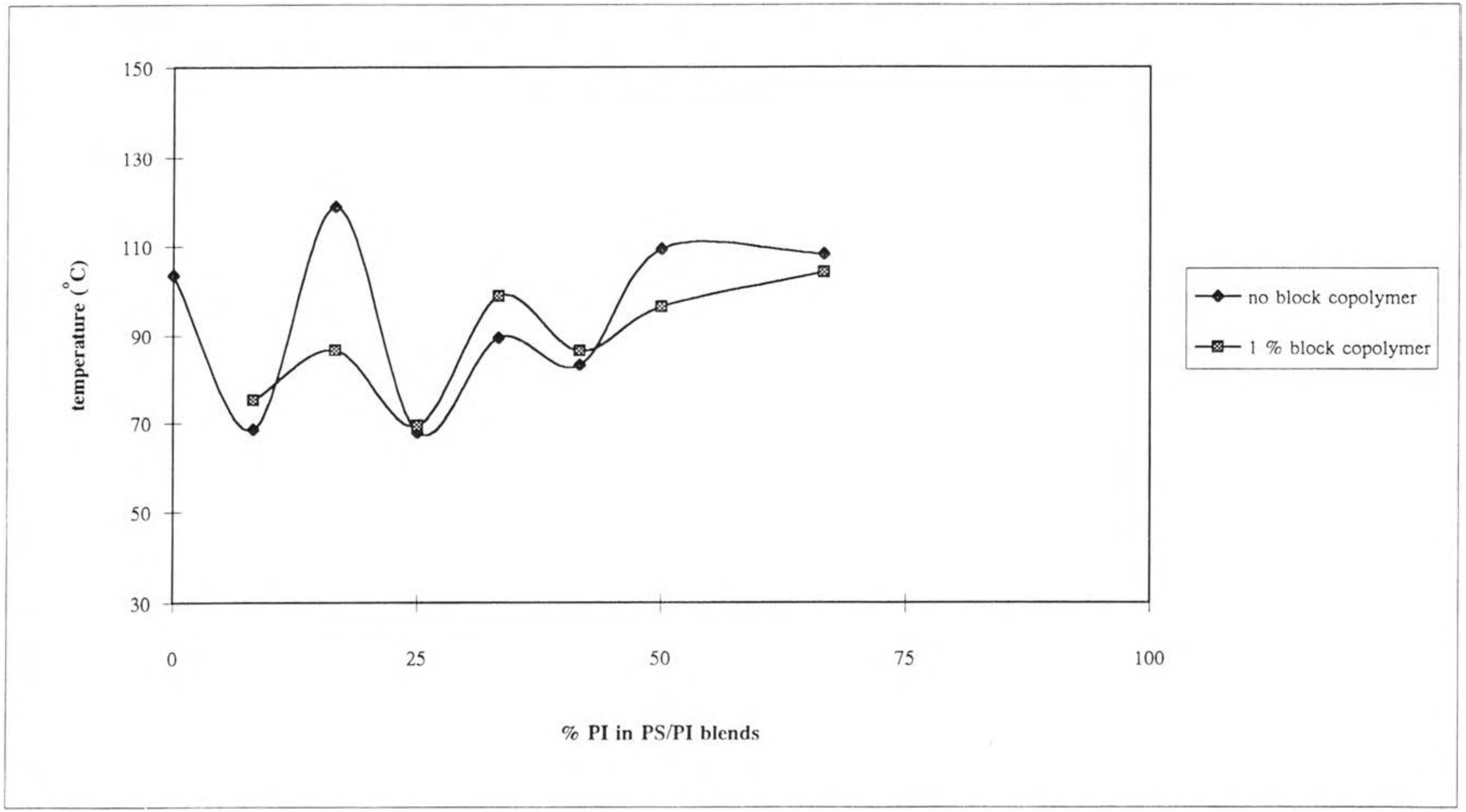

Figure 3.16 The transition temperature of PS-storage modulus inflection as a function of % PI with and without the diblock copolymer.

