

Computer modelling of rubber-toughened plastics

PART III *High-impact polystyrene surface model*

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A computer model has been developed which shows that high-impact polystyrene (HIPS) surface roughness (gloss) depends heavily on rubber phase volume and rubber particle size distribution parameters. The model has been developed in a series of steps. First, several tools have been created for isolation and display of rubber particles near the surface of computer-generated resins. Next, a technique for choosing surface points has been devised, using an algorithm which allows the surface to be disturbed by any particle near the surface. In step three, a non-linear fit of the surface points produces an abstract surface in the form of a grid. The variability in the array of grid points is a measure of surface roughness. The measured surface roughness of conventional high-impact polystyrene resins correlates to the variables identified by the model. A high percentage of the surface roughness variability has been explained in a correlation using average rubber particle size and rubber phase volume, showing the linear regression approach to be good for prediction of the surface roughness of conventional HIPS resins.

1. Introduction

Polystyrene can be toughened by incorporation of spherical rubber particles which contain (occluded) polystyrene. An effort has been made to model the geometry of the high-impact polystyrene (HIPS) system using the computer. Past work has focused on modelling of core-shell particles in a plastic material, as the simplest way to consider the geometric effects of occluded polymer (core) and the rubber shell on resin properties [1]. The tools developed in the early modelling work are used to model geometries of HIPS, where rubber particle distributions are placed at random in a three-dimensional space until a specified rubber phase volume requirement is satisfied [2]. Calculation of spatial parameters, like interparticle distance, in our laboratories and elsewhere have helped to explain rubber reinforcement in rubber-modified materials [2,3].

Surface gloss is a function of surface roughness. The specular reflection from a glossy surface is visible over a small viewing angle, but the intensity of the specular reflection (when visible) is large. The specular reflection is visible over a wider viewing angle for dull surfaces, but the intensity of specular reflection for a given viewing angle is weakened by scattering of light striking the rough surface. The rubber particles in a rubber-modified polymer can disrupt the surface, making it rough and dull.

In the development of computer models to understand the influence of imbedded rubber particles on a polymer surface, it is possible to construct a surface map, where the rubber particles near the surface cause either depressions or elevations. Processing of the polymer influences the surface characteristics. For example, in the injection moulding operation, the surfaces of thermoplastics usually conform to the mould surface when the resin is quenched under pressure. In extrusion, when the resin is allowed to cool slowly, the surface roughness is altered by the rubber particles close to the surface. Particles may cause depressions in the surface if the particle volume shrinks more than the matrix. Elevations would occur if the matrix shrinks more than the rubber. From a comparison of thermal expansion coefficients, polybutadiene should shrink more than the matrix, causing depressions. Stereo microscopic examinations of HIPS extruded sheet show the surfaces can be complex, with rubber particles associated with depressed and/or elevated regions in the frozen matrix.

Phase volume changes from thermal contraction, and many other factors, make the HIPS surface very complex and difficult to model. To date, only intuitive models exist which explain the effects of the rubber phase on gloss. Surface gloss of HIPS is inversely proportional to particle size and rubber level (other variables constant). The logic is that rubber particles

close to the surface may alter surface roughness, depending on moulding conditions. Large particles near the surface have a higher probability of altering the surface roughness than small particles. At high rubber level, there are more particles near the surface and these surface particles may affect the roughness.

Several steps are described in this report for creation of abstract surface representations for hypothetical HIPS resins. Testing of the model on real HIPS resins is also discussed, where modelled surface roughness is compared to measured values.

2. Experimental procedure

2.1. HIPS resin selection and characterization

Several resins were selected for the study (Table I). The resins were characterized for rubber particle size distribution using image analysis [4]. Rubber phase volume was determined using a modified Ruffing gel test procedure [5, 6].

The resins were extruded into 0.5 mm sheet. The extruded sheet take-up equipment was operated to minimize the effect of take-up roll surface on the surface of the sheet, by keeping the contact roll relatively cool and by keeping the roll from touching the sheet on the matt side until the sheet was cooled below 100 °C. Surface characterization (gloss and surface roughness measurements) was conducted on the matt side of the extruded sheet.

