

Chemical Resistance Evaluation of Polystyrene/Polypropylene Blends: Effect of Blend Compositions and SEBS Content

Sani Amril Samsudin^{1*}, Azman Hassan¹, Munirah Mokhtar¹,
Syed Mustafa Syed Jamaluddin²

¹Department of Polymer Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

²Plastics Technology Group, SIRIM Berhad, 1, Persiaran Dato' Menteri, 40911 Shah Alam, Selangor, Malaysia

*Corresponding author: saniamril@fkkksa.utm.my

ABSTRACT: The present study investigates the effect of styrene-*b*-(ethylene-co-butylene)-*b*-styrene (SEBS) and blend ratio on the chemical resistance of PS/PP blends. Using a Brabender PL2000 twin-screw extruder, blends of PS rich PS/PP (composition ranging of 90–60 wt % PS) containing different amount of SEBS were prepared and injection moulded to be evaluated for chemical resistance. The results showed that the chemical resistance of PS to acetone and tetrahydrofuran (THF) increased with increasing PP content. The chemical resistance of PS/PP blends increased with increasing SEBS content at relatively lower PP content but decreased with increasing SEBS content at higher PP content. Dynamic mechanical analysis showed that 60/40/25 PS/PP/SEBS blends had better miscibility than 60/40/5 PS/PP/SEBS blends. However better miscibility did not result in enhanced chemical resistance since SEBS itself was effected by the chemicals.

Keyword: polystyrene, polypropylene, styrene-*b*-(ethylene-co-butylene)-*b*-styrene, chemical resistance, polymer blends

1.0 INTRODUCTION

Blending of polymers provides an efficient way of developing new materials with tailored properties, and thus has received much attention from academia and industry. By blending different polymers, several properties can be improved, while retaining some of the original properties. However, the desire of polymer scientists and engineers to produce improved products by blending a particular pair of polymers is often frustrated by their low compatibility. The incompatibility between polymer pairs and their consequently poor phase morphology are responsible for the poor mechanical properties of most polymer blends. As a result, there is a strong need to enhance compatibility, and the compatibilization of polymer blends by the addition of block or graft copolymer has become an important feature of polymer science and technology [1].

This present study focuses on the blending of polystyrene (PS) with polypropylene (PP). For many years PS has been very successfully used in packaging, building and construction, and in injection moulding applications. PS is an amorphous polymer with a glass-transition temperature (T_g) between 90 to 110°C; it has the advantages of being clear, hard, easily processed and low cost. Because of the excellent properties described above, PS is now used in electrical/electronic, automotive, and industrial films applications.

Although PS has many desirable properties, its disadvantages are low impact strength and poor chemical resistance at room temperature, especially to ketones and ethers [2]. On the other hand PP can be considered a tough material at room temperature and it also

possesses good chemical resistance. Thus, blending of PS with PP can be a convenient way to increase the impact strength and chemical resistance of PS. PS/PP blends seem to be promising materials for various purposes in packaging and for components that need improved resistance to oils in the automotive industry [3].

However, the PS/PP blend system is considered immiscible and incompatible, because PS contains aromatic benzene rings, while PP contains straight carbon chains of an aliphatic kind. Many researchers have reported on the optimization of immiscible PS/PP blends through the use of compatibilizers such as styrene-*b*-(ethylene-co-butylene)-*b*-styrene (SEBS) [3-11]. SEBS is an effective compatibilizer for PS/PP blends, because the PS and EB blocks of SEBS are miscible with PS and PP respectively.

Recently Samsuddin *et al.* [12] reported that the mechanical properties of PS/PP blends are dependent on blend composition (ratio of PS/PP) and SEBS content. The impact strength and elongation at break of the uncompatibilized PS/PP blends increased with PP content. However, the tensile strength and flexural modulus decreased with PP content. The impact strength and elongation at break of the PS/PP blends increased with SEBS content, at the expense of tensile strength and flexural modulus. The improvement in impact strength and elongation at break with the addition of SEBS are due to the improved interfacial adhesion between the PP dispersed phase (PP) and matrix phase (PS). The effectiveness of SEBS in enhancing the compatibility of the blends depends on the blend composition. A significant improvement was observed on addition above 10 phr of SEBS into the 70/30 and 60/40 PS/PP blends. However, not much improvement in impact strength was observed upon addition of 10 phr SEBS to 90/10 and 80/20 PS/PP blends.

Many plastics and composites are widely used because of their chemical resistance, low weight and mechanical strength. Indeed, plastics find widespread use in chemical plants, in distribution systems for natural gas and water, and in effluent and sewage disposal networks. The chemical interactions with plastics materials can be categorized into direct chemical attack, preferential chemical attack, environmental stress cracking (ESC), surface attack and swelling [2]. Combined effects of stress cracking and photodegradation in polystyrene was recently reported by Sousa *et al.*[13]. They found out that butanol causes significant modification in PS with extensive surface crazing as well as reduction in mechanical properties. Studies on chemical resistance of plastics blends including PS/PP blends have received very little attention among the researchers. Therefore, the present study was carried out to investigate the effects of PP and SEBS contents on chemical resistance of PS/PP blends. Two chemical reagents from different groups were used in this study, acetone which is a ketone and tetrahydrofuran (THF) from ether group.