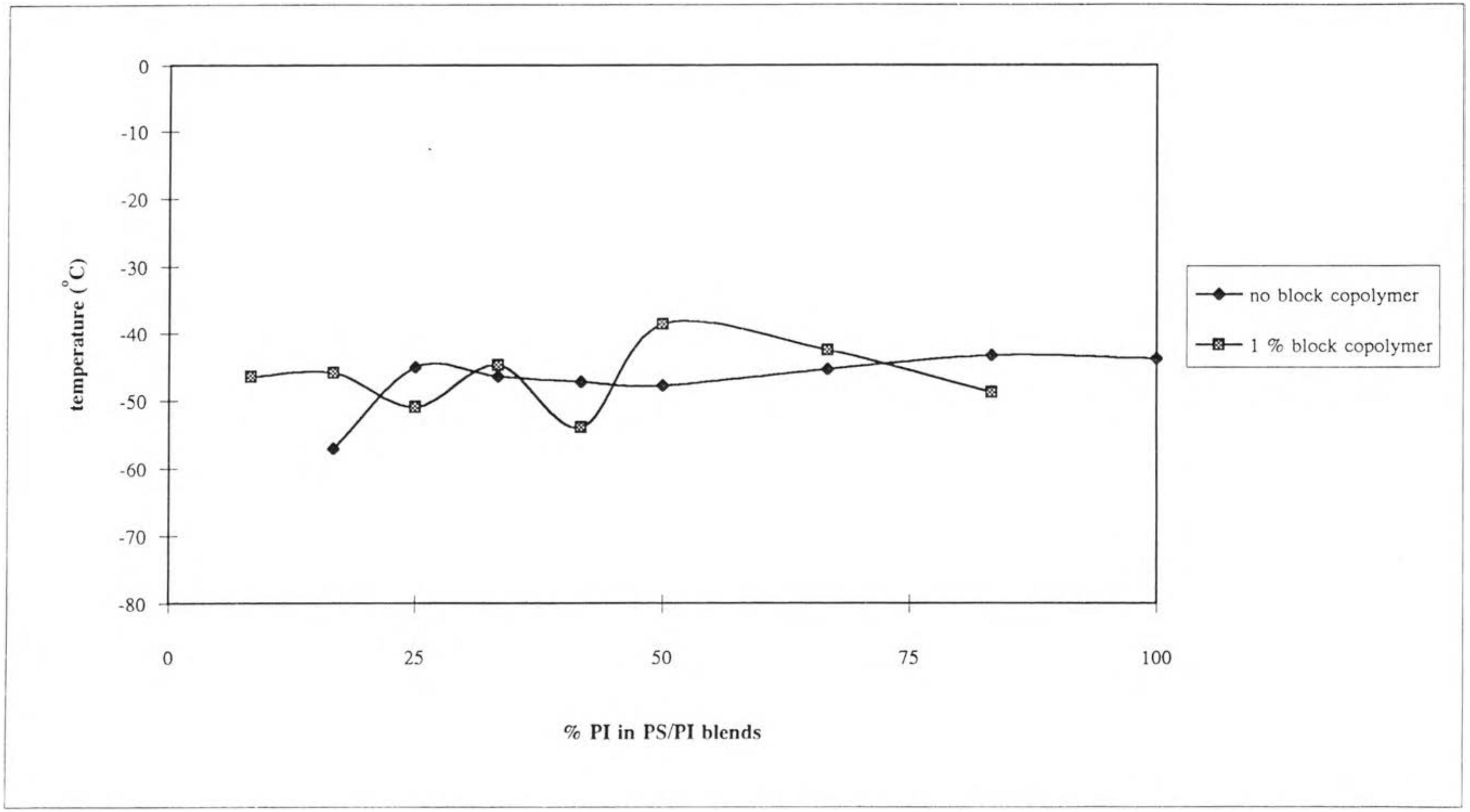

Figure 3.17 The transition temperature of PI-storage modulus inflection as a function of % PI with and without the diblock copolymer.