2.2. Computer generation of hypothetical and real HIPS resins

The basic concept of the programs and computer visualization techniques have been explained previously [1, 2]. In a representative experiment, a file holding the diameters of rubber particles (either as output from a random number generator or actual particle measurements) was read by the program, until enough particles were picked to satisfy a rubber phase volume requirement. The rubber phase volume could be a measured value, or could be arbitrarily chosen by the user. After sorting the array of particles, the particles were placed in the user-specified three-dimensional space, making sure each placed particle did not overlap with a previously placed particle, and that the particle was within the desired three-dimensional boundary.

For generation of hypothetical resins, seven rubber particle size distributions were generated using

STATGRAPHICS, to study the effects of rubber phase characteristics on surface roughness [7]. The particle diameters for each distribution were stored in a data file to be input for the gloss-model program. The program was run on a personal computer in batch mode overnight. After placement of the particle distributions and identification of the rubber particles interacting with a plane 1 μm from one face of the computer-generated structure, files were generated to view the hypothetical materials.

In the computer simulations of real resins, the rubber particle diameters (measured using image analysis) were held in a file. The diameters were read by the program until enough particles were picked to satisfy a rubber phase volume requirement. The rubber phase volume was a measured value. After sorting the array of particles, the particles were placed in the user-specified three-dimensional space, making sure each placed particle did not overlap with a previously placed particle, and that the particle was within the desired three-dimensional boundary.

2.3. HIPS surface map algorithm

For each hypothetical resin, an array of points (x, y, z coordinates) was obtained describing an imaginary surface of the structures created by the particle-placement routine. The algorithm projected circles of points on a boundary surface, directly above each surface sphere. Each circle diameter was equal to an associated surface sphere diameter. In addition, the centre of each sphere, which was close to the surface, was added to the array of surface points. The complete array of surface points was written to a file to be used to grid the surface.

2.4. HIPS surface grids and calculation of surface roughness

A surface grid for each hypothetical resin was obtained using a software package called SURFER [8]. The array of surface points was input to the GRID utility within SURFER. A minimum curvature algorithm, with a maximum error of 0.001, was employed to obtain surface grid maps [9]. Once these maps were available, various plots were made to display the surfaces and compare the generated surface maps to particles close to the surfaces in the original computer-generated resins.

About 5000 grid points for each hypothetical resin (output from the GRID option within SURFER) were

TABLE I Selected resins used in the polystyrene surface modelling study in order of decreasing surface roughness

Resin source	Particle size (μm)		Rubber phase volume (%)	Surface roughness (μm)		Surface gloss	
	Microtrac ^a	ITC-PS ^b		Abstract	Real		
A	Pilot plant	11.5	4.5	27.7	0.808	1.589	3.8
B	Pilot plant	12.1	5.6	25.6	1.183	1.472	3.8
C	Pilot plant	10.5	3.1	26.9	0.536	1.096	4.4
D	Pilot plant	9.2	2.8	27.7	0.633	1.013	4.5
E	Commercial	6.0	2.2	23.0	0.345	0.490	7.3
F	Commercial	4.1	1.4	25.2	0.201	0.289	8.2

^aLaser light scattering.

^bImage analysis.

evaluated statistically. The points fit a normal distribution, and the average deviation of the grid point elevations was taken as a measure of surface roughness for each abstract surface.

3. Results and discussion

3.1. Surface particle displays and abstract surfaces of HIPS

Rubber particles in HIPS are positioned at random in the polystyrene matrix. Other rubber-modified materials also contain randomly placed rubber particles. In the modelling of these materials, random placement of spheres inside a rectangular solid also places spheres at random near the boundary surface. This is guaranteed if particles are allowed to fill the entire three-dimensional volume made available during the placement operation. The particles close to the surface affect surface roughness of the real materials, and the models can show the effects of rubber particles on surface characteristics.

An example of a computer-generated structure containing flagged surface particles is shown in Fig. 1. Fig. 1a shows a hypothetical rubber-modified resin, with the rubber particles highlighted which are within $1\ \mu\text{m}$ of the resin's top face. This depth is an arbitrary selection. Particles deeper than $1\ \mu\text{m}$ may influence the surface roughness, and the depth may have to be altered when real materials are considered. A side view of the hypothetical material is shown in Fig. 1b. Graphic displays like the ones in Fig. 1 stimulate the

