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Computer modelling of rubber-toughened plastics

Part II *Geometric models of high-impact polystyrene and calculation of interparticle distance parameters*

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Coarse models of high-impact polystyrene (HIPS) have been created by computer simulation of the rubber particle spacing in the resin. Interparticle surface–surface distance parameters can be calculated from the models to help explain properties of real materials and predict the properties of hypothetical impact-polystyrene resins. Calculations of the geometric spacing of rubber particles in a group of hypothetical HIPS resins show that a narrow rubber-particle size distribution gives smaller interparticle distance and more reinforcing particles compared to broad distributions for a given average particle size.

1. Introduction

Computer programs have been developed in our laboratory which build geometric models of rubber-modified materials. Models of plastics reinforced with monosized, spherical particles have been described in the first report in this series [1]. These programs have now been expanded to allow placement of rubber particle distributions in a three-dimensional space [2].

Geometric simulation of high-impact polystyrene (HIPS) is the logical extension of methods for characterization of rubber-particle size distribution and rubber-phase volume [3, 4]. Generation of a reasonable geometric model of HIPS in the computer requires knowledge of both the rubber-particle size distribution and the rubber-phase volume. Random placement of the rubber particles of real HIPS in a three-dimensional space, until the rubber-phase volume is just exceeded, geometrically simulates the real material.

This stochastic approach does not place the rubber particles in the same location as they existed in the real material, but the technique provides a useful model for calculation of particle spacing parameters. The parameters can be related to rubber-particle-dependent resin properties. Using this approach, questions can be answered about the effects of rubber-particle size and size distribution on interparticle distance – a parameter associated with toughness of rubber-modified plastics [5, 6].

2. Experimental procedure

2.1. Resin selection and characterization

Three commercial resins were selected for the modelling study. Determination of rubber-phase cross-linking was performed using a modification of the Ruffing gel test [7]. The procedures for measurement of rubber-particle size [3] and rubber-phase volume [4] have been described previously. In the determination of rubber-particle size distribution using image analysis, at least 350 particles were sized for each resin, and the diameters were transferred to a data file to be used as input for the modelling programs. Rubber-particle size distribution was also measured using a laser light-scattering method [8]. Molecular weight was determined using GPC. All other characterizations were conducted using ASTM methods. Physical properties and analyses of the materials are summarized in Table I.

2.2. Description of programs for geometric simulation of HIPS

The basic concept of the programs has been explained previously [1]. Modifications of the Pascal programs for geometric simulation of core–shell reinforced materials were made to allow placement of distributions of rubber particles.

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 sufficient particles were picked to satisfy a rubber-phase volume requirement. The rubber-phase volume could be a measured value or could be chosen arbitrarily 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.

Runs of the program on a personal computer were slow, given the trial-and-error method of selection of

TABLE I Characterization of resins used in modelling studies

	Resin A	Resin B	Resin C
Molecular weight			
Number average	65 000	70 000	68 000
Weight average	166 000	203 000	208 000
Melt flow rate (g/10 min)[a]	5.8	2.1	2.2
Izod impact strength (J m^{-1})[b]	76.3	72.6	69.9
Tensile properties[c]			
Yield strength (MPa)	19.7	30.8	30.4
Ultimate strength (MPa)	23.9	32.7	32.8
Elongation (%)	84	41	37
Dry gel (%)[d]	28.2	18.9	17.7
Swelling factor	11.1	9.4	9.5
Microtrac particle size			
Volume average diameter (μm)	4.24	5.46	5.30
ITC particle size			
(lognormal average, S.D.)	2.08 (1.24)	2.05 (1.39)	2.18 (1.60)
Phase volume (%)	31.8	20.1	19.4
Nearest-neighbour interparticle surface–surface average distance in craze array (μm)	0.261	0.647	0.743
Backdoor-neighbour interparticle surface–surface average distance in craze array (μm)	0.805	1.700	2.178

[a] ASTM method D 1238.

[b] 1/4 in. bar, ASTM method D 256.

[c] ASTM method D 638.

[d] Modified Ruffing gel test.

candidate particle coordinates. A C-language version of the program was written for creation of large models using the Cray-2 supercomputer at the Minnesota Supercomputer Center.

