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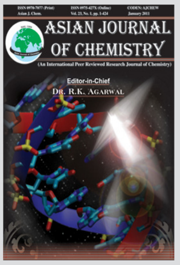

Impact Modification and Toughening of Polystyrene: Part-2. Blending with Medium and High Molecular Mass Elastomers

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The impact properties and morphology of polystyrene by blending with two types of thermoplastic elastomer [styrene-ethylene-propylene-styrene (SEPS)] with the same styrene content were studied to determine the effect of varying molar mass, percentage thermoplastic elastomer content and particle size on the PS/SEPS blends. The impact properties of PS/SEPS blends containing 10-40 % medium molar mass elastomers were found to be superior to those containing 10-40 % high molar mass elastomers with the phase morphology of the former blends show better distribution of rubber particles which are more spherical in shape with reduced size within the PS phase.

Key Words: Polystyrene, Impact modification, Rubber blends, Morphology, Elastomers, Impact properties.

INTRODUCTION

The blending of polymers is an effective way of developing new materials with tailored properties, which is relatively quick and and more cost-effective means of achieving a desired set of properties than synthesizing a new polymeric material. Polymer blending are widely used in many diverse industries and form the basis for engineering plastics, structural adhesives and materials for composite materials[1-6]. By combining two polymers it is possible to produce an immiscible blend. The blend is then made of two phases where one type of polymer molecule predominates. Toughened grade of polystyrene known as toughened PS (HIPS) are used in many applications, where impact abuse is encountered. Recent technology have centred on the use of triblock copolymers such as thermoplastic elastomers to obtain a critical particle size allied to optimum impact resistance. Therefore, a decrease in stiffness and an increase in impact strength of PS can be achieved by adding elastomer with substantially higher impact strength. The influence of thermoplastic elastomer addition on the impact properties of the PS/elastomer blends have been reported[7-20]. This work reports the effect of styrene-ethylene propylene-styrene (SEPS) molar mass on the morphology obtained by means of SEM and the influence of the amount of SEPS on the fracture properties and the correlation between morphology and mechanical properties of the PS/SEPS blends.

EXPERIMENTAL

The thermoplastic elastomers [(styrene-ethylene-propylene (SEPS)] were produced by Kuraray Chemical company Ltd. of Japan (Table-1) with the following structure and composition as shown:

15%	70%	15%
Styrene block	Ethylene/propylene block	Styrene block

In SEPS the central block consists of the rubber like ploymer and the terminals are formed from PS segments.

TABLE-1
DETAILS OF THE THERMOPLASTIC ELASTOMERS

Details	Septon 4033 Medium molar mass	Septon (4055) High molar mass
Composition	SEPS	SEPS
Predominant architecture	Triblock	Triblock
Structure	Linear	Linear
Glass transition temperature of rubber block	≈ -50 ºC	≈ -50 ºC
$M_n \times 10^3$	78.51	147.48
$M_w \times 10^3$	92.48	222.34
M_w/M_n	1.178	1.508

Polystyrene used was Atactic polystyrene, Dow styrene 678E GPPS; $M_n = 72.5 \times 10^3$, $M_w = 220 \times 10^3$, $M_w/M_n = 3.05$.

Compounding: The blends produced were of PS with SEPS 4033 and 4055. Thermoplastic contents were varied from 10 to 40 % by weight. Batches were prepared by Betol BT530 twin-screw extruder with intensive mixing profile, with the zone temperature of 140/145/155/155/165 ºC and at 80 rpm. The dispersion of rubber particles in the blends were carried out under fixed conditions in which screw speed for the blends and the rate feed into the extruder was kept unaltered throughout. The laces of material on existing the die, were quenched in a water bath and passed through a strand cutter to be granulated ready for injection moulding.

Injection moulding: The blends were injection moulded on a Boy 15S injection moulding machine with the barrel temperature of 175-190 ºC (190 ºC at nozzle) at screw speed 230 rpm, to produce impact test pieces of dimensions 110 mm × 10 mm × 4 mm. The blends were all moulded under identical conditions.