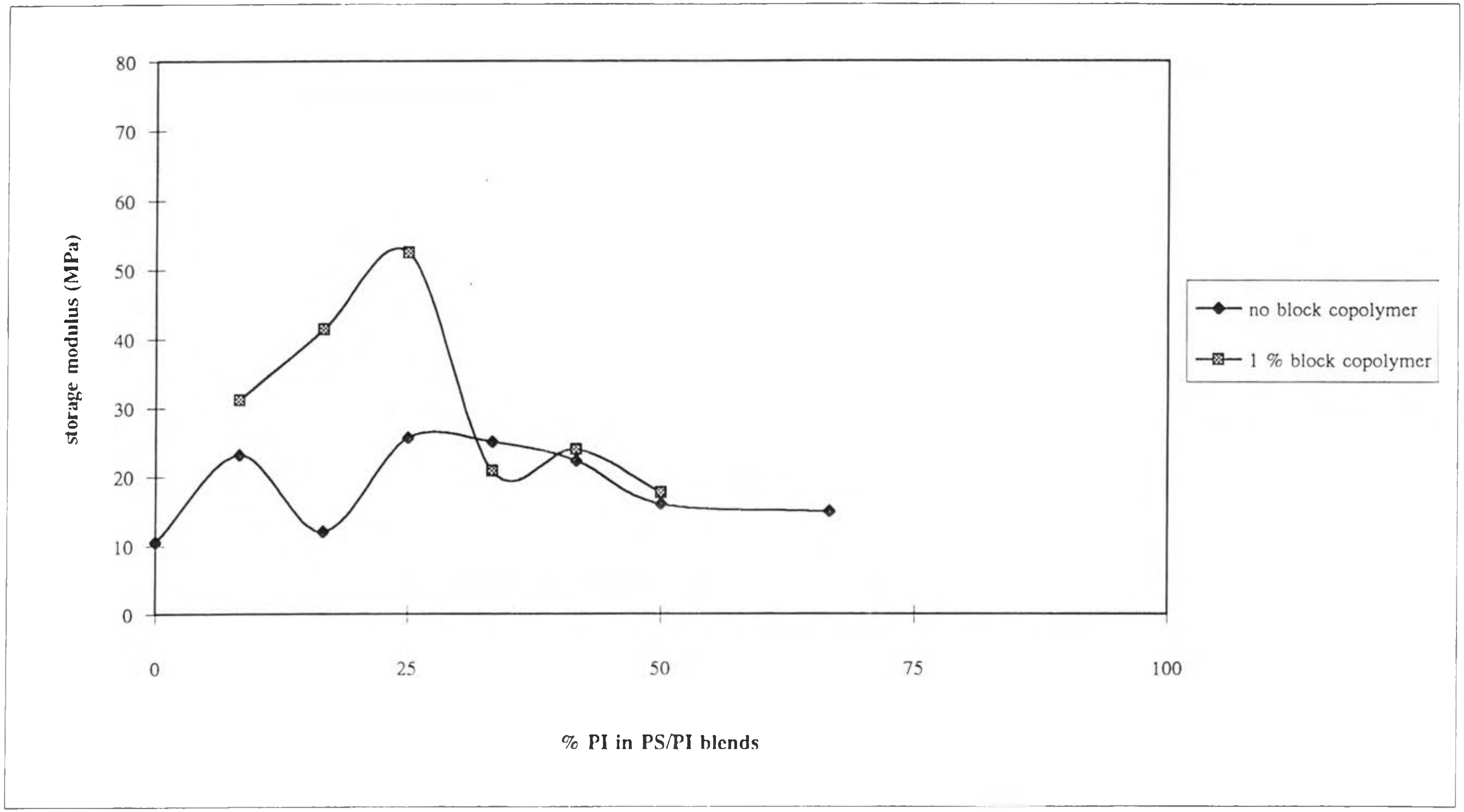

Figure 3.18 The PS-storage modulus peak as a funciton of % PI with and without the diblock copolymer.

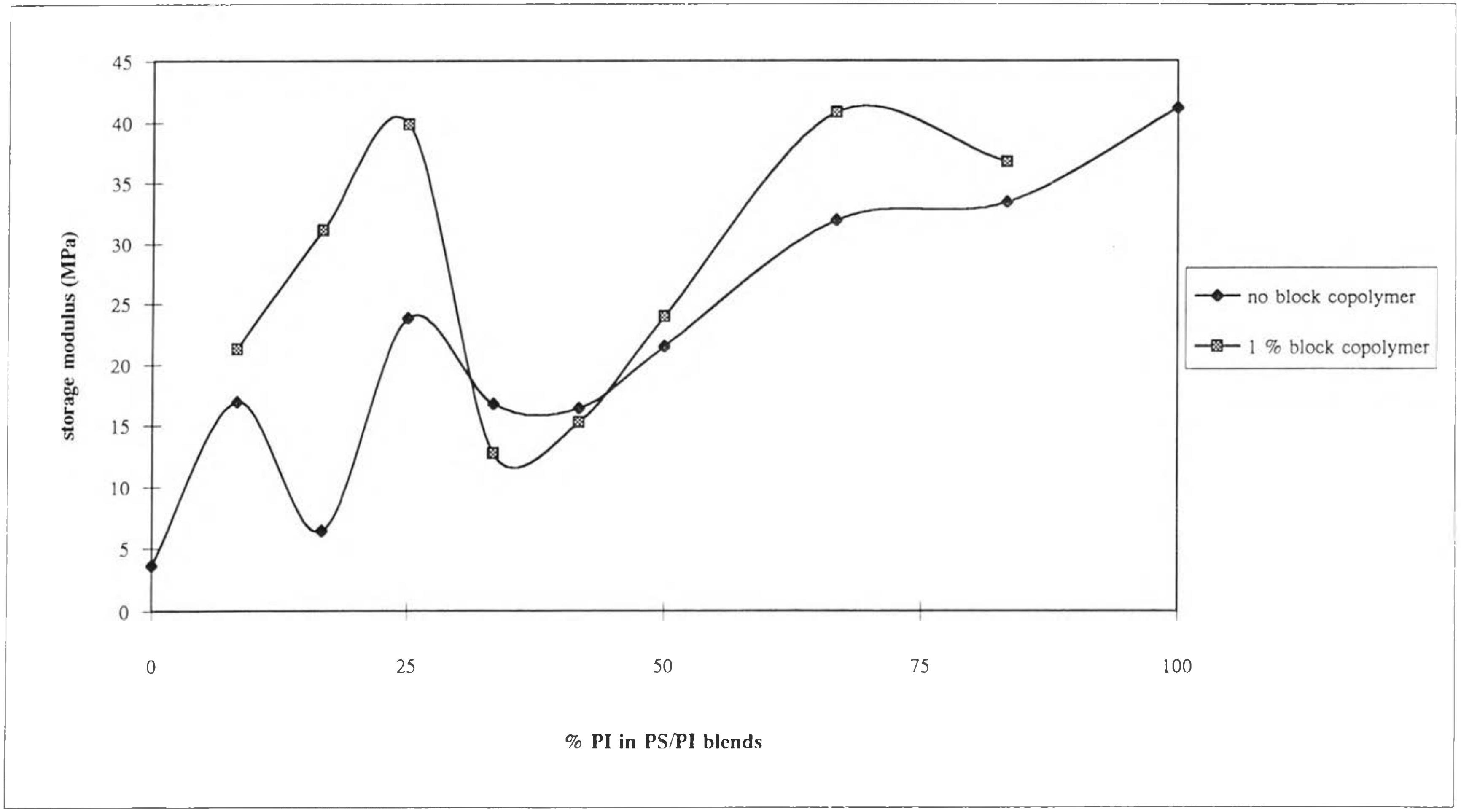

Figure 3.19 The PI-storage modulus plateau as a function of % PI with and without the diblock copolymer.

