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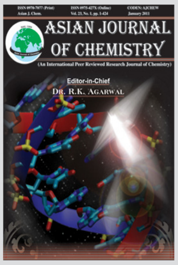

Impact Modification and Toughening of Polystyrene: Part-1. Blending with Low and Medium Molecular Mass Elastomers

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Rubber toughened polystyrene (RTPS) materials were prepared by blending polystyrene with two types of thermoplastic elastomer [styrene-ethylene-propylene-styrene (SEPS)] which include low molar mass and medium molar mass with the same styrene content. The effect of particle morphology, varying molar mass and percentage thermoplastic elastomer content on the fracture properties were evaluated. The properties of polystyrene modified with 30-40 % low and medium molar mass elastomers were found to be superior to those containing 10-20 % low and medium molar mass elastomers with phase morphology of 30-40 % medium molar mass blends show better distribution of rubber particles with reduced size within the PS phase.

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

INTRODUCTION

Polymer blending are widely used in many diverse industries and form the basis for engineering plastics, structural adhesives and materials for fibre-composite materials. The materials are usually multiphase polymers. The dispersed phase consists of rubbery or thermoplastic domain and the continuous phase is a cross linked thermosetting or thermoplastic polymer matrix. The basic reason for toughening a plastic, that is normally brittle at room temperature is to improve its crack resistance and toughness without significantly decreasing other important properties such as the load bearing modulus and the mechanical properties at elevated temperatures[1-10].

It is widely recognized amongst manufacturers that the development of new polymer is not the way forward in trying to help meet demands by the more challenging thermoplastics applications. For these reason polymer blending has been widely acknowledged as the way forward, due to the large reductions in capital investment required and also the reduction in time to market place. Thus, polymer blending is a relatively quick and efficient way of tailoring a material properties to suit a particular market application. Recent developments in toughened thermoplastic technology have centred upon the use of triblock copolymers to obtain a critical particle size allied to optimum impact resistance. Therefore, optimum toughness is achieved for a given rubber phase contents and a given particle size, that is small enough to maximise the volume fraction of craze matter in the stretched polymer but also large enough to initiate crazes from interfaces of such particles[11-20]. This paper studies the effect of styrene-ethylene-propylene-styrene (SEPS) molar mass on the particle morphology obtained by means of SEM and the influence of the amount of SEPS in blends and on the fracture properties of PS/SEPS blends.

EXPERIMENTAL

The thermoplastic elastomers [(styrene-ethylene-propylene-styrene (SEPS)] were produced by Kuraray Chemical company Ltd. of Japan (Table-1). In SEPS the central block consists of the rubber like polymer (70 %) and the terminals are formed from PS segments (30 %).

TABLE-1
DETAILS OF THE THERMOPLASTIC ELASTOMERS

Details	Septon 2007 Low relative molar mass	Septon 4033 Medium molar mass
Composition	SEPS	SEPS
Predominant architecture	Triblock	Triblock
Structure	Linear	Linear
Glass transition temperature of rubber block	≈ -50 ºC	≈ -50 ºC
$M_n \times 10^3$	60.49	78.51
$M_w \times 10^3$	77.88	92.48
M_w/M_n	1.228	1.178

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 2007 and 4033. 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 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 following equation was used:

$$\text{SEI} = \frac{\text{MN}}{\text{r}}\ \text{amps/kg}$$

where SEI is apparent specific energy input, M is motor load (amps), N is screw speed (rpm) and r is rate of feed (kg/h). The apparent specific energy input for the blends during extrusion compounding is shown in Table-2.

Mechanical properties: The mechanical properties of the blends investigated are shown 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

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

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 $BD\phi$ whose slope is G_c.

