Journal of Reinforced Plastics
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Journal of Reinforced Plastics and Composites 1997 16: 1523
DOI: 10.1177/073168449701601605

On the Influence Zone and the Prediction of Tensile Strength of Particulate Polymeric Composites

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ABSTRACT: An intended numerical investigation is carried out. The results indicate that, even if a perfect adhesive bond is preserved between the particles and matrix materials, the two-phase element cell model is unable to predict the strength increment of the particulate polymeric composites (PPC). To explore the main reinforcing mechanism, additional microscopic experiment is performed. An "influence zone" was observed around each particle which is measured about 2 to 10 micrometers in thickness for a glass-polyethylene mixture. Then, an improved computational model is presented to include the "influence zone" effect and several mechanical behaviors of PPC are well simulated through this new model.

1. INTRODUCTION

Because of its low cost and ease in manufacturing, the particle-filled polymeric composite (PPC) is becoming one of the most competitive materials in modern industry (Katz and Milewski, 1978). The inorganic inclusions dispersed in the polymeric matrix greatly improve the rigidity of composites, and at certain cases, improve the tensile strength and toughness, also. A number of theories have been developed for the prediction of elastic modulus of particulate composites. However, few well-defined studies have been made in an effort to explain the strength behavior (Papanicolaou and Bakos, 1992). The reinforcing mechanism of PPC in the aspect of tensile strength is obviously different from that of the traditional fibre-reinforcing composites (FRC) (Jayaraman et al., 1993a; 1993b). To understand this issue seems crucial not only to the material advancement but also to the development of pertinent sciences, especially composite mechanics.

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0731-6844/97/16 1523–12 $10.00/0

Pioneering studies could date back to the analysis of a single inclusion embedded in an infinite elastic medium (Eshelby, 1957) and the representative volume element (RVE) model proposed by Hashin (1962). However, most of the successive research works were focused on the investigation of increment of elastic modulus (bulk or shear moduli), following the primitive motivation of chemical industry. Only from the 1980s did people begin to pay attention to the strength of composites and its reliance to the microstructures (Miller et al., 1989; Wu et al., 1987; Theocaris, 1985). Some of the common experimental results reported in literature are summarized as follows:

1. The interfacial bond between the phases has an effect on the final composite strength: a weak bond weakens the strength.
2. Smaller fillers in diameter deduce a relatively higher composite strength (Wu et al., 1987; Katz and Milewski, 1978).
3. The composite strength is also affected by the volume fraction of the fillers (Wu et al., 1987; Katz and Milewski, 1978). The result 2 and result 3 are illustrated in Figure 1 (reprinted from Wu et al., 1987, according to Table 1 and Figure 3 in the paper).

The adhesive strength of the interface has been regarding as the main contribution to the composite strength. As a result, commercial attention has long been paid to the choice of the so-called "coupling agent" in order to get the strongest surface adhesion. However, present study on a mixture of HDPE/glass shows that to improve the overall strength, a strong interface is far from sufficiency. Three additional conditions seem more important:

1. Around each particle the matrix forms an influence zone.

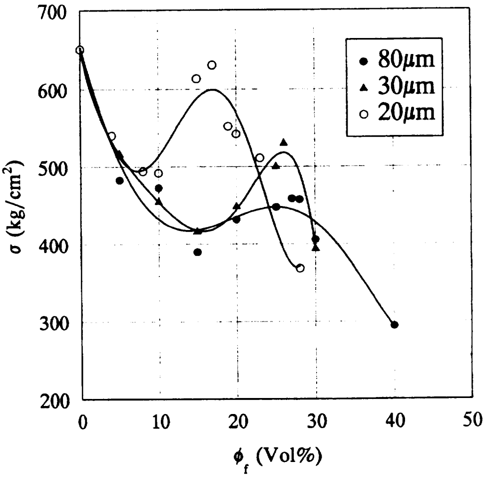

Figure 1. *The tensile strength of the composites is affected by the volume fraction of the fillers (reprinted from Figure 3, Wu et al., 1987).*

2. The local tensile strength of the zone must be higher than that of the original polymeric matrix.
3. To obtain the maximum of the composite strength, the content of the influence zone should be controlled at a proper ratio.

2. A STRONG INTERFACE DOES NOT LEAD TO AN IMPROVED STRENGTH

With the introduction of secondly phased particles to polymeric matrix, the defects, impurities in matrix increase, too. When the composite is loaded, these defects will certainly induce local stress concentration as well as microdamage evolution (Yan, 1990). Therefore, logically, the strength of the composites should be lower than that of the original matrix in most cases if the physical structures of components do not change during the mixing at all.

Neglecting the interaction or change of the constituent components is the main character of the two-phase model, in which only the matrix phase and particle phase are considered. The distribution of particles in the matrix is also assumed to be a periodic structure for the sake of simplicity. The tiniest part of the periodic structure with the periodic boundary conditions is usually called an element cell (Hashin and Rosen, 1964).

As shown in Figure 2, an axis-symmetric element cell was often used in the previous analyses (Zhang and Lu, 1994). The interface between the particle and matrix is assumed to be perfect and strong enough that any stress or strain can pass through it. For simplicity, both the radius and the height of the quarter-cell are assumed as a, respectively. The radius of the particle is r and its Young's modulus, Poisson's ratio, strength limit are E_f, ν_f, and σ_f^b, respectively. In sequence, the Young's modulus, Poisson's ratio, strength limit of matrix are E_m, ν_m, and σ_m^b, respectively.

When the particulate composites are subjected to a tension load along the z-axis, the stress field of matrix was unavoidably distributed by the fillers. Nevertheless,

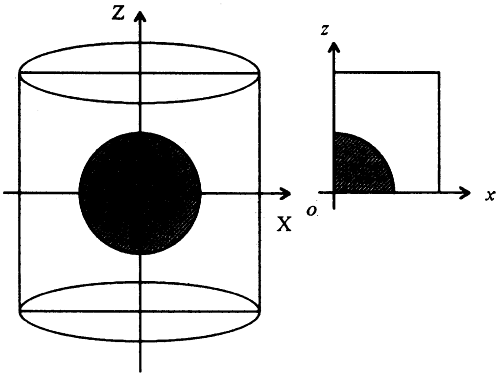

Figure 2. An axis-symmetric element cell.

the principle stress along the tensional axis, i.e., σ_z, will dominate among the stress components. Therefore, once the σ_z at an arbitrary point of the cell element reaches its original strength limit first (the filled matrix has been assumed to be as the same as the unfilled matrix in the two-phase model), the average stress at the upper surface of the cell is defined as the composite strength, σ_c^b.

The following computational results indicate that no matter how soft or hard the particle is, the composite strength cannot surpass the original matrix strength (Figure 3). In other words, a strong interface does not lead to an improved strength.

Compared to the experimental results listed in section 1, the two-phase model has two shortcomings:

1. The stress or strain distribution in the matrix or particles given by the two-phase model cannot reflect the size effects of the fillers: once the volume fraction of the fillers is specified, no matter how large the particle is, its relative scale to the whole cell is the same and so are the computational results.
2. Even if the cell analysis can give an exact stress distribution, the model itself cannot illustrate the reason of reinforcement. Just examining the