Charpy impact tests: Impact testing was performed on a Charpy zwick impact test machine, according to ASTM D 256. A test span of 40 mm was used. The specimen, average dimensions 10 mm in depth (D) and 4 mm in thickness (B), were notched with a hacksaw and using sharp knife to give sharp notch sizes between 0.5 mm and 6.0 mm. The energy of impact was recorded for later analysis.

Scanning electron microscopy (SEM): Scanning electron microscopy (Cambridge Stereoscan 250) was used at high magnification (2000x) to study the phase morphology of the blends which were etched in *n*-hexane to remove rubber particles from the surface of the samples. Specimens upto a few mm in each dimension, from the fracture surface of etched samples, were stuck onto small aluminium mounting stubs and sputtered with a thin gold layer in a vacuum evaporator.

RESULTS AND DISCUSSION

The increasing rubber content for a given blend at constant screw speed and feed rate, led to an increase in energy consumption during compounding of the blends due to the viscosity of rubber being higher than polystyrene. The compounding energy also shows an increase as the average molar mass of the rubber increased. This is due to the increase in the viscosity of the elastomer as molar mass increased. To assess the work being done under these fixed conditions the SEI apparent specific energy input (SEI) was used (Table-2).

TABLE-2
APPARENT SPECIFIC ENERGY INPUT OF THE BLENDS

Blend	SEI** = MN/r amps/kg
GPPS	30.76
Septon* 4033	
10M	10.00
20M	12.00
30M	13.33
40M	16.00
Septon* 4055	
10 H	12.97
20H	13.33
30H	15.55
40H	17.35

*First two digits denote the mass percent and the letter, M and H denote the medium molar mass and high molar mass elastomer, respectively. **M is motor load (amps), N is screw speed (rpm) and r is rate of feed (kg/h).

TABLE-3
ENERGY (U) *versus* BDϕ

Materials	UV BDϕ	UV BDϕ (corrected)
GPPS	Linear C = 0.0766 J G_c = 0.945 kJ/M^2	
10M (Septon 4033)	Linear C = 0.075 J G_c = 2.19 kJ/M^2	Linear C = 0.07 J G_c = 2.50 kJ/M^2
10H (Septon 4055)	Linear C = 0.12 J G_c = 2.2 kJ/M^2	Linear C = 0.1 J G_c = 2.73 kJ/M^2
20M (Septon 4033)	Non-linear C = 0.114 J G_c = 4.76 kJ/M^2	Linear C = 0.108 J G_c = 5.52 kJ/M^2
20H (Septon 4055)	Linear C = 0.16 J G_c = 2.15 kJ/M^2	Linear C = 0.098 J G_c = 3.32 kJ/M^2
30M (Septon 4033)	Non-linear C = 0.385 J G_c = 11.88 kJ/M^2	Linear C = 0.174 J G_c = 17.54 kJ/M^2
30H (Septon 4055)	Non-linear C = 0.311 J G_c = 2.24 kJ/M^2	Linear C = 0.2 J G_c = 13.77 kJ/M^2
40M (Septon 4033)	Non-linear C = 0.098 J G_c = 75.45 kJ/M^2	Linear C = 0.336 J G_c = 75.45 kJ/M^2
40H (Septon 4055)	Non-linear C = 0.376 J G_c = 14.35 kJ/M^2	Linear C = 0.276 J G_c = 33.5 kJ/M^2

Mechanical properties: The mechanical properties of the blends investigated are shown in Table-3. The results of the Charpy impact tests indicated that a modification of a typical brittle PS with SEPS elastomers resulted in improved impact properties. Impact tests have acquired a rather poor reputation in recent years which has arisen from their lack of reproducibility and variation between test methods. However, the use of energy (U) is a pragmatic solution to find the impact resistance of a given material. The analysis of impact fractures where the linear elastic fracture mechanics (LEFM) requires no modification and the fracture initiation condition is defined in terms of G_c which is critical strain energy release rate. Where

G_c = Change in strain energy/Crack growth

$$i.e., G_c = \frac{U}{BD\phi}$$

where ϕ (phi) is an energy calibration factor which is dependant on specimen geometry. A typical graph which is shown in Fig. 1 is obtained by plotting U as a function of BD whose slope is G_c.