2.3. Interparticle distance calculations and visual displays

Interparticle distance parameters were calculated on the models. The algorithms, calculating these parameters, were used without modification from a previously written code [1]. For each simulation, several runs were made to determine averages for the number of particles placed and averages for calculated parameters.

Two interparticle distance parameters were calculated after the particles were placed within the boundary. Interparticle nearest-neighbour surface–surface distance was calculated for each particle interacting with a planar craze through the model. In the algorithm, each particle was compared to all others interacting with the craze to identify the closest neighbour. Nearest-neighbour distances for all particles were held in an array. After each particle's nearest-neighbour distance was calculated and stored in the array, the average was calculated and sent to program output. The other interparticle distance was the average nearest-backdoor-neighbour surface–surface distance for particles interacting with a planar craze through the model. If a rubber particle intersects a developing craze at the particle's front door, then the next particle to interact with the craze – in close proximity to the first particle – will be at the backdoor of the first particle. A backdoor neighbour was defined as a particle under the particle in question, and each particle was compared to all others to identify the closest-backdoor-neighbour for a given particle. Keeping in mind that the craze is parallel to the Y–Z plane and grows to increasing values of Y, the selection criteria to identify a backdoor neighbour were:

$$Y(\text{neighbour}) > Y(\text{particle})$$

and

$$Z(\text{neighbour}) > Z(\text{particle}) - r(\text{particle}) - r(\text{neighbour})$$

and

$$Z(\text{neighbour}) < Z(\text{particle} + r(\text{particle}) + r(\text{neighbour})$$

where Y and Z are the centre coordinates for particles of radius r. After each particle's nearest-backdoor-neighbour distance was calculated and stored in the array, the average was sent to program output.

Chem-X [9] was the graphics application used to display the models. Output files from the particle-placement routines were in MACCS [10] format or custom format for input to Chem-X. A tandem file, containing Chem-X instructions for assigning sizes to particles, was also output from the particle-placement routines. The tandem file was a script file needed within Chem-X to assign correctly particle diameters for display.

2.4. Simulation of hypothetical HIPS

Three rubber-particle size distributions were generated using Statgraphics [11] to study the effects of rubber-particle distribution parameters on interparticle distance. The particle diameters for each distribution were stored in a data file to be input for the interparticle distance calculation program. The program was run on a personal computer in batch mode overnight, because some runs took several hours to complete. The program read particles from the data file until the specified rubber-phase volume (arbitrarily chosen at 20%) was just exceeded. After sorting this array, particles were placed at random in the three-dimensional space ($20 \times 50 \times 50$ µm^3), working from the largest to smallest particles. Without the sorting, the volume would become blocked before achieving the desired rubber-phase volume. After placement and identification of the rubber particles interacting with a planar craze through the HIPS, interparticle distance parameters were calculated on the geometric array of rubber particles interacting with the craze. Finally, an output file, which could be viewed using the Chem-X molecular modelling package, was generated to view the hypothetical HIPS structure.

3. Results and discussion

3.1. Geometric model of HIPS

Simulation of the rubber-particle spacing in HIPS can be done using computer programs. The size of the model is restricted when the programs are run on a personal computer because of the time required for model creation. However, using the Cray-2 supercomputer, large geometric models of HIPS can be created quickly. As an example, a fairly large model of Resin B (Table I) is shown in Fig. 1. The figure simulates a $50 \times 50 \times 50$ µm^3 block of HIPS and contains about 2000 particles. It requires a small amount of CPU time on the Cray-2 to generate a model such as that in Fig. 1, whereas several hours would be required on a personal computer to solve the same problem. The Cray-2 has not been used for much of the work described in this document. However, for more refined simulation of HIPS, where polystyrene occlusions are accounted for, a supercomputer would be required.

3.2. Calculation of interparticle distance

The computer programs, which can create geometric models of HIPS, have been used to simulate several real materials. The results show to be inversely proportional to the interparticle distance parameters polystyrene rubber reinforcement (Table I).