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 bends 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

TABLE-2
APPARENT SPECIFIC ENERGY INPUT OF THE BLENDS

Blend	SEI (amps/g)
GPPS	30.76
Septon* 2007	
10L	9.62
20L	9.65
30L	10.00
40L	12.30
Septon* 4033	
10M	10.00
20M	12.00
30M	13.33
40M	16.00

*First two digits denote the mass percent and the letter, L and M denote the low molar mass and medium molar mass elastomer, respectively.

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	
10L (Septon 2007)	Non-Linear C = 0.06 J G_c = 2.26 kJ/M^2	Linear C = 0.045 J G_c = 2.50 kJ/M^2
10M (Septon 4033)	Linear C = 0.075 J G_c = 2.19 kJ/M^2	Linear C = 0.070 J G_c = 3.55 kJ/M^2
20L (Septon 2007)	Non-Linear C = 0.07 J G_c = 2.56 kJ/M^2	Linear C = 0.1 J G_c = 3.31 kJ/M^2
20M (Septon 4033)	Non-linear C = 0.114 J G_c = 2.12 kJ/M^2	Linear C = 0.05 J G_c = 4.54 kJ/M^2
30L (Septon 2007)	Linear C = 0.374 J G_c = 7.55 kJ/M^2	Linear C = 0.108 J G_c = 13.94 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
40L (Septon 2007)	Non-linear C = 0.515 J G_c = 36.5 kJ/M^2	Linear C = 0.31 J G_c = 67.79 kJ/M^2
40M (Septon 4033)	Non-linear C = 0.0.98 J G_c = 0.945 kJ/M^2	Linear C = 0.336 J G_c = 75.45 kJ/M^2

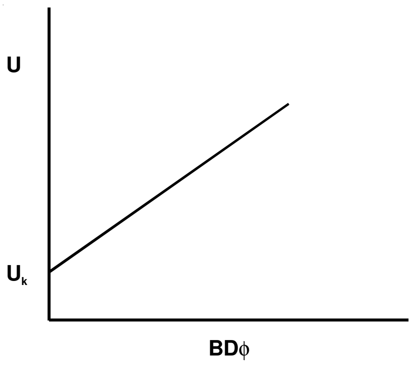

Fig. 1. Energy (U) *versus* BDϕ for LEFM behaviour

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].

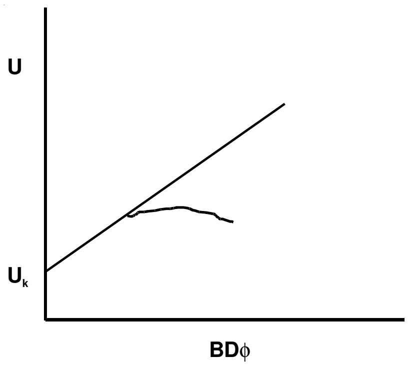

Fig. 2. Corrected energy (U) *versus* BDϕ for large plastic zone

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. The results in Table-3 show that for all the blends the value of G_c increased with increasing rubber content[2-4]. The value of G_c observed for blends containing 30-40 % by weight of both low and medium molar mass rubber are significantly higher than those containing 10-20 % by weight. However, a graph of energy (U) *versus* BDϕ for GPPS shows linearity with the intercept equal to 0.0766 J and the values of G_c equal to 0.945 kJ/M^2 (Fig. 3 for GPPS). With ductile failure such as rubber toughened polystyrene, corrected energy (U) *versus* BDϕ is linear. This is due to the gross plastic deformation in head of the crack propagation of the specimens resulting in a large energy absorption. For the blends containing 10 % rubber content of varying molar mass, the 10L/10M shows linearity when corrected energy (U) is plotted *versus* BDϕ, which gives the value of G_c = 2.50 kJ/M^2 and G_c = 3.55 kJ/M^2 which are slightly lower than those of 20L/20M for which G_c are 3.31 kJ/M^2 and 4.54 kJ/M^2, respectively (Figs. 4 and 5 for 10L/10M and 20L/20M, respectively). For blends containing 30 % rubber content, same plot give linearity with the value of G_c for 30M blend which is higher than 30L for which G_c is 17.54 kJ/M^2