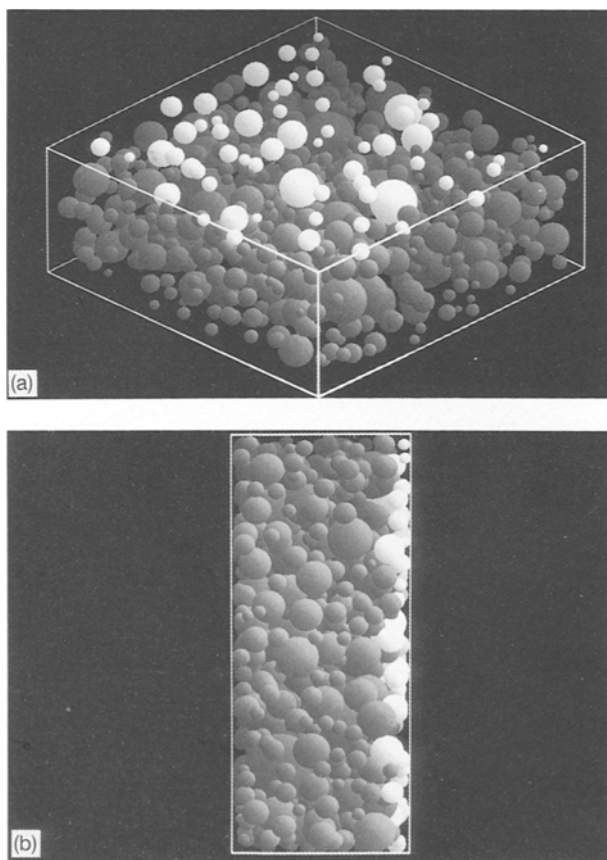


Figure 1 Computer-generated HIPS with surface particles highlighted: resin volume = $50 \times 50 \times 20\ \mu\text{m}^3$, and rubber phase volume = 20%; (a) perspective view, and (b) side view.

imagination, allowing visualization of the potential effects of rubber particles on surface gloss and possibly other surface properties.

Converting visual effects into quantitative information is more difficult. In the case of rubber-modified thermoplastic surface modelling, the surface of a fabricated part depends on the conditions used to obtain the part. Furthermore, the surfaces may be very complex, as in the case of HIPS extruded sheet. In this study, an abstract surface has been created for rubber-modified materials, which is based on the size of particles, the amount of particles and the proximity of particles to the surface. Large particles near the surface disrupt the surface more than small ones. The surface is also disrupted more when a large number of particles are close to the surface, as in the case of high rubber phase volume. This abstract surface model should show the directional effects of these rubber phase characteristics on gloss. The model, once developed, will have to be tested on real materials.

The abstract surface of the modelled HIPS is generally planar, with deviations from planarity occurring where rubber particles exist. These deviations can be either depressions or elevations (user's choice), and the magnitude of the deviation is greater when the rubber particle is large. In Fig. 2, the topology of the abstract surface is mapped to the surface particles. Large particles cause deep depressions in the surface.

Similarly, surface disruptions can be seen when the surface particles are compared to a grid of the abstract surface (Fig 3). The grid surface is shown as depressions where particles exist, but the effect of particles could have been displayed easily as elevations. The variability in grid point elevation is the same for depressions as for elevations in the abstract surface.

It is apparent, from examination of Figs 2 and 3, that the surface particles have been mapped to form an abstract surface. The grid points of the abstract surface can be analysed. The standard deviation of grid point elevation values (taken as a parameter proportional to surface roughness) has been calculated in several hypothetical HIPS resins (Table II) and found to correlate with rubber particle size, rubber particle size distribution breadth and rubber phase volume (as discussed in later sections).

3.2. Effect of phase volume on modelled surfaces

Surfaces of the hypothetical rubber-modified materials are disrupted more when the rubber phase volume is high. This can be seen graphically in Figs 4 and 5. Fig. 4 shows the isolated surface particles for two hypothetical materials varying in rubber phase volume (5 and 25%). Both materials contain particle samplings from the same rubber particle size distribution (log normal $2\ \mu\text{m}$ average diameter and a standard deviation of 1.0). Fig. 5 is a comparison of the grid surfaces of the materials.