2.0 EXPERIMENTAL

2.1 Materials

The polystyrene used was a general-purpose grade (GPPS HH-30) supplied by Petrochemicals (M) Sdn. Bhd. Polypropylene homo-polymer TITANPRO 6531 (isotactic type) with a specified melt flow index of 3.5 g/10 minutes was supplied by Titan PP Polymers (M) Sdn. Bhd. The properties of GPPS HH-30 and TITANPRO 6531 are summarized in Table 1. Both of these resins were originally in the form of extruded pellets. The compatibilizer used was SEBS (Kraton 1652G) (PS blocks $M_w = 7,500$ and an EB mid-block segment $M_w = 37,500$) supplied by Tiram Kimia Sdn. Bhd.

Table 1: The properties of GPPS HH-30 and TITANPRO 6531

Properties	GPPS HH-30	TITANPRO 6531
Specific gravity	1.1	0.9
Melt Flow Rate (g/10min.)	5.0 (at 200°C)	3.5 (at 230°C)
Tensile stress at yeild (MPa)	45.1	35.3
Elongation at Break (%)	2.6	12
Flexural modulus (GPa)	2.7	1.7

2.2 Blend Preparation

The various formulations of uncompatibilised PS/PP blends and PS/PP/SEBS blends were prepared in a twin-screw extruder (Brabender PL2000 with L/D= 30 and D= 25 mm). The compositions prepared in this study are listed in Table 2. Before that, pellets of PS, PP and SEBS powder (Kraton 1652G) were mixed in a tumbler mixer for 5 -10 minutes to produce a uniform composition throughout the batch size. This uniformly mixed feed was then melt blended in a co-rotating twin-screw extruder. The extrusion was conducted at a speed of 50-55 r.p.m. with barrel temperatures of 190°C, 225°C, 230°C from feeding zone to die zone, respectively. The residence time of the blends in the extruder was kept at about 60 seconds. The compound was extruded via a twin, 4 mm rod-die. The extruded strands were then air-dried and palletized. The blends were extruded and pelletised twice to allow good dispersion of the PP phase within the PS matrix. The dumbbell tensile specimens (ASTM D 638, type I) were injection-moulded on an Arburg Allrounder 750-310D. The barrel temperature ranged from 200-235°C, while the mould temperature was 40°C.

2.3 Chemical Resistance Evaluation

Two chemical reagents from different groups were used in this study; acetone which is a ketone and tetrahydrofuran (THF) from ether group. The chemical resistance towards acetone is measured through swelling effect and weight loss, while for THF only weight loss method was used.

This testing was carried out according to ASTM D543-87. The specimens were immersed in the appropriate reagent for a specified time under the Standard Laboratory Atmosphere of 23±2°C and 50±5 % relative humidity. For the swelling effect, changes in mass and appearance were reported for time duration of 24, 96 and 168 hours which represent short, intermediate and long period of the tests. Five tests were carried out for each blend sample. The degree of swelling (DS) was calculated using the following equation:

$$DS = (m_2 - m_1) / m_1 \times 100 \text{ ----- (1)}$$

where m_1 and m_2 are the weight of the dry and swollen samples respectively. Weight loss was determined after 168 hours of immersion in acetone. The weight was determined after a drying process and the samples have reached a consistent weight. For the chemical resistance towards THF, weight loss was determined after 24 hours of immersion.

2.4 Dynamic Mechanical Measurement

Dynamic mechanical measurements were carried out on a Perkin Elmer DMA 7e in accordance to MS 1473 (1999) consisting a temperature programmer and controller. The experiment was performed in flexural mode from -60 to 140 °C at a frequency of 1 Hz

with a programmed heating rate of 5 °C/min. Liquid nitrogen was used to achieve sub-ambient temperature. The Tg was taken as the temperature of the onset of a decrease in storage modulus.

Table 2: Blends Formulations

SAMPLE DESIGNATION				
No	CODE	Composition		
		Polymers (%)		Compatibilizer (part per hundred)
		GPPS (HH-30)	Homo PP (6431)	
1	PS	100	0	0
2	PP	0	100	0
3	SEBS	0	0	100
4	A1	90	10	0
5	A2	90	10	10
6	A3	90	10	25
7	B1	80	20	0
8	B2	80	20	10
9	B3	80	20	25
10	C1	70	30	0
11	C2	70	30	10
12	C3	70	30	25
13	D1	60	40	0
14	D2	60	40	10
15	D3	60	40	25

3.0 RESULT AND DISCUSSIONS

3.1 Resistance to Acetone

Swelling is a type of chemical attack which normally occurred before total dissolution. The swelling effect is represented by the percentage of weight increase after the immersion. The effects of acetone on pure samples after 24 hrs immersion are given in Table 3. PS dissolved completely after immersion in acetone which indicates that PS has a weak chemical resistance towards acetone. The weight increased in PP after immersion in acetone is only minimal (<1%) which indicates that PP has a good resistance towards acetone. After 24 hours of immersion in acetone, pure SEBS increased by about 15% which indicates that the resistance is better than PS but inferior to PP.