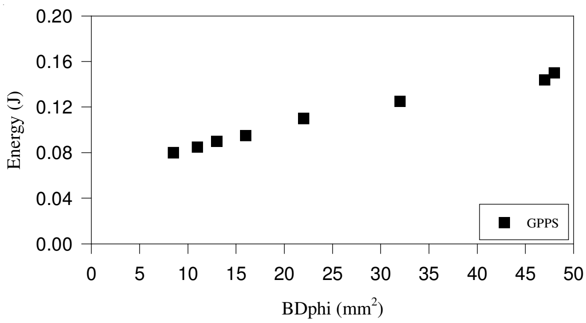

Fig. 3. Shows energy *versus* BDphi for GPPS

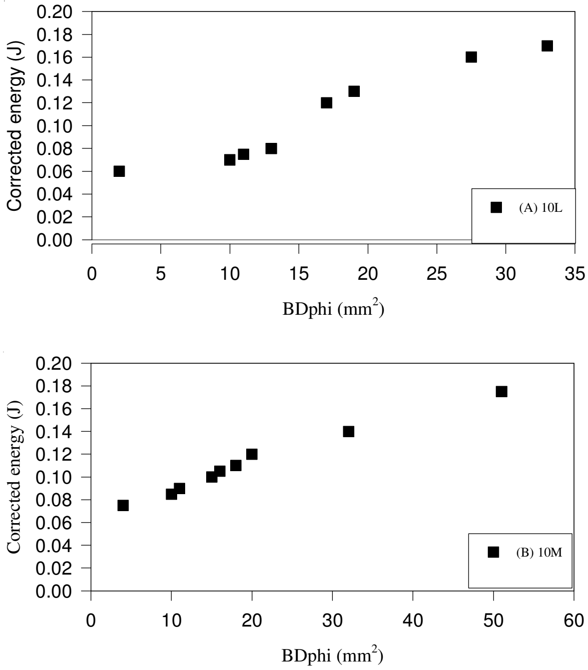

Fig. 4. Shows corrected energy *versus* BDphi for (A) 10 % low molar mass elastomer (10L) and (B) 10 % medium molar mass elastomer (10M)

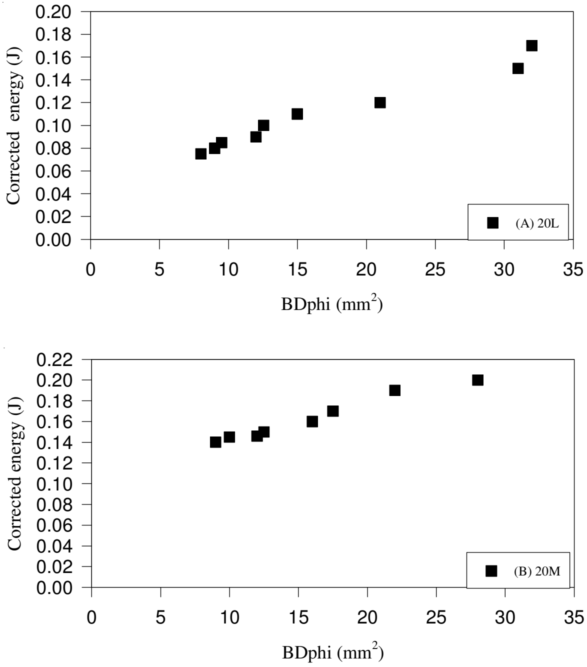

Fig. 5. Shows corrected energy *versus* BDphi for (A) 20 % low molar mass elastomer (20L) and (B) 20 % medium molar mass elastomer (20M)

(Fig. 6 for 30L/30M). Again, for 40 % rubber blends, similar plot give linearity with the value of G_c for 40M blend which is higher than 40L for which G_c is 75.45 kJ/M^2 (Fig. 7 for 40L/40M).