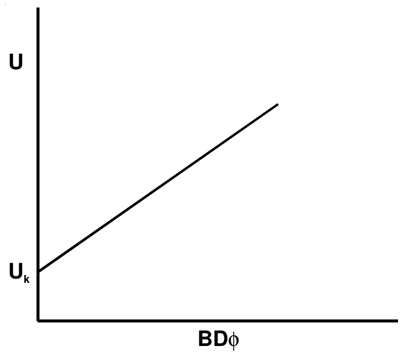

Fig. 1. Energy (U) *versus* BDϕ for LEFM behaviour

Where U_k is kinetic energy. To characterize the ductile failure, LEFM analysis of impact fracture does not work. For tough/ductile materials such as RTPS blends the presence of a large plastic zone (r_p) which occurs in the region of the notch, alters the results and corrections are therefore necessary. It is assumed that the plastic zone acts as a crack length extension so the real crack length is ($a + r_p$) from which the corrected G_c values may be calculated. The presence of a large plastic zone typified by ductile materials can be detected when corrected energy (U) as a function of BDϕ graphs is plotted. Where the data points do not follow the straight line but fall below with curvature, once corrected the energy (U) is linear with BDϕ as shown in Fig. 2[21-24].

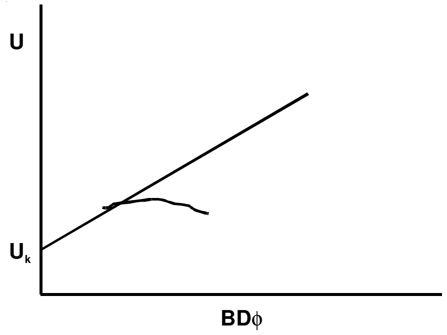

Fig. 2. Corrected energy (U) *versus* BDϕ for large plastic zone

The improvement in fracture properties of brittle GPPS upon rubber modification is well reflected in the values of G_c for rubber toughened polystyrene which are significantly higher than PS for which G_c is 0.945 kJ/M^2 (Fig. 3 for GPPS). The results in Table-3 show that for all the blends the value of G_c increased with increasing rubber content. For the blend containing 10 % rubber content of varying molar mass, the 10M and 10H show linearity when corrected energy (U) is plotted *versus* BDϕ, which give slightly similar value of G_c = 2.50 kJ/M^2 and G_c = 2.73 kJ/M^2, respectively (Fig. 4 for 10M/10H). Whereas, by plotting corrected energy (U) *versus* BDϕ for blends containing 20 % rubber content, all blends show linearity with value of G_c for 20M blend which is higher than 20H blend for which G_c is 5.52 kJ/M^2 (Fig. 5 for 20M/20H). Again, for blends containing 30 % rubber content, same plot give linearity with the value of G_c for 30M blend which is higher than 30H blend for which G_c is 17.54 kJ/M^2 (Fig. 6 for 30M/30H). Similarly, for 40 % rubber blends, same plot give linearity with the value of G_c for 40M blend which is again higher than 40H for which G_c is 75.45 kJ/M^2 (Fig. 7 for 40M/40H). However, the results obtained for all the blends indicated that incorporation of elastomer with medim molar mass and with varying rubber content has significantly improved the impact properties of the PS/SEPS blends which is well reflected in the the values of G_c for these blends[1-3]. The higher values of G_c obtained for the medium molar mass blends is due to the gross plastic deformation in head of the crack propagation of the specimens resulting in a large energy absorption in comparison with those of higher molar mass blends.