Fig. 5 illustrates the effect of rubber phase volume on surface roughness. Each grid-line intersection is a surface elevation value. Calculation of the standard deviation of the grid-point surface elevations is proportional to surface roughness. Fig. 5 shows a much

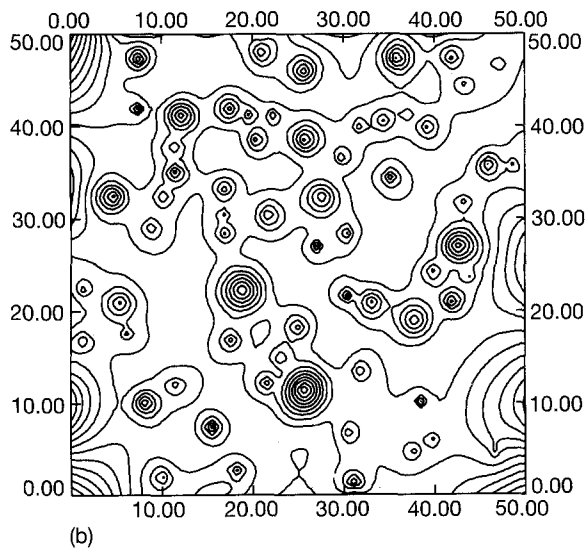
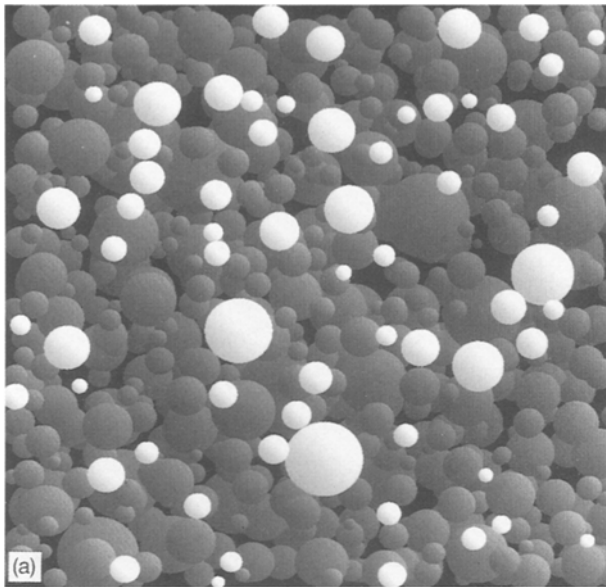


Figure 2 Contour map (b) generated from surface particles (a) in HIPS.

greater variation in surface grid-point elevation when the rubber phase volume is 25%.

At constant rubber phase volume, the surfaces of modelled rubber-modified materials are disrupted more when the rubber particle size is large or when the breadth of the particle size distribution is wide. These effects can be shown graphically in the same way surface roughness has been shown to increase with increasing rubber phase volume.

3.3. Roughness as a function of phase volume and particle parameters

Regression analyses have been carried out using the data in Table II to determine how well the rubber phase volume and particle parameters explain the calculated surface roughness. In a simple linear regression of surface roughness against three variables: the rubber phase volume; the rubber particle size; and the rubber particle size distribution (standard deviation), all three variables are significant at greater than 95% confidence. This correlation also explains over 80% of

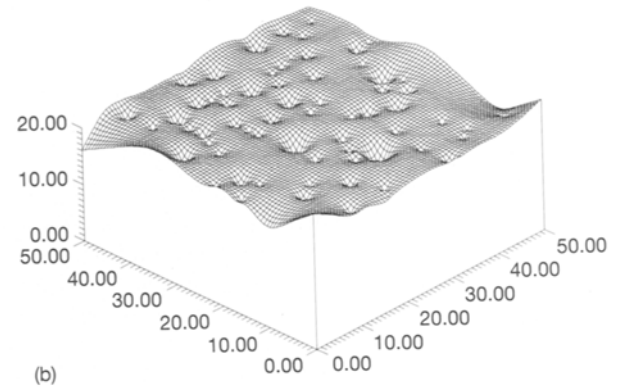
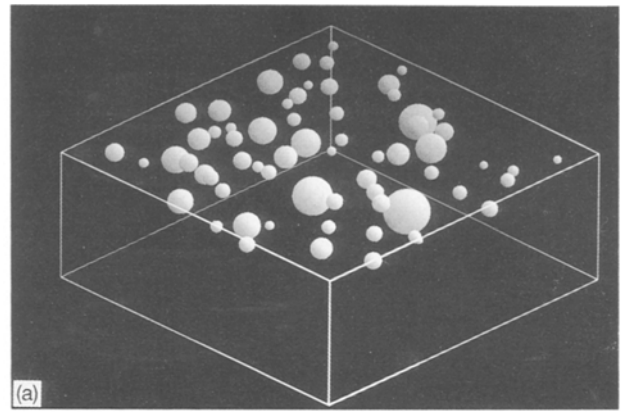


Figure 3 Grid surface (b) generated from HIPS surface particles (a).