Table 3: Effect of acetone on swelling effect of neat samples after 24 hrs immersion

Sample	Weight increased (%)
PP	0.7
PS	Total dissolution
SEBS	15

PS is an amorphous polymer, which in general is more prone to chemical attack. The weakness of PS to the chemical attack of acetone is probably due to the presence of benzene ring in the polymer structure causing it to have relatively more open structure. Due to the structure, PS is more susceptible to environment related damage; in particular, there is a much stronger tendency towards chemical dissolution than in the case with semi-crystalline polymers such as PP.

A strong interaction between a plastics material and a chemical is favoured when the chemical nature of the materials are similar. For instance, if the solvent is highly polar and the plastics material also has a polar group, the plastics material is likely to be strongly affected by the chemical. This observation of chemical similarity in dissolving phenomena has been expressed in traditional chemistry as "like dissolves like" which implies that polar solvents strongly affect polar plastics and non-polar solvent have a strong interaction with non-polar plastics. Therefore in this case there would be strong interaction between PS and acetone which are both non-polar.

Figure 1 shows the swelling effect of the various PS/PP blend samples after immersion in acetone for 24, 96 and 168 hours. The result also shows that the chemical resistance of the PS/PP blends increased with increasing PP content. The uncompatibilized 90/10 PS/PP (A1) blend showed the highest percentage of weight increase than the other blends whereby the weight increases by 74 % after 168 hours. The percentage of weight increase reduced significantly as the PP content increased to 40 % (D1), whereby the weight increased only by 13 % after 168 hours.

From Figure 1, it can also be seen that dramatic weight change occurred for all blends composition upon increasing the time of immersion from 24 hours to 168 hours. For example sample B1 (80:20 PS/PP blend) increased by more than 3 times as the time of immersion increased from 24 to 168 hours. This clearly indicates that the compatibility between the PS and PP weaken with time in the presence of the acetone.

Figure 1 also shows that SEBS is effective in enhancing the chemical resistance of PS/PP blend. The weight increase in the 90/10 PS/PP blend (A1) was reduced when 10 % SEBS was added into the blend. A further increase of SEBS content from 10 to 25 % reduced the weight increase from 68 to 57 %. The weight increase was reduced because of the overall increase of SEBS in the blend samples, which has a better resistance to acetone than PS. The other probable factor is the increased compatibility between PS and PP with the presence of SEBS.

Interestingly, it was observed for the 20, 30 and 40% PP content in the PS/PP blends, an increment in weight was observed with increasing SEBS contents. This is because the overall ratio of PP (which was previously shown to have better chemical resistance than SEBS) in the blend decreases with increasing SEBS content. The possible reason is that the samples were modified due to the increased compatibility between PP and PS in the presence of SEBS.