In the creation of the models, the rubber-particle size distributions and rubber-phase volumes of the resins are determined experimentally. In each calculation, the computer program reads the particle sizes at random from a file until the real rubber-phase volume is just exceeded. Then, after sorting, the particles are placed in a three-dimensional space. Interparticle distances are calculated on the array of placed spheres interacting with a planar craze through the simulated materials. The interparticle distance parameters have been explained previously [1]. Models of two simulated materials, showing craze penetration through $25 \times 25 \times 25$ µm^3 resin blocks are shown in Figs 2 and 3. Isolated craze fields of $12 \times 50 \times 50$ µm^3 blocks are shown in Figs 4 and 5.

The higher rubber-phase volume in Resin A is accounted for by an increased number of rubber particles in Resin A compared to Resins B and C (Table II). The surface–surface interparticle average distance is much less for Resin A. Reinforcement in these materials is ordered in the same way as the interparticle surface–surface distance. The order is intuitively predictable based on phase volume, but the model gives the value of a parameter which can relate size distribution to properties. More important, the

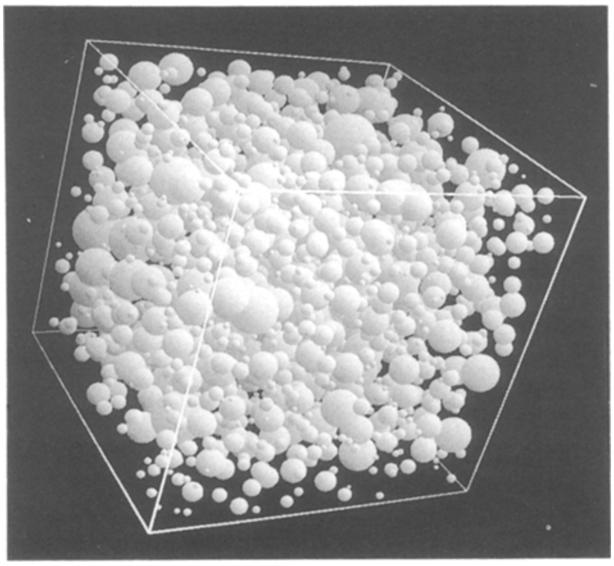


Figure 1 Computer simulation of HIPS using the Cray-2 supercomputer. 1939 particles in $50 \times 50 \times 50$ µm^3.

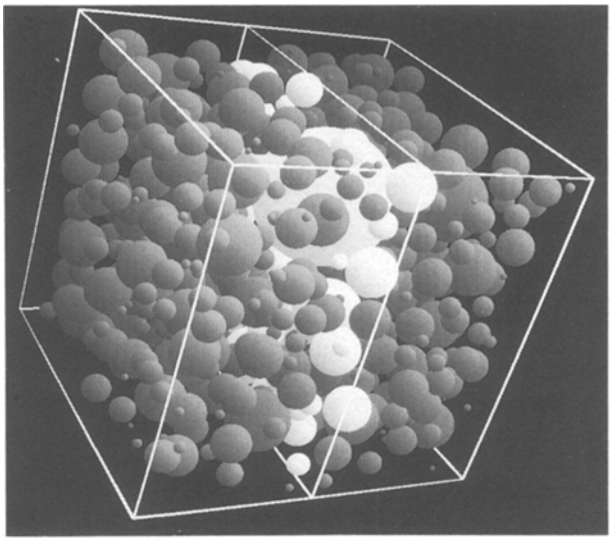


Figure 2 Computer-simulated HIPS Resin A ($25 \times 25 \times 25$ µm^3).

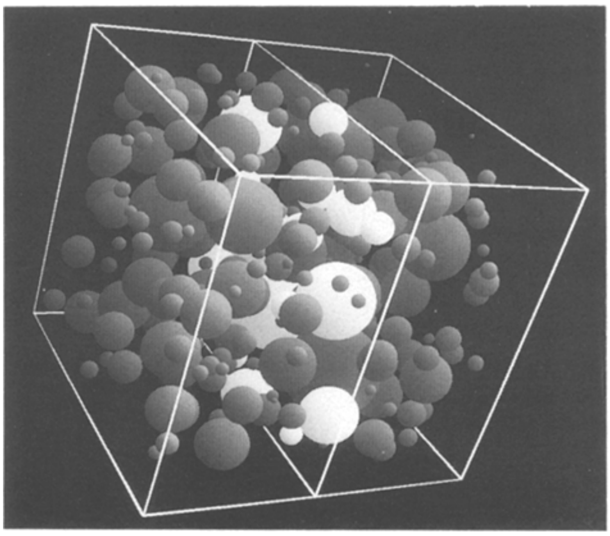


Figure 3 Computer-simulated HIPS Resin C ($25 \times 25 \times 25$ µm^3).