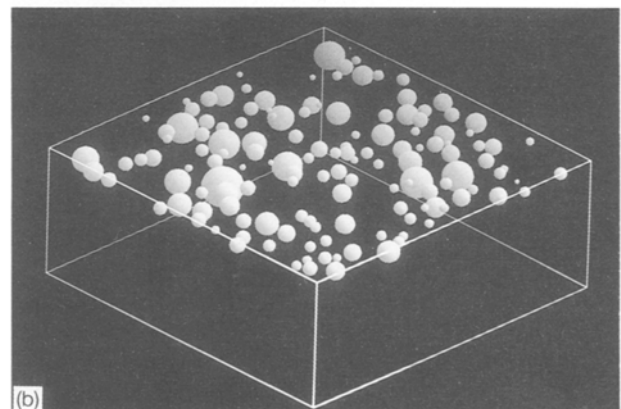
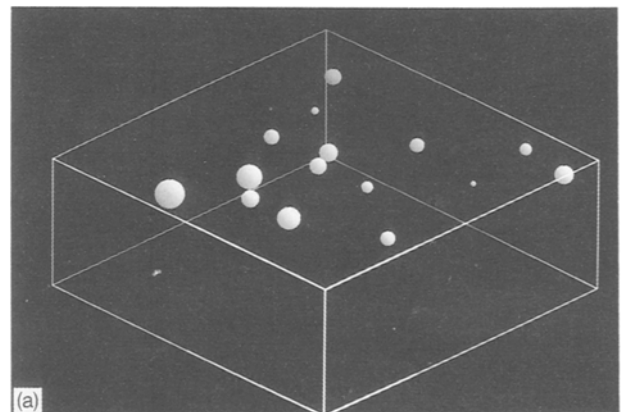


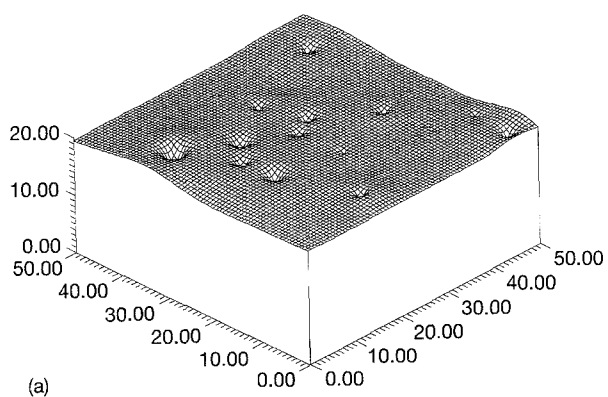
Figure 4 Surface particles from two computer-generated resins varying in rubber phase volume: (a) 5%, and (b) 25%.

TABLE II Calculation of surface roughness for a group of hypothetical HIPS resins ^{a b}

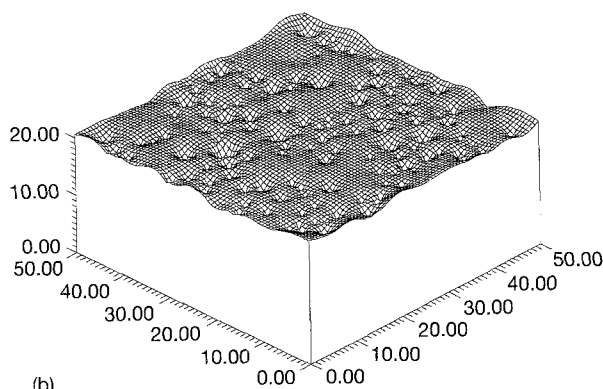
Case	1	2	3	4	5	6	7	8	9	10	11
Log normal size distribution of random numbers											
Average diameter (μm)	1.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.5
Standard deviation	1.0	1.5	0.5	1.0	1.0	1.0	1.0	1.0	1.5	0.5	1.0
Rubber phase volume (%)	20	20	20	5	10	15	20	25	20	20	20
Surface particles	121	61	138	15	36	62	90	140	82	89	65
Surface roughness (grid-point standard deviation, μm × 10 exp 3)	401	482	442	328	447	371	510	473	608	518	656

^aBoundary conditions: z-axis = 20 μm, x-axis and y-axis = 50 μm; volume = 50 000 μm³.