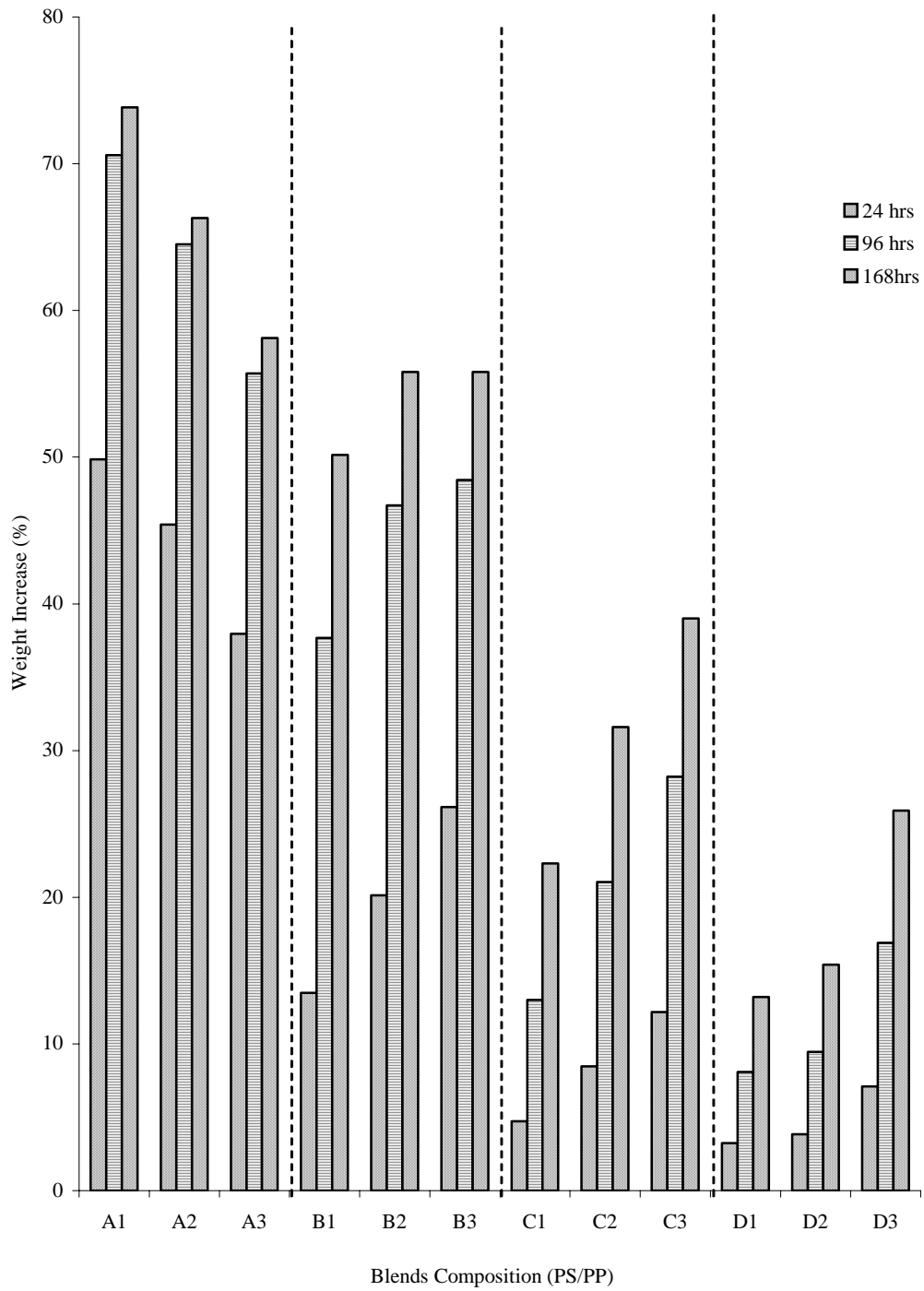


Figure 1: Swelling effect of various PS/PP blends samples after immersion in aceton

Another method to determine chemical resistance is through polymer dissolution. The effects of acetone on dissolution of pure samples after 168 hrs immersion are given in Table 4. This determination of loss weight was done after the samples achieved consistent weight during the drying process. Weight loss being determined indicates the amount of polymer dissolved in the chemical. The trend is similar to the swelling effect whereby PP has the best chemical resistance followed by SEBS and PS was the weakest. PP lost only 0.2% of the weight after the drying process as compared to PS, which is totally dissolved. It was also observed that the weight loss for SEBS is around 60%.

Table 4: Effect of Acetone on Dissolution of Pure samples after 168 hrs immersion

Sample	Weight Loss (%)
PP	0.2
PS	Total dissolution
SEBS	60

Figure 2 displays the percentage of loss weight occurred after PS/PP blend samples immersion in acetone for 168 hours. The result illustrates that the trend of PS/PP blends weight loss effect was similar to the swelling effect, whereby the chemical resistance increased with PP content. This observation was proven by the photographs in Figure 3, where less surface distortion and dimension change was observed in the 60/40 PS/PP samples as compared to 90/10 PS/PP samples.

The effect of SEBS on the weight loss of PS/PP blends is also shown in Figure 2. The result shows that only the 90/10 PS/PP blends improved upon the incorporation of 10 phr of SEBS. No significant improvement occurred with further increase of SEBS from 10 to 25 phr. However, in the blends with 20, 30, and 40 % PP content, increasing SEBS contents decrease the chemical resistance. This is because as previously mentioned SEBS also has poor resistance to acetone whereby about 60 % weight loss was observed as shown in Table 4.

The photographs in Figure 4 illustrate the effect of SEBS on the chemical resistance of the 90/10 PS/PP blend. It is clear that the surfaces distortions occurred was more severe in the uncompatibilized blends compared to compatibilized blend with SEBS.