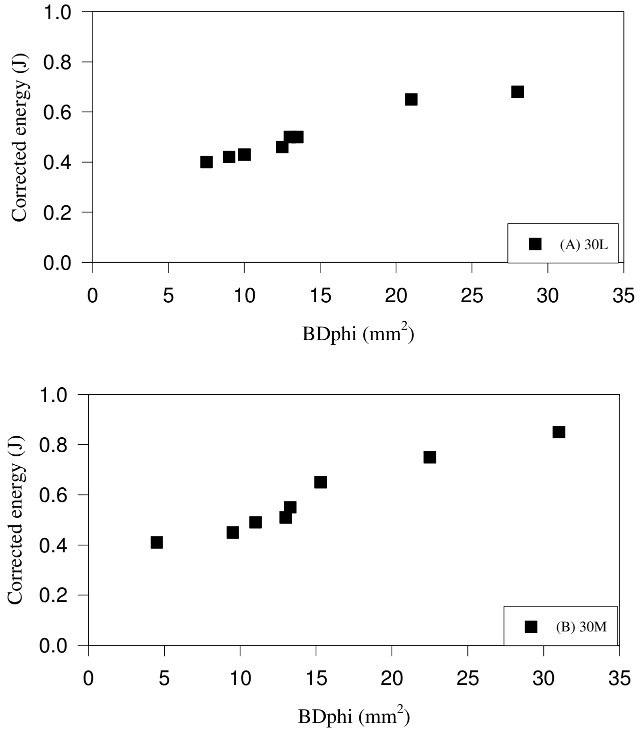

Fig. 6. Show corrected energy *versus* BDphi for (A) 30 % low molar mass elastomer (30L) and (B) 30 % medium molar mass elastomer (30M)

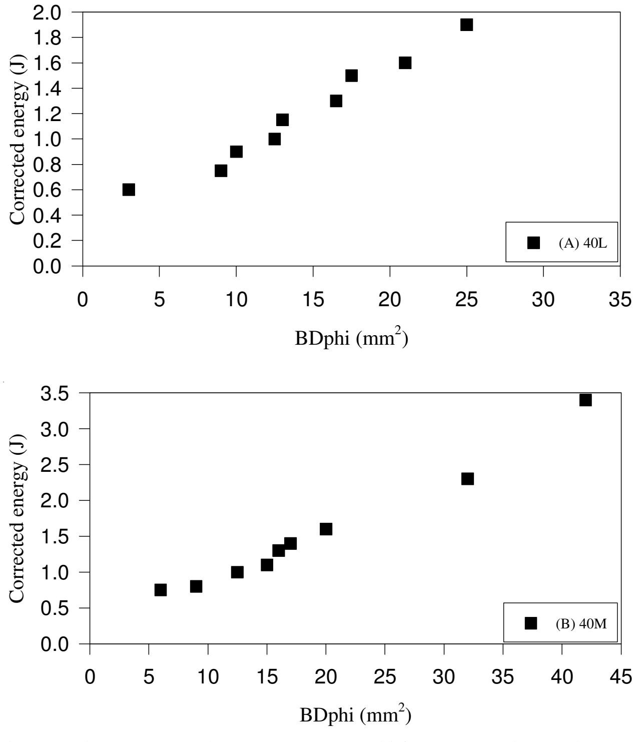

Fig. 7. Shows corrected energy *versus* BDphi for (A) 40 % low molar mass elastomer (40L) and (B) 40 % medium molar mass elastomer (40M)

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. The micrograph for 10-20L blends show distribution of elongated rubber particles within the white PS phase. Whereas, the micrograph for 10M blend shows distribution of coarser rubber particles and that of 20M blend show smaller