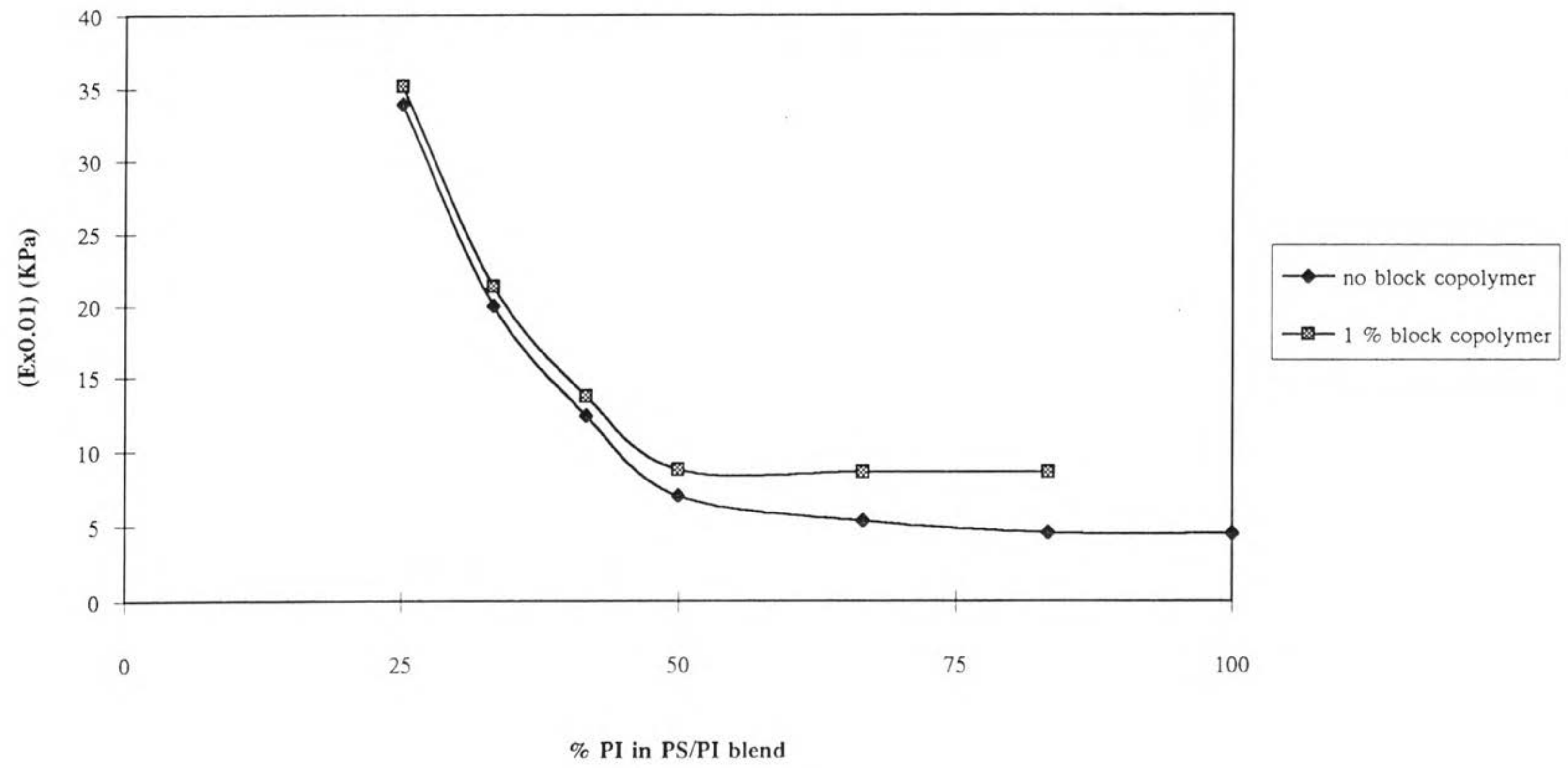

Figure 3.20 Effect of composition ratio on Young's modulus.