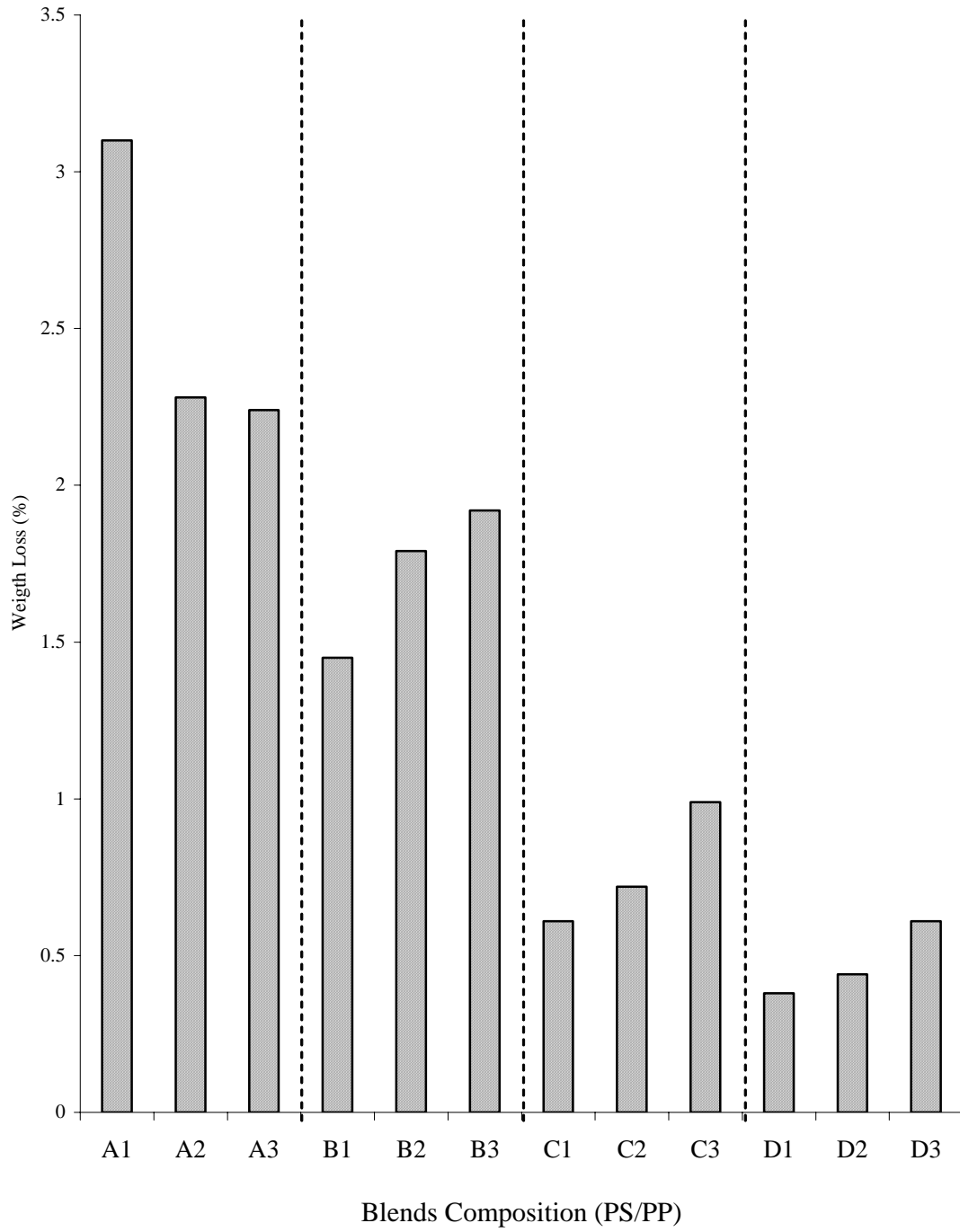


Figure 2: Effect of immersion in acetone for 168 hours on weight loss

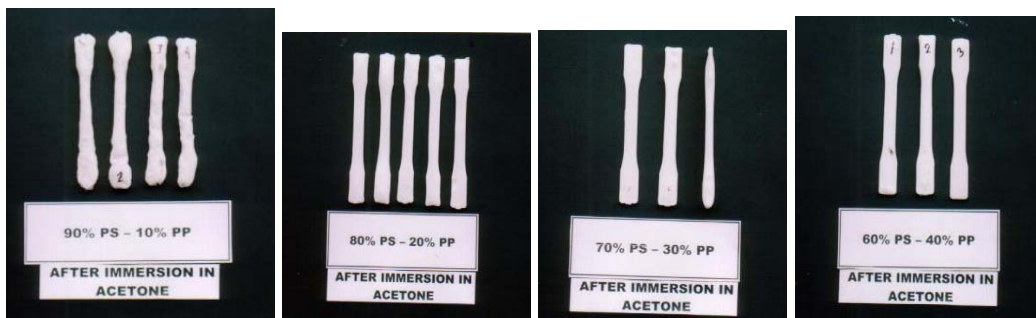


Figure 3: Effect of blend compositions on surface distortion of PS/PP blend due to acetone.

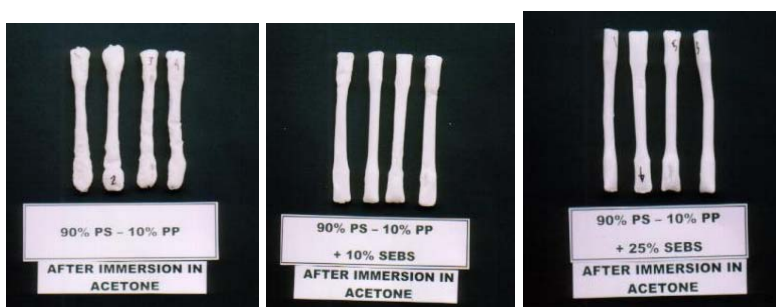


Figure 4: Effect of SEBS contents on surface distortion due to acetone on 90/10 PS/PP blends

3.2 Resistance to Tetrahydrofuran

The effects of THF on pure samples are given in Table 5. The determination on resistance to THF of PS/PP blends was done by studying the weight loss after immersing in THF for 24 hours. The chemical resistance of PS/PP blends to THF was found to be weaker than acetone. Therefore, it was not possible for the swelling effect to be studied and the duration of immersion was reduced to 24 hours.

Table 5: Effect of THF on weight loss of neat samples after 168 hours immersion

Sample	Weight loss (%)
PP	0.07
PS	Total dissolution
SEBS	Total dissolution

The result shows that both PS and SEBS dissolved after immersion in THF for more than one hour, which indicates that PS and SEBS have weak chemical resistance towards THF. Only 0.07% loss weight of PP samples occurred after immersion in THF was recorded, which indicates that PP has strong chemical resistance towards THF.

Figure 5 illustrates the effect of PS/PP blends composition on the chemical resistance to THF. The results show that the weight loss decrease with increasing PP content as expected. An increase from 10 to 20 % PP reduced the weight loss from 77 to 47 % which is relatively significant. However a further increase from 20 to 40 % decreases the weight by only 16 %. The weight loss was consistent with the extent of dimension and shape distortion as shown in Figure 6. The photographs show that the dimensions of

90/10 PS/PP blend changed significantly as compared to 60/40 PS/PP blend. However, this effect is reduced drastically with increasing PP contents in the blend.