TABLE II

Resin	Phase volume (%)	Image analysis particle size average (S.D.)	Particles in $12 \times 50 \times 50\ \mu m^3$ three-dimensional space	Particles in X–Z craze	Surface–surface average distance in craze array	
					Nearest-neighbour	Backdoor-neighbour
Resin A	31.8	2.08 (1.24)	1144	181	0.261	0.805
Resin B	20.1	2.05 (1.39)	609	105	0.647	1.700
Resin C	19.4	2.18 (1.60)	470	79	0.743	2.178

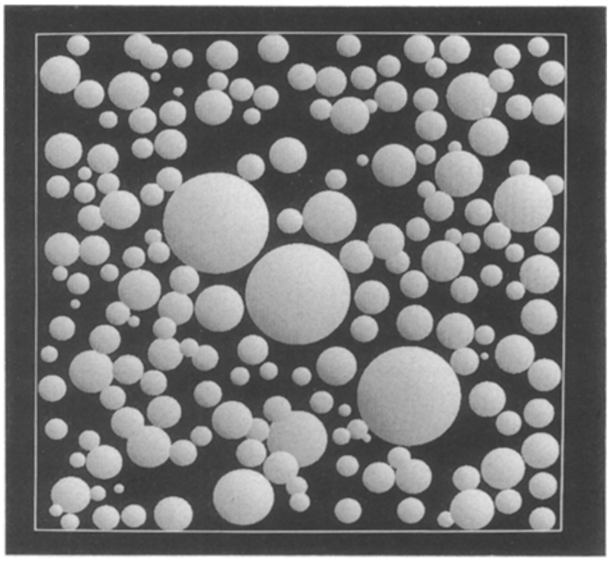


Figure 4 Craze field from computer-simulated HIPS Resin A ($50 \times 50\ \mu m^2$ craze).

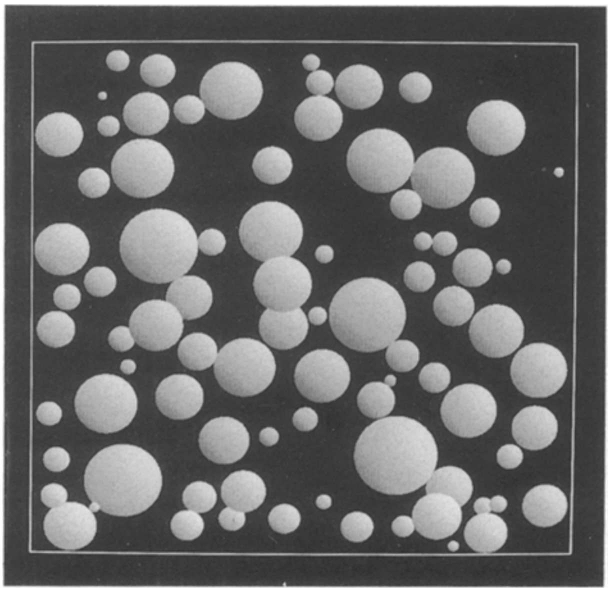


Figure 5 Craze field from computer-simulated HIPS Resin C ($50 \times 50\ \mu m^2$ craze).

modelling tool may provide a way to predict particle-dependent properties of hypothetical HIPS resins which could possibly be made.