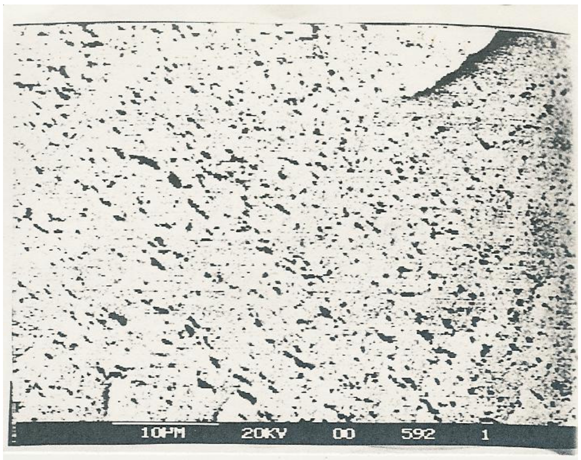

Fig. 8. Shows SEM migrograph of 10L blend (dark phase shows distribution of elongated rubber particles within the white phase PS)

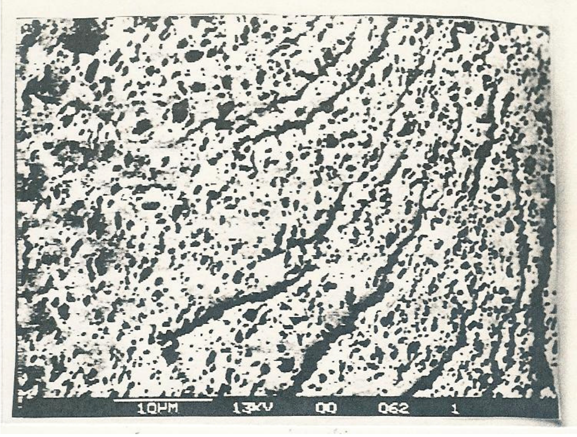

Fig. 9. Shows SEM migrograph of 20L blend (dark phase shows distribution of elongated rubber particles within the white phase PS)

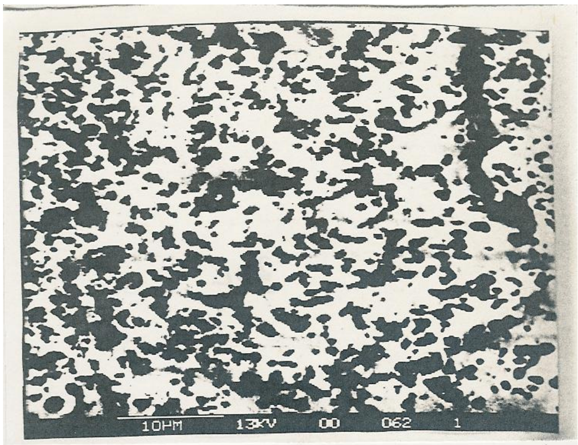

Fig. 10. Shows SEM migrograph of 30L blend (dark phase shows distribution of larger and elongated rubber particles within the white phase PS)

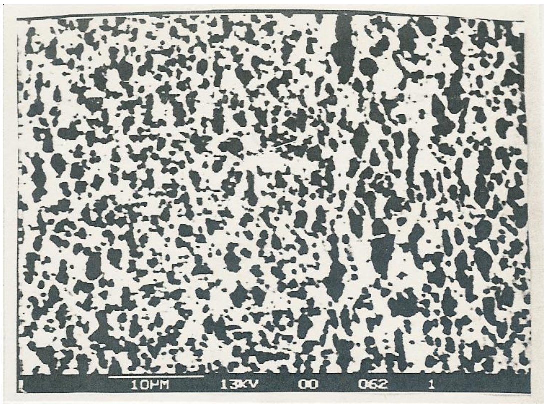

Fig. 11. Shows SEM migrograph of 40L blend (dark phase shows distribution of larger and more even rubber particles within the white phase PS)