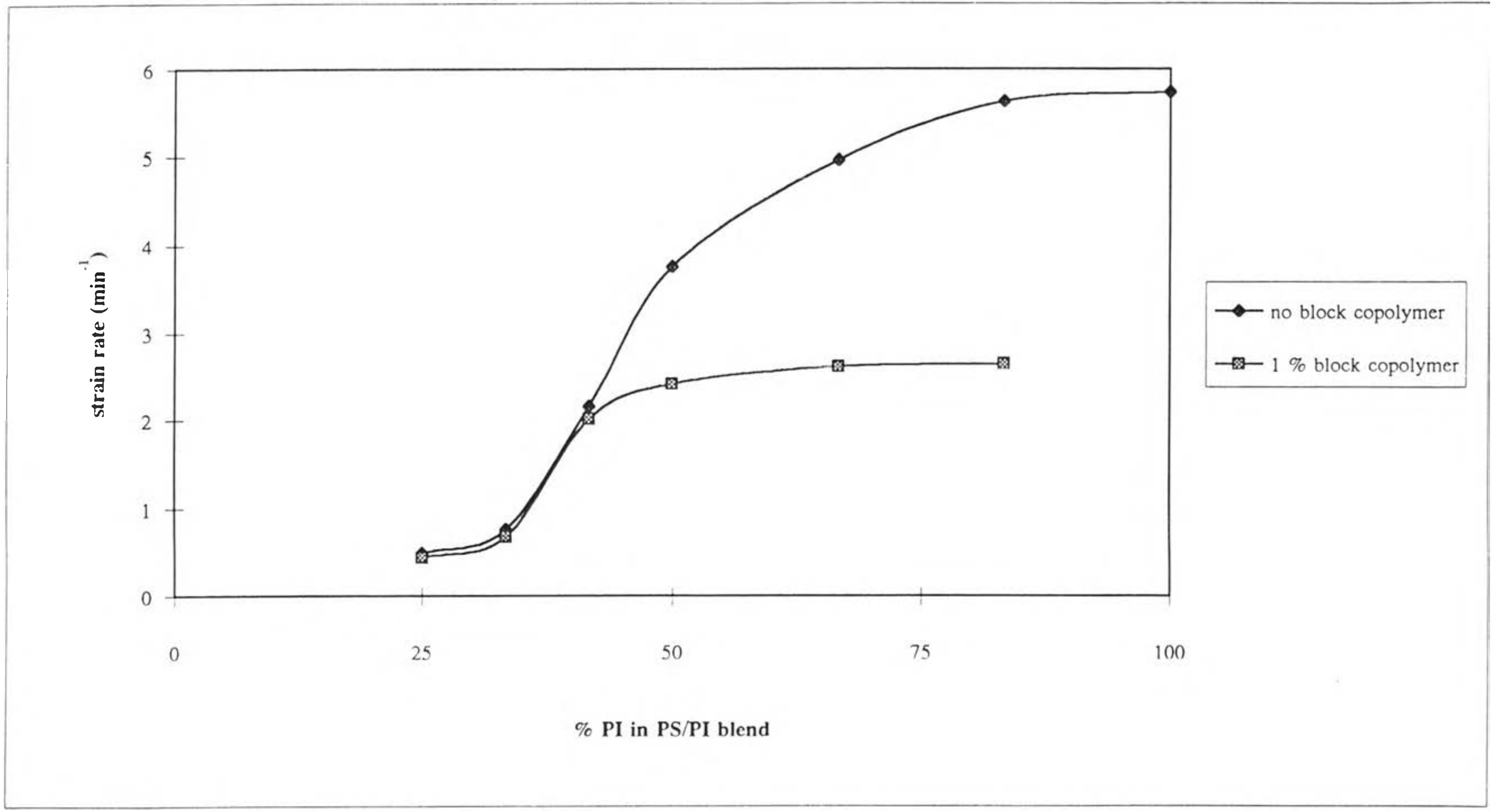

Figure 3.21 Effect of composition ratio on strain rate (stress rate = 10mN/min).

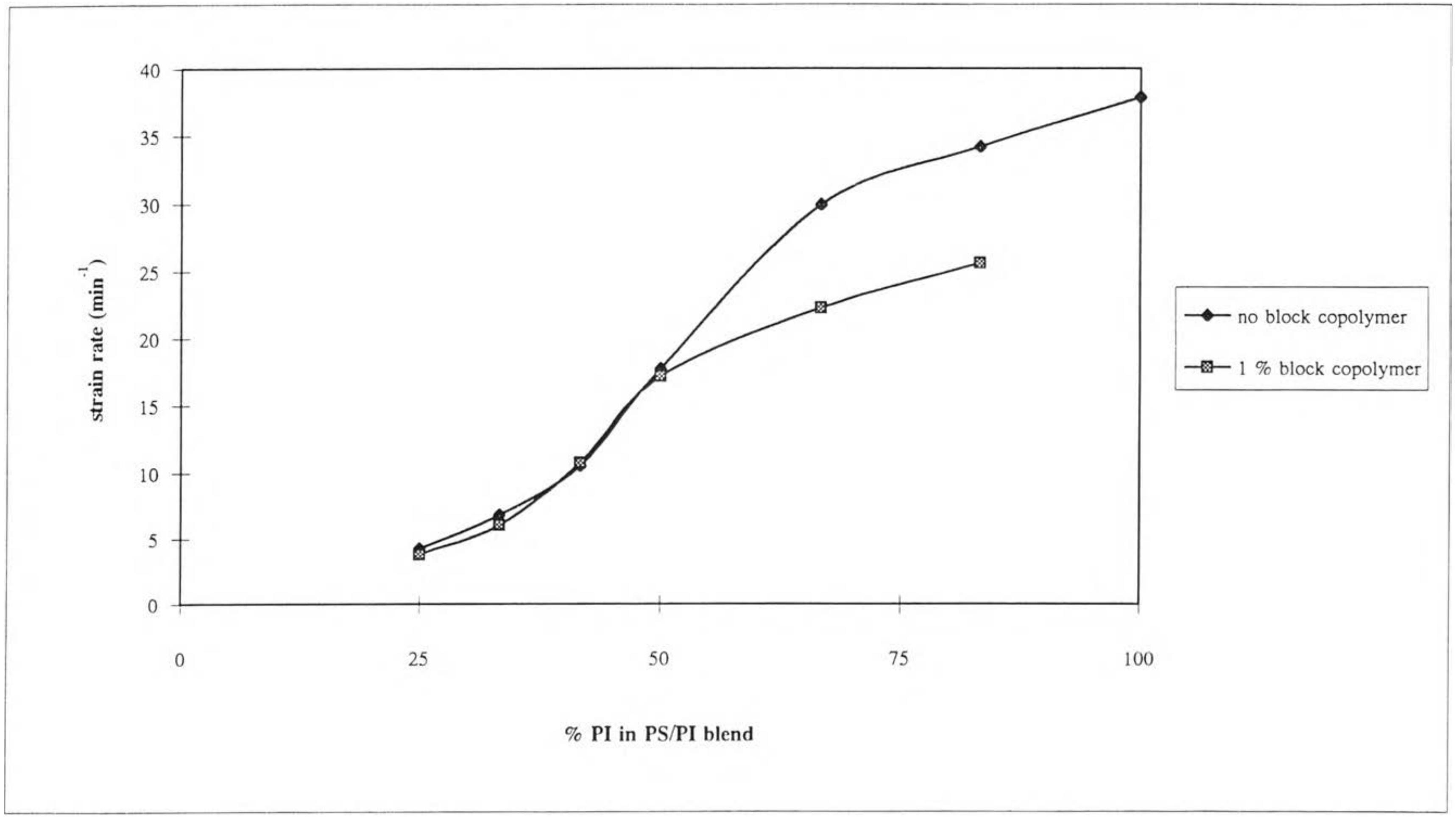

Figure 3.22 Effect of composition ratio on strain rate (stress rate = 100mN/min).