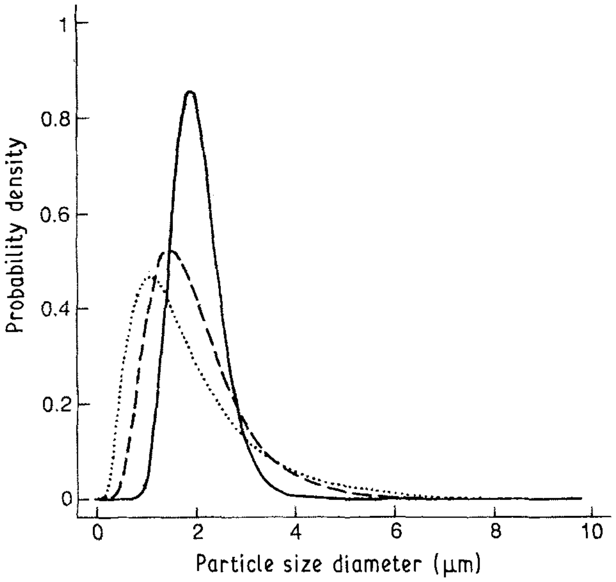


Figure 6 Lognormal probability distributions used in nearest-neighbour calculations. Average = 2.0 μm, S.D.: (———) 0.5; (– – –) 1.0; (· · ·) 1.5.

3.3. Geometric spacing of rubber particles in hypothetical HIPS

HIPS rubber-particle size distributions measured in the past have fit a lognormal distribution [3]. Computer programs have been written to place lognormally distributed rubber-particle size distributions in a three-dimensional space. These programs are useful in graphic simulation of rubber-modified materials. The user of these programs can specify boundary conditions, rubber-phase volume, and particle size distribution as input. The rubber-particle size distributions can be actual distributions (determined from image analysis of real HIPS samples) or randomly generated distributions (from computer algorithms in software packages like Statgraphics).

Particles generated using Statgraphics have been placed in a three-dimensional space to create three hypothetical HIPS resins. Examples of the distributions are shown in Fig. 6, where the standard deviation is varied for three lognormal distributions, each having an average of 2.0 μm. Perspective views of particles interacting with a craze are shown in Fig. 7. Representations of particles interacting with crazes after placement of the three particle size distributions in Fig. 6 are shown in Fig. 8.

Interparticle distances can be calculated, given any HIPS sample modified with lognormally distributed

TABLE III Calculation of interparticle distance parameters for a group of hypothetical HIPS resins

	Case 1	Case 2	Case 3
Lognormal size distribution of random numbers			
Average diameter (μm)	2.0	2.0	2.0
S.D.	0.5	1.0	1.5
Number of particles placed[a]	1968	1335	1082
Interactions within craze[b]	193 (8.5)	129 (2.9)	91 (2.7)
Nearest neighbours within craze			
Surface–surface mean (μm)	0.49 (0.06)	0.61 (0.09)	0.82 (0.07)
Centre–centre mean (μm)	2.60 (0.04)	3.19 (0.02)	3.63 (0.05)
Backdoor neighbours within craze			
Backdoor pairs	183 (8.5)	117 (2.9)	80 (2.1)
Surface–surface mean (μm)	1.57 (0.27)	1.81 (0.10)	2.36 (0.31)

[a] Boundary conditions: X-axis = 20 μm, Y- and Z-axes = 50 μm; volume = 50 000 μm^3. Craze orientation: parallel with the Y–Z plane, centred on the X-axis.

[b] Standard deviations based on three calculations are in parentheses.