Morphology of the blends: Scanning electron microscopy was used to obtain micrographs of the PS/SEPS blends at a magnification of 2000x. These reveal details of the phase structure with the dispersed rubber phase appearing as dark features against a lighter PS continuous phase as shown in Figs. 8-15. However, the blends containing medium molar

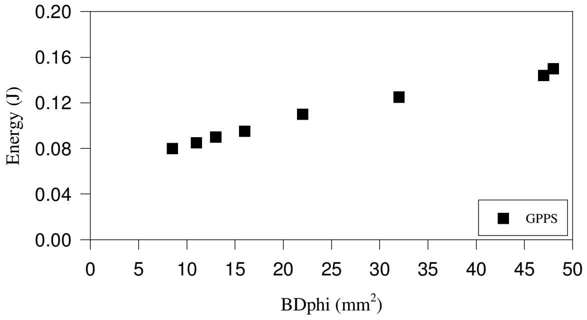

Fig. 3. Shows energy *versus* BDphi for GPPS

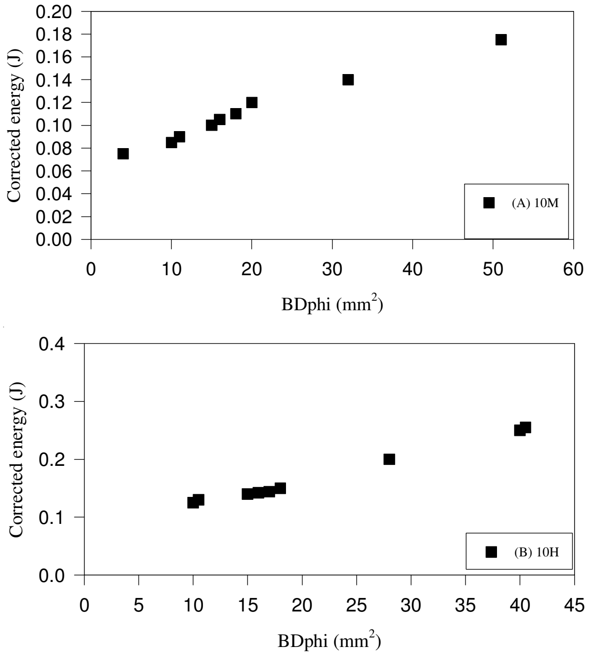

Fig. 4. Shows corrected energy *versus* BDphi for (A) 10 % medium molar mass elastomer (10M) and (B) 10 % high molar mass elastomer (10H)

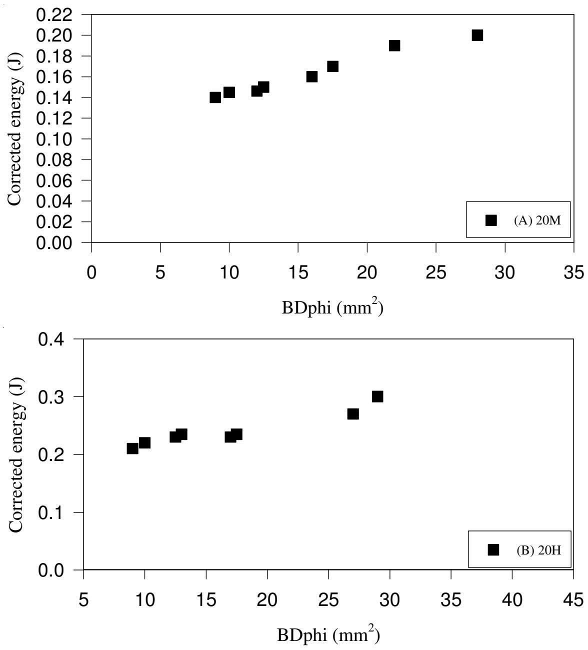

Fig. 5. Shows corrected energy *versus* BDphi for (A) 20 % medium molar mass elastomer (20M) and (B) 20 % high molar mass elastomer (20H)