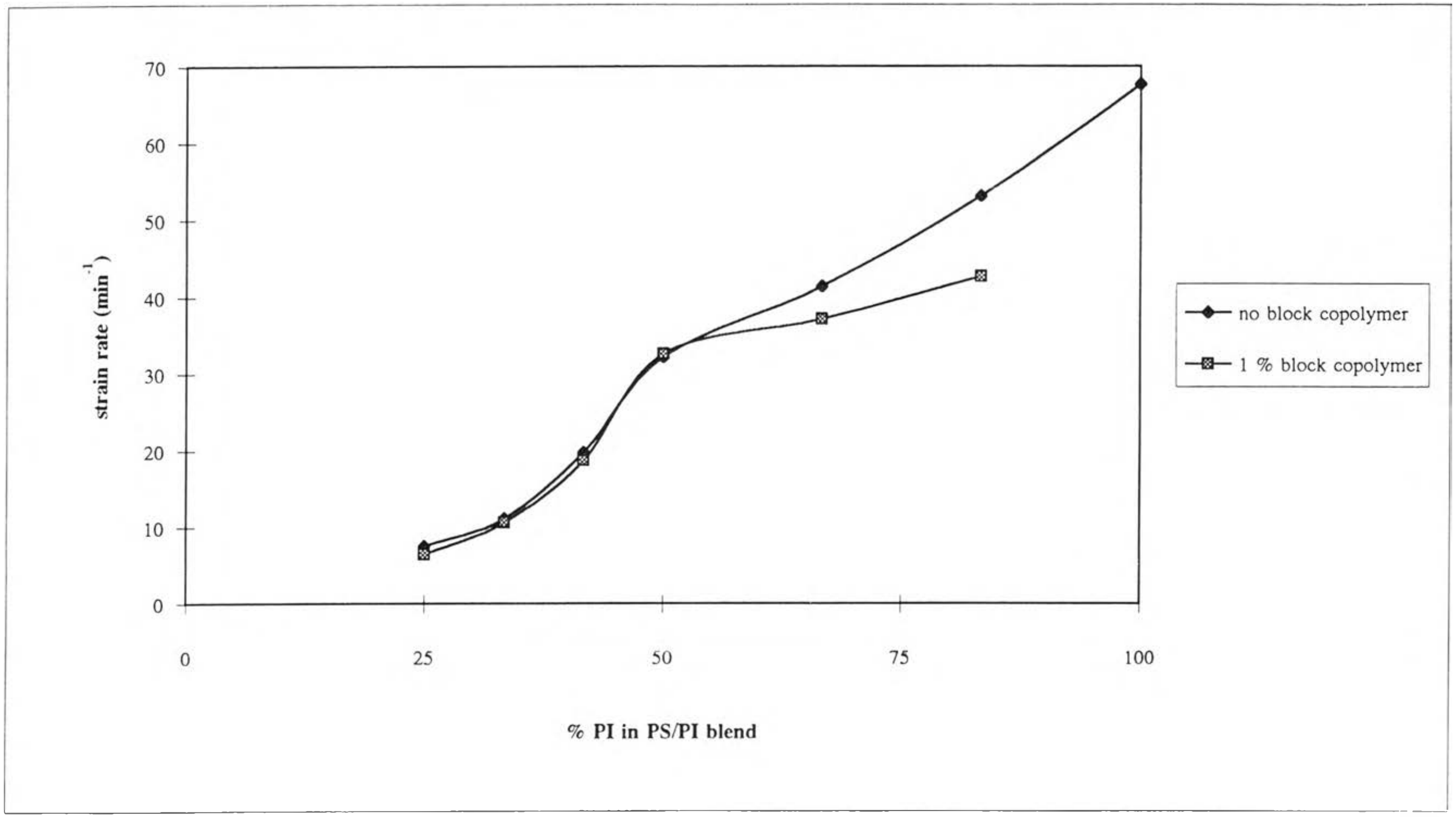

Figure 3.23 Effect of composition ratio on strain rate (stress rate = 200mN/min).