^bSurface particle selection criteria: touching a plane parallel to the x-y plane, 1.0 μm from the x-y top face.



(a)



(b)

Figure 5 Grid surfaces for two computer-generated HIPS resins varying in rubber phase volume: (a) 5%, and (b) 25%.

the variability in the gridded surface roughness (R squared = 80.5%).

Additional regression analyses have been carried out on real resins using the data in Table I to determine how well the rubber phase volume and particle parameters explain the measured surface roughness. In a simple linear regression, the rubber phase volume and the average rubber particle size, as independent variables, explain over 97% of the variability in the measured surface roughness. Both variables are significant at greater than 95%.

This excellent correlation shows that a simple regression model can be used to predict the surface roughness (and hence the gloss) of conventional HIPS resins, when fabricated into thin sheet using the ex-

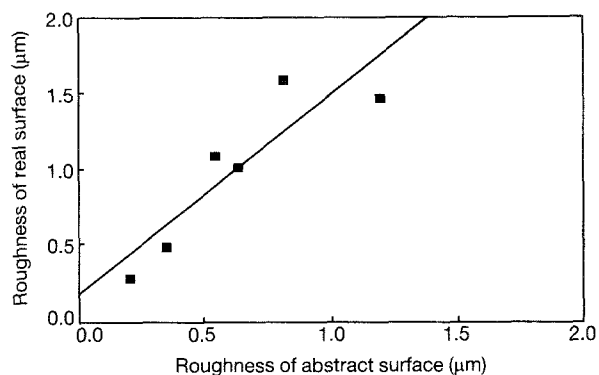


Figure 6 Surface roughness of HIPS extruded sheet.

trusion operation. The regression equation is:

$$Ra = -2.59 + 0.104 (\% \text{ rubber phase volume}) + 0.267 (\text{ITC-PS})$$

where Ra is the surface roughness in micrometers and ITC-PS is the average particle diameter in micrometers. It should be noted that the rubber particle size average must be obtained using image analysis or some other method which gives an accurate measure. An accurate measure of rubber phase volume must also be used in the calculation. The correlation holds for polystyrene reinforced with log normal rubber particle distributions.

3.4. Comparison of measured and modelled surface roughness of real HIPS

The steps to obtain an abstract surface for hypothetical HIPS resins have been applied to the real resins in Table I. The surface roughness of the real materials is the arithmetic average of the absolute distances of all profile points from the mean line of profile points. This value has been calculated from grid surfaces, like those in Fig. 5, for all resins in Table I. The calculated abstract surface roughness correlates to the measured surface roughness ($r = 0.80$), but the abstract surfaces are smoother. This is illustrated in Fig. 6. The abstract surface is idealized, and close microscopic examination reveals the real surfaces to be more complex than the abstract representations.

Other factors may explain the discrepancy between the measured and modelled surface roughness values.

It is possible that particles deeper in the material than those flagged by the computer program, affect the surface roughness. This hypothesis should be investigated to determine if a close agreement can be achieved between the measured and calculated surface roughness values, while maintaining a good correlation between the two.

4. Conclusions

Over the past two years, several tools have been developed to model the geometry of rubber-toughened materials. These tools allow recreation of real HIPS resins in the computer, and allow calculation of geometric parameters which relate to resin toughness. More importantly, the tools facilitate the study of hypothetical materials which are difficult or impossible to synthesize in the laboratory.

In the current study, the HIPS geometry-simulation tools have been modified and used to obtain a surface model for HIPS. This model predicts that surface roughness of HIPS is directly proportional to rubber phase volume, and parameters associated with the rubber particle size distribution.

The model has been used to explain the surface roughness of a group of real HIPS resins, showing an excellent correlation when rubber particle size and

rubber phase volume are used as independent variables. The correlation can be used to predict the extruded sheet surface roughness of conventional HIPS resins.

Acknowledgements

Amoco Chemical Co. is gratefully acknowledged for providing resources and releasing this document for publication. Screen photography was performed by Bruce Blackwell.

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*Received 23 August 1993
and accepted 13 April 1994*