Overall the results revealed that THF had a stronger effect on PS/PP blends, compared to acetone where the weight loss occurred above 30% for all blend compositions as can be seen in Figure 6. Previously, Figure 2 shows that the weight loss effect of PS/PP blends after immersion in acetone was below 3%.

Figure 5 also clearly shows that for 90/10 and 80/20 PS/PP blends, increasing SEBS contents significantly reduced the weight loss of the samples. On the contrary for 70/30 and 60/40 PS/PP blends, increasing SEBS contents showed increment in weight loss of the samples. The low chemical resistance at high SEBS concentration is probably due to solubility of SEBS in THF. In general the trend in THF was similar to acetone with the exception of 80/20 PS/PP blend. For the 80/20 PS/PP blend, the chemical resistance to acetone decreased with increasing SEBS content whereas for THF the chemical resistance increased.

The photographs in Figure 6 illustrate the effect of PP content on the chemical resistance of the PS/PP blend. It is clear that the surfaces distortions decreased in severity with increasing PP content which correlates with the weight loss effect given in Figure 5.

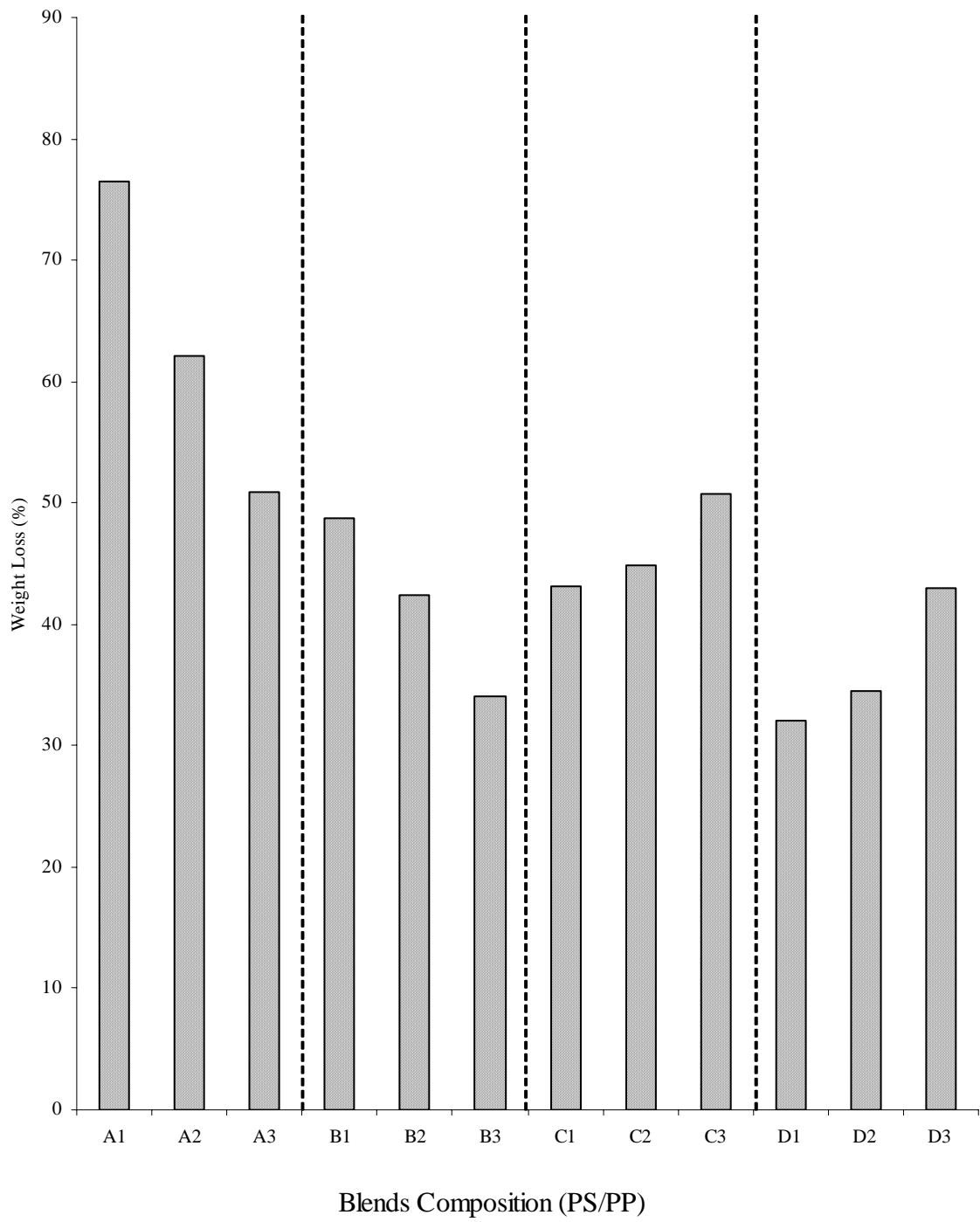


Figure 5: Effect of THF on weight loss of PS/PP blends

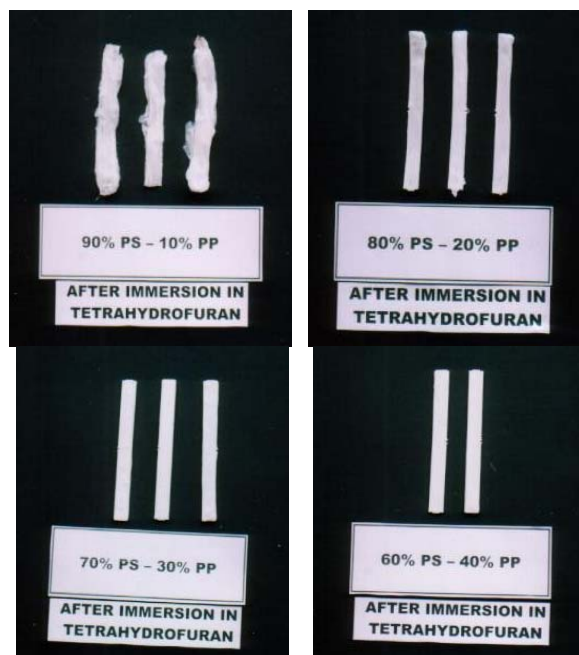


Figure 6: Effect of blend compositions on surface distortion of PS/PP blends due to THF

3.3 Dynamic Mechanical Analysis

Figure 7 illustrates the Dynamic Mechanical Analysis (DMA) thermogram of the 60/40 PS/PP blends. Two glass transitions for the 60/40 PS/PP blend were observed, representing the T_g of each component in the PS/PP blend. The T_g of the PS component was found to be around 105°C and that of the PP component was about -5 °C which indicate that the blends were immiscible. This result is consistent with the result found by D'Orazio *et al.* [7] who also found two T_gs in the iPP/aPS blend. On the other hand, the DMA thermogram of the 60/40/25 PS/PP/SEBS blends showed a single endothermic peak at 102°C (Figure 8), which indicates an improvement in miscibility.

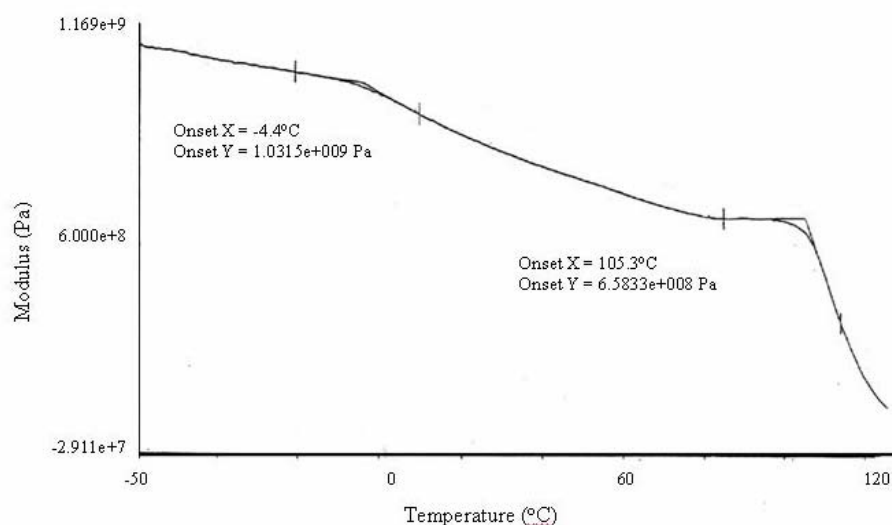


Figure 7: A DMA thermogram showing the T_g of the 60/40 PS/PP.

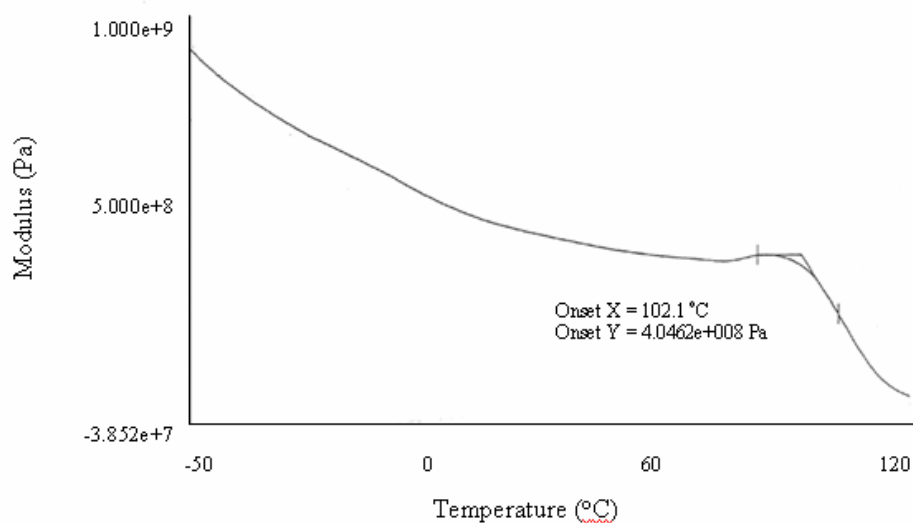


Figure 8: A DMA thermogram showing the Tg of the 60/40/25 PS/PP/SEBS.