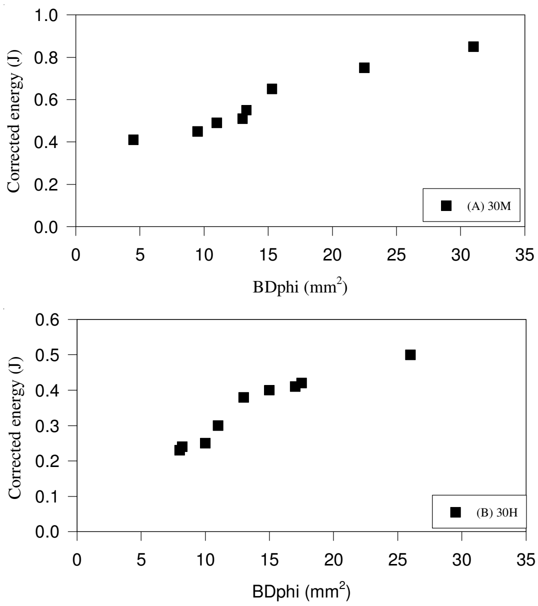

Fig. 6. Shows corrected energy *versus* BDphi for (A) 30 % medium molar mass elastomer (30M) and (B) 30 % high molar mass elastomer (30H)

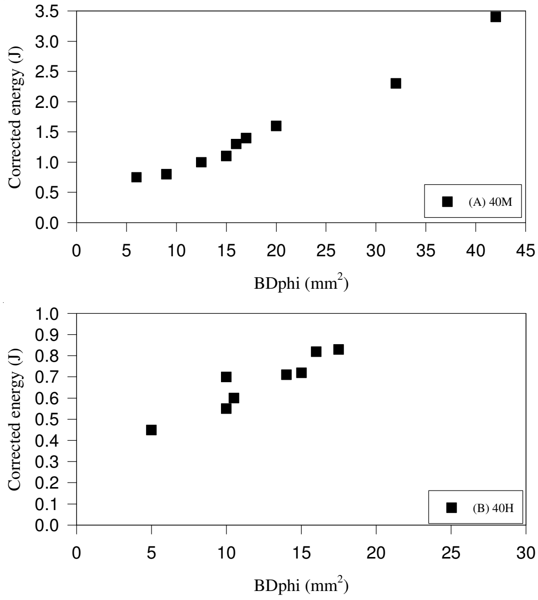

Fig. 7. Shows corrected energy *versus* BDphi for (A) 40 % medium molar mass elastomer (40M) and (B) 40 % high molar mass elastomer (40H)

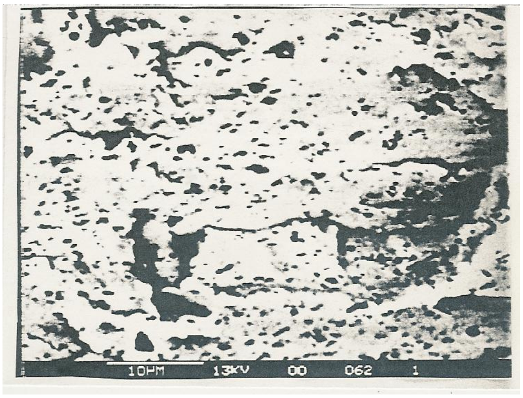

Fig. 8. Shows SEM migrograph of 10M blend (dark phase shows distribution of coarser rubber particles within the white phase PS)

Fig. 9. Shows SEM migrograph of 20M blend (dark phase shows distribution of smaller rubber particles within the white phase PS)

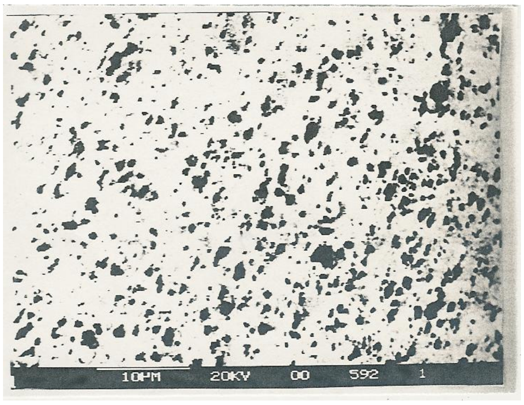

Fig. 10. Shows SEM migrograph of 30M blend (dark phase shows distribution of smaller rubber particles within the white phase PS)