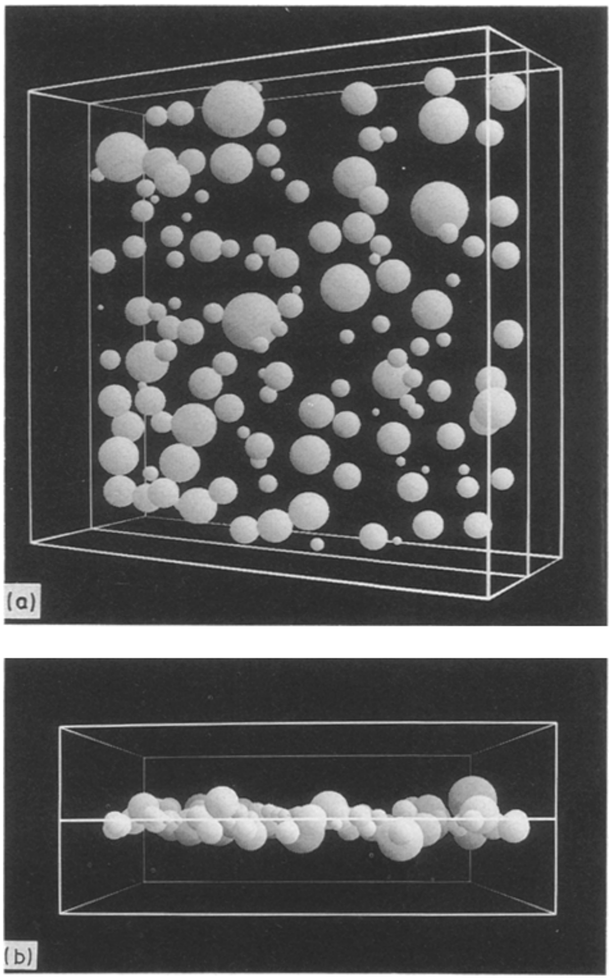


Figure 7(a, b) Perspective views of rubber particles interacting with a craze through hypothetical HIPS.

rubber particles. Calculations have focused on particles interacting with a craze (microcrack) that would occur in failure of a material like HIPS, assuming the craze is planar within the dimensions of the three-dimensional model. The nearest-neighbour parameters have been described previously [1].

The results of all calculations are summarized in Table III. Considering the placement of the distributions with the 2.0 μm average diameter, the following trends are observed.

1. The number of reinforcing particles and the number of backdoor pairs in the craze decrease as the standard deviation increases.
2. All interparticle distance parameters increase as the standard deviation increases.

If one assumes that interparticle surface–surface distance affects polystyrene reinforcement, then the above results show that the breadth of the rubber particle size distribution is important for achieving good reinforcement in HIPS. Narrowing the lognormal distribution makes the rubber-phase volume, which is spent on a large particle, available for many small particles. Other particle-dependent properties can be balanced in polystyrene reinforced with narrow particle distributions. For example, gloss can be balanced with reinforcement if the particle size is kept small and the particle size is kept above the reinforcement threshold.

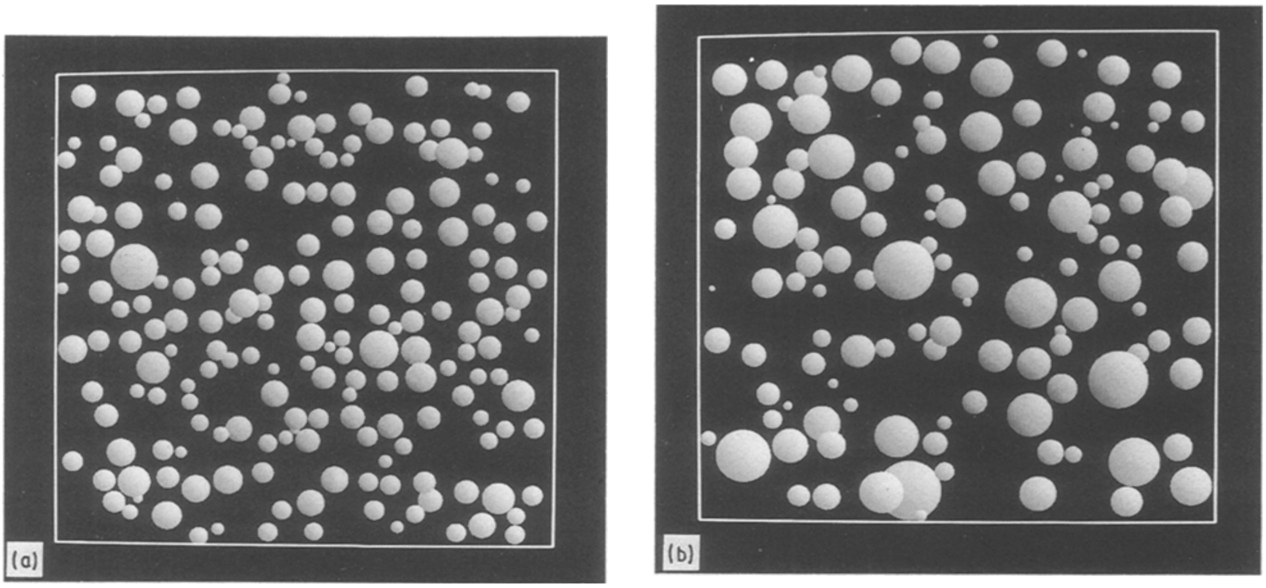
Calculation of interparticle distance values on randomly placed HIPS rubber-particle size distributions gives theoretical parameters, which can be used to predict the effects of changes in particle size distributions on polystyrene reinforcement. The theoretical work needs to be verified by more experimental data to increase the understanding of rubber reinforcement of polystyrene with rubber.