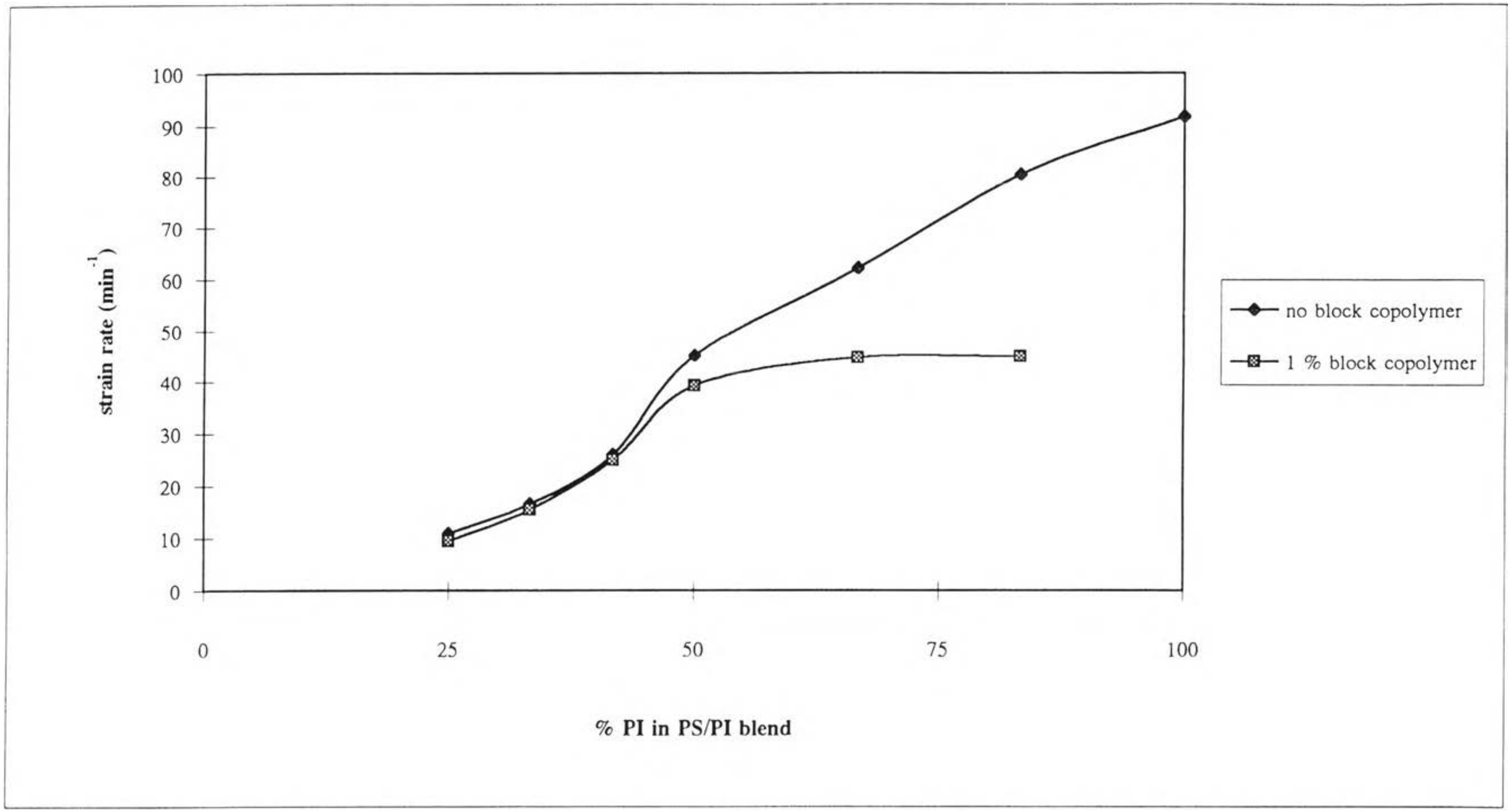

Figure 3.24 Effect of composition ratio on strain rate (stress rate = 300mN/min).