4.0 CONCLUSION

The study has investigated the effect of SEBS and blend ratio on the chemical resistance of PS/PP blends. The chemical resistance of PS/PP blends towards acetone and THF increased with PP content. However, the effect of SEBS depends on the PP content in the blends. For the 90/10 and 80/20 PS/PP blends, the chemical resistance towards acetone increased with increasing SEBS content. On the other hand, for 70/30 and 60/40 PS/PP blends, the chemical resistance decreased with increasing SEBS content. Similar trend was observed in the chemical resistance towards THF with a slight variation whereby for the 80/20 PS/PP blend, the chemical resistance towards THF decreased with increasing SEBS content. From the studies it is concluded that the uncompatibilized 60/40 PS/PP blend showed the best chemical resistance among the compositions studied. For the compatibilized blends, 80/20/25 PS/PP/SEBS showed the best chemical resistance towards THF and for acetone 70/30/10 PS/PP/SEBS was the best. Dynamic mechanical analysis showed that 60/40/25 PS/PP/SEBS blends had better miscibility than 60/40 PS/PP blends. However better miscibility did not result in enhanced chemical resistance since SEBS itself was affected by the chemicals.

5.0 ACKNOWLEDGMENT

The authors would like to thank staff of Plastics Technology Group, SIRIM Berhad for overall cooperation. Also thank Petrochemicals (M) Sdn. Bhd. and Titan PP Polymers (M) Sdn. Bhd. for material support.

6.0 REFERENCES

- [1] Sudhin Datta and David, J. L. (1996). "Polymeric Compatibilizers: Uses and Benefits in Polymer Blends". Munich, Vienna and New York: Hanser/Gardner Publications, Inc., Cincinnati.
- [2] Birley, A.W., Haworth, B., and Batchelor, J. (1992). "General Chemical Resistance." Physics of Plastics, New York, Hanser Publisher. 488-492.

- [3] Horak, Z., Kolarik, J., Sipek, M., Hynek, V., and Vecerka, F. (1998). *Journal of Applied Polymer Science*, 69 2615 – 2623.
- [4] Adewole, A. A., Denicola, A., Gogos, C. G., and Mascia, L. (2000). "Compatibilization of Polypropylene – Polystyrene Blends: Part 2, Crystallization Behavior and Mechanical Properties." *Advances in Polymer Technology*, 19 (3) 180-193.
- [5] Radonjic, G., Musil, V. and Smit, I. (1998). "Compatibilization of Polypropylene/Polystyrene Blends with Poly (styrene-b-butadiene-b-styrene) Block Copolymer". *Journal of Applied Polymer Science*, 69; 2625 – 2639.
- [6] Hlavata, D., Horak, Z., Hromadkova, J., Lednický, F., and Pleska, A. (1999). "Compatibilization of Polystyrene/Polypropylene Blends by Styrene-Butadiene Block Copolymers with Differing Polystyrene Block Lengths." *Journal of Polymer Science: Part B: Polymer Physics*, 37; 1647-1656.
- [7] D'Orazio, L., Guarino, R., Mancarella, C., Martuscelli, E., and Cecchin, G. (1997). "Isotactic Polypropylene/Polystyrene Blends: Effects of the Addition of a Graft Copolymer of Polypropylene with Styrene". *Journal of Applied Polymer Science*, 65 ; 1539 – 1553.
- [8] Radonjic, G. (1999). " Compatibilization Effects of Styrenic/ Rubber Block Copolymer in Polypropylene/Polystyrene Blends." *Journal of Applied Polymer Science*, 72; 291-307.
- [9] Adewole, A. A., Denicola, A., Gogos, C. G., and Mascia, L. (2000). "Compatibilization of Polypropylene – Polystyrene Blends: Part 1, Effect of Mixing Intensity on Morphology and Rheological Properties." *Plastics, Rubber and Composites*, 29; (2), 70-79.
- [10] Mustafa, S. S. J., Nor Azlan, M. R., Ahmad Fuad, M. Y., Mohd Ishak, Z. A., and Ishiaku, U. S. (2001). " Polypropylene/Polystyrene Blends – Preliminary Studies for Compatibilization by Aromatic-Grafted Polypropylene". *Journal of Applied Polymer Science*, 82; 428 – 434.
- [11] Halimatudahliana, Nasir, M., and Ismail, H. (2001). "Compatibilizing effect of Ionomer on Mechanical Properties of Polystyrene and Polypropylene Blend". National Symposium on polymeric Material 2000, USM. 211-215.
- [12] Samsudin, S.A, Hassan, A. Mokhtar, M. and Mustafa, S.J.S. (2005). "Effect of SEBS on the Mechanical Properties and Miscibility of Polystyrene Rich Polystyrene/Polypropylene Blends" *Journal of Progress in Rubber, Plastics and Recycling Technology*, 21;(4), 261-276.
- [13] Sousa, A.R., Amorim, K.L.E., Medeiros, E.S., Melo, T.J.A and Rabello, M.S., (2005). "The combined effect of photodegradation and stress cracking in polystyrene". *Polymer Degradation and Stability*, 91;1504-1512.