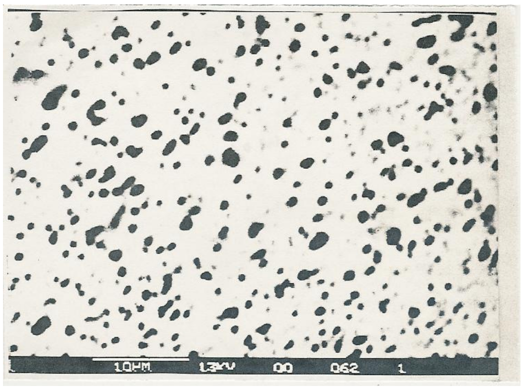

Fig. 11. Shows SEM migrograph of 40M blend (dark phase shows even distribution of rubber particles within the white phase PS)

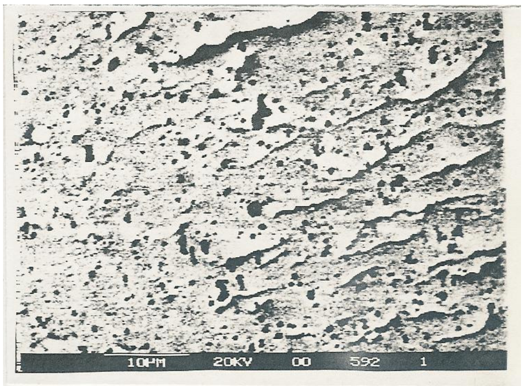

Fig. 12. Shows SEM migrograph of 10H blend (dark phase shows more continuous distribution of rubber particles within the white phase PS)

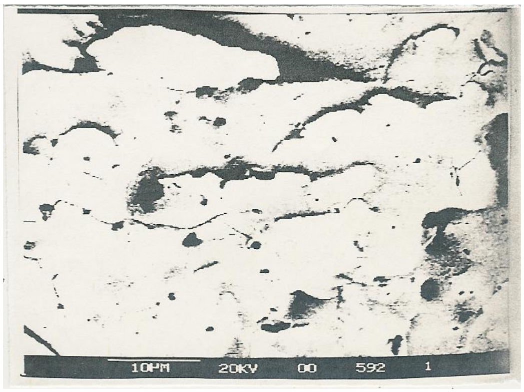

Fig. 13. Shows SEM migrograph of 20H blend (dark phase shows larger and continuous distribution of rubber particles within the white phase PS)

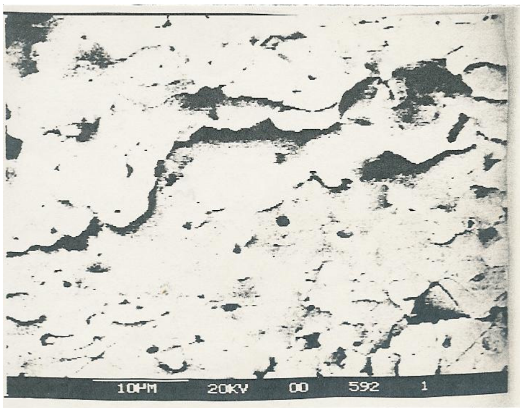

Fig. 14. Shows SEM migrograph of 30H blend (dark phase shows continuous distribution of rubber particles within the white phase PS).

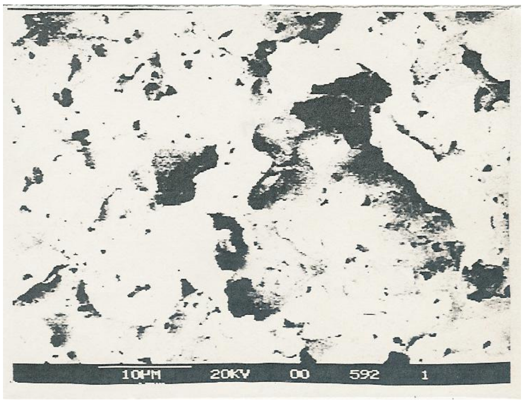

Fig. 15. Shows SEM migrograph of 40H blend (dark phase shows continuous distribution of rubber particles within the white phase PS)

mass rubber (10-40M), their phase morphology show better distribution of rubber particles. As it can be seen from micrographs, the rubber particles increased with increasing rubber content. The blends show good interfacial adhesion with no holes observed in these materials. The 10-40H blends show different phase morphology with regard to their rubber particles size and shape. In contrast to the 10-40M blends the blends containing higher molar mass rubber do not show good distribution of rubber particles within the PS continuous phase. These blends show the rubber dispersed particles are more elongated than blends containing medium molar mass rubber which show a better distribution of rubber particles which are more spherical in shape within the PS phase. The fact that 10-40M blends have higher G_c values indicate a strong dependence upon particle structure with these materials.

Conclusion

(1) Blending polystyrene with varying molar mass and with increasing rubber content led to the improvement of fracture properties of brittle GPPS upon rubber modification which is well reflected in the values of G_c for these materials. (2) The incorporation of elastomer with medim molar mass and with varying rubber content appeared to be substantially more efective in improving the impact properties of the PS/SEPS blends in comparison to those of PS/SEPS blends with high molar mass. (3) The PS/SEPS blends with medium molar mass showed better dispersion of rubber particles, in contrast to those of PS/SEPS blends with high molar mass which showed much broader distribution of rubber particles within the PS phase.

REFERENCES

1. O.H. Tack, H.R. Kim, J.K. Kim and J.Y. Park, *J. Korea-Australia Rheol.*, **13**, 83 (2003).
2. S. Mitra and S. Chattopadhyay, *Nanoscal. Res. Lett.*, **4**, 420 (2009).
3. J. Mosnacek, J. Ae Yoon, A. Juhari, K. Koynov and K. Matyjaszewski, *Polymer*, **50**, 2087 (2009).
4. W. Brostow, T.H. Grguric, O. Olea-Mejia, V. Rek and J. Unni, *e-Polymer*, No. 33 (2008).
5. F. Parres, R. Balart and G. Garcia, *J. Mater. Sci.*, **43**, 3203 (2008).
6. J.H. Laurer, S.A. Khan and R.J. Spontak, *Langmuir*, **15**, 7947 (1999).
7. S.M. Lai, W.C. Chen and C.M. Chen, *Eur. Polym. J.*, **44**, 3535 (2008).
8. M. Abu-Abdeen and I. Elamer, *Mater. Design*, **31**, 808 (2010).
9. J. Li, H. Li, C. Wu, Y. Ke, D. Wang, C. Li, L. Zhang and Y. Hu, *Eur. Polym. J.* , **45**, 2619 (2009).
10. C.B. Bucknall, Toughened Plastics, Applied Science (1977).
11. J.A. Manson and L.H. Sperling, Polymer Blends and Composites, Plenum Press (1975).
12. S.J. Monte and G. Sugeman, Developments in Plastics Technology 2, Elsevier, London, Ch. 3 (1985).
13. D.R. Paul and S. Newman, Polymer Blends, Academic Press, New York (1978).
14. H.G. Elias and F. Vohwinkel, New Commercial Polymers 2, Gordon and Breach, New York (1986).
15. M.J. Folkes, Processing, Structure and Properties of Block Copolymers, Elsevier Applied Science, London and New York (1985).
16. I. Goodman, Developments in Block Copolymers-1, Applied Science Publishers, London (1982).
17. I. Goodman, Developments in Block Copolymers-2, Applied Science Publishers, London (1982).
18. N.R. Legge, G. Holden and H.E. Schroeder, Thermoplastic Elastomers, Hanser Publishers, Munich, Vienna and New York (1987).
19. A.D. Thom, Thermoplastic Elastomers, Rubber and Plastics Research Association, Shawbury, Shrewsbury, England (1980).
20. B.M. Walker, Handbook of Thermoplastic Elastomers, Van Nostrand Reinhold, New York, edn. 2 (1988).
21. A. Whelan and K.S. Lee, Developments in Rubber Technology, Applied Science Publishers, London and New York (1982).
22. R.J. Crawford, Plastics Engineering, Butterworth-Heinemann, Oxford, edn. 3 (1999).
23. J.G. Williams, Fracture Mechanics of Polymers, Ellis Horwood, Chicester (1984).
24. L.A. Utracki, Two Phase Polymer System, Hanser Publisher, Munich (1991).