3.4. An example of interparticle distance reduction

To illustrate the effect of narrowing the distribution on interparticle distance in Resin C, a hypothetical resin model (Resin D) has been constructed. This material has the same rubber-phase volume as real Resin C, but the narrower rubber-particle size distribution of Resin B (Table I) has been used to construct the hypothetical resin. Resin D is imaginary, but not outside the realm of possibility (Table IV). The narrow rubber-particle size distribution gives more rubber particles and a smaller interparticle surface–surface distance. Resin D should have better reinforcement than Resin C without increasing the rubber-phase volume.

TABLE IV

Resin	Phase volume (%)	Image analysis particle size average (S.D.)	Particles in $12 \times 50 \times 50\ \mu m^3$ three-dimensional space	Particles in X–Z craze	Surface–surface average distance in craze array	
					Nearest-neighbour	Backdoor-neighbour
Resin C	19.4	2.18 (1.60)	470	79	0.743	2.178
Resin D	19.4	2.05 (1.39)	583	100	0.702	1.895



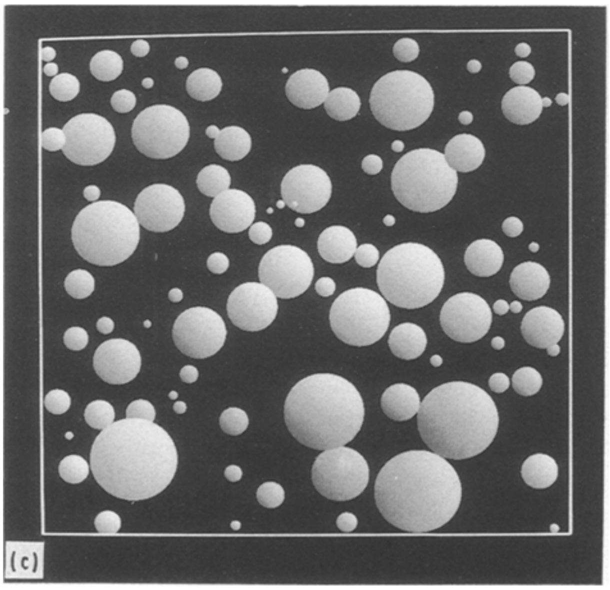


Figure 8 HIPS craze fields for three rubber-particle size distributions in hypothetical HIPS. Average = 2.0 μm, S.D.: (a) 0.5, (b) 1.0, (c) 1.5.

4. Conclusions

The geometric spacing of rubber particles in HIPS has been modelled using computer programs written for a personal computer. These programs generate output files which allow the user to view the simulated HIPS on graphics systems available to the Chem-X molecular modelling application. Larger models can be created using C-language versions of the programs to run on the Cray-2 supercomputer. Output files from the C-language versions are also viewed through Chem-X.

Construction of the models requires rubber-particle size and rubber-phase volume as input variables. The output parameters associated with geometric spacing of rubber particles in the polystyrene matrix can be used in correlations to help explain the rubber-phase-dependent HIPS properties. Computer simulation of real HIPS resins has shown a general correlation of rubber reinforcement of the polystyrene with interparticle surface–surface distance. However, more work needs to be done to establish this relationship firmly.

The most important result of the HIPS modelling work is generation of hypothetical resins in the computer. This allows the researcher to consider a variety of materials which would be difficult or impossible to synthesize. This has been demonstrated by modelling a group of hypothetical HIPS resins, by varying the rubber-particle size distribution breadth.

The study of the hypothetical materials shows, from a particle-geometry standpoint, that it is important to control rubber-particle size distribution. Calculations show that interparticle distance can be reduced by narrowing the rubber-particle size distribution in HIPS.

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