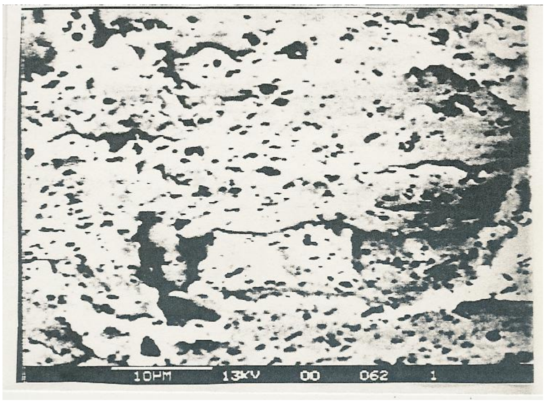

Fig. 12. Shows SEM migrograph of 10M blend (dark phase shows distribution of coarser rubber particles within the white phase PS)

Fig. 13. Shows SEM migrograph of 20M blend (dark phase shows distribution of smaller rubber particles within the white phase PS)

with even dispersion of rubber particles within PS phase. The blends show good interfacial adhesion with no holes observed in these materials. The blends 30-40L and 30-40M show different phase morphology with regard to their rubber particles size and shape. For example, 30-40L blends show more elongated with much larger rubber particles to those of 30-40M blends which show rubber particles are more spherical in shape with reduced size of the rubber dispersed particles within the PS phase. The fact that 30-40M blends have higher G_c values indicate a strong dependence upon particle structure with these materials.

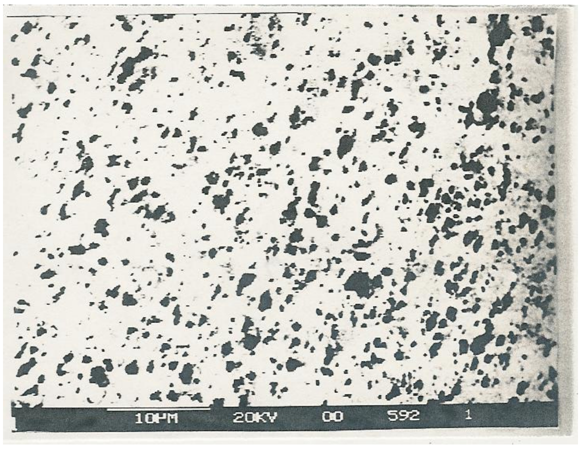

Fig. 14. Shows SEM migrograph of 30M blend (dark phase shows distribution of smaller rubber particles within the white phase PS)

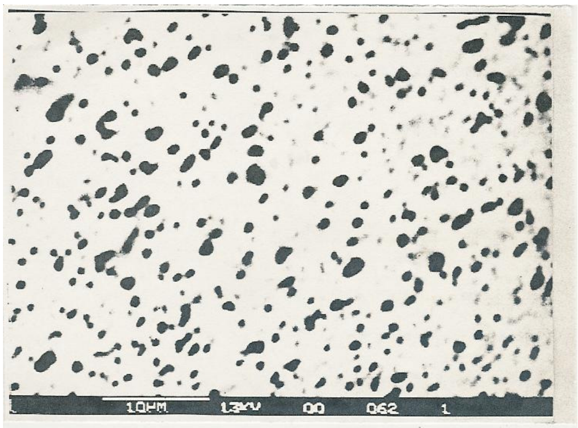

Fig. 15. Shows SEM migrograph of 40M blend (dark phase shows even distribution of rubber particles within the white phase PS)

Conclusion

(1) The incorporation of thermoplastic elastomers [styrene-ethylene-propylene-styrene (SEPS)] with varying molar mass and rubber content into polystyrene resulted in improvement of impact properties of PS/SEPS blends. (2) The values of G_c obtained for blends containing 30-40 % by weight of both low and medium molar mass rubber are significantly higher than those containing 10-20 %. (3) The phase morphology of blends containing 30-40 % medium molar mass elastomer showed better distribution of rubber particles than blends containing 30-40 % low molar mass elastomer which resulted in higher impact properties.

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