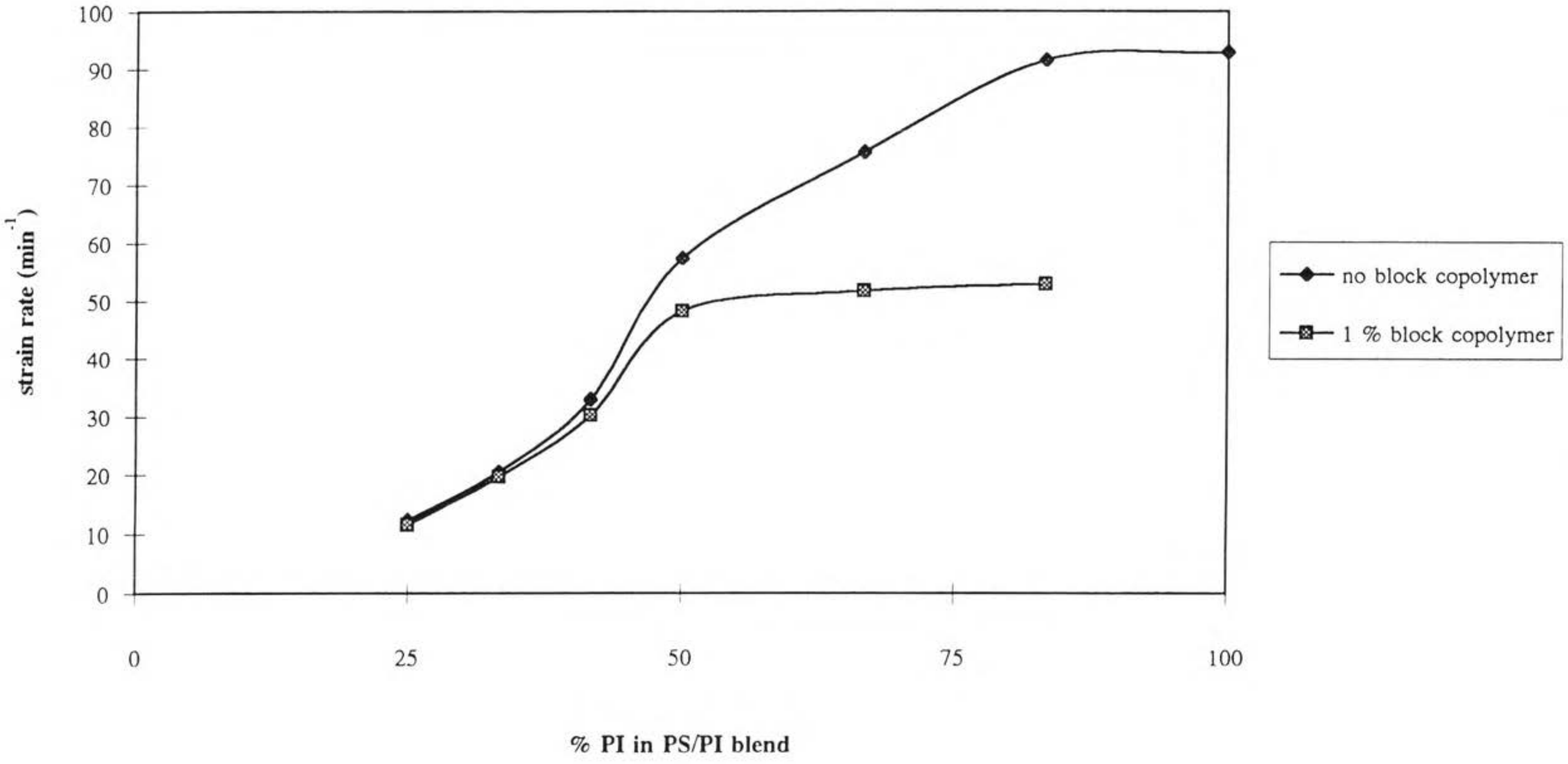

Figure 3.25 Effect of composition ratio on strain rate (stress rate = 400mN/min).

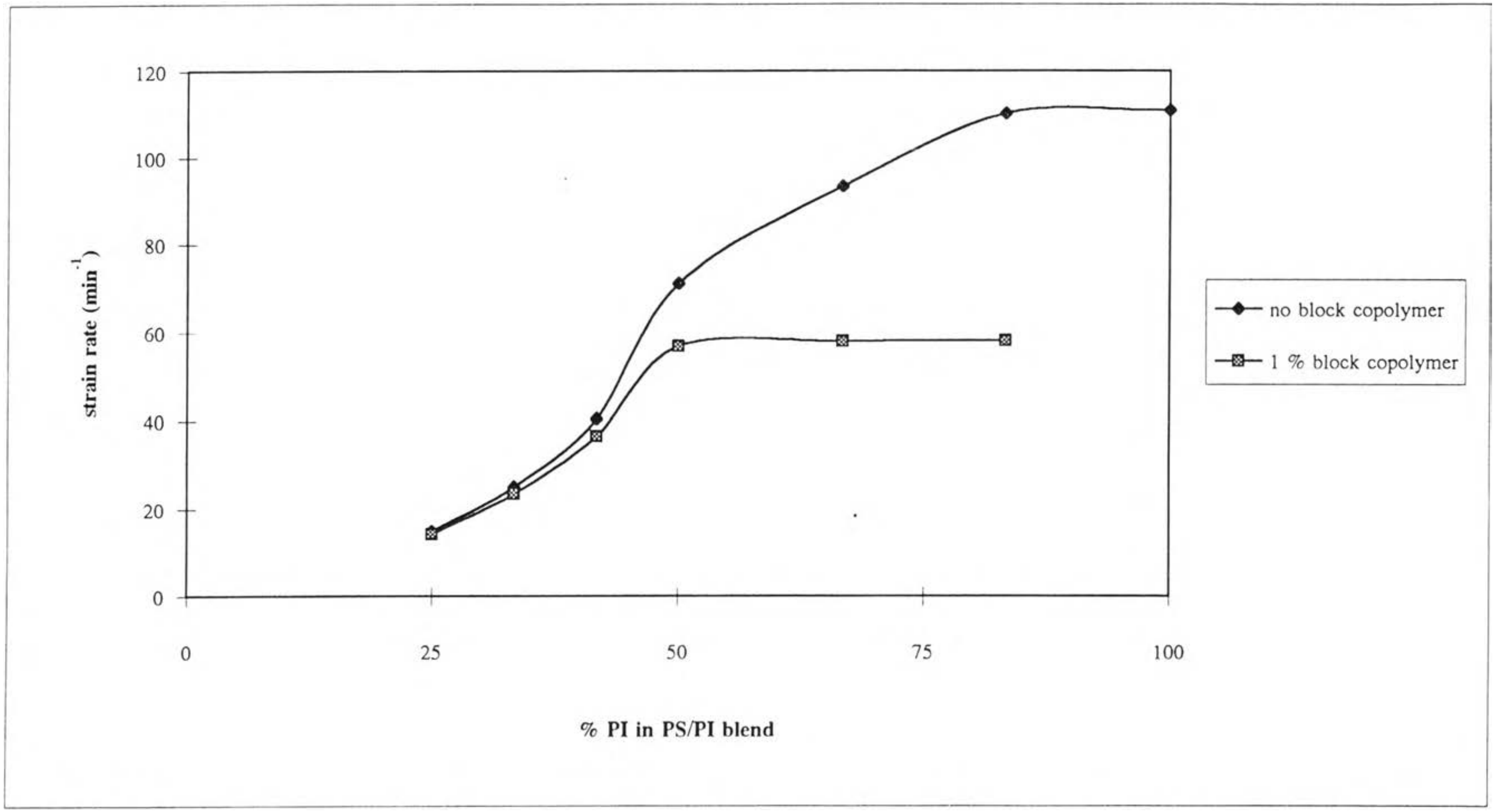

Figure 3.26 Effect of composition ratio on strain rate (stress rate = 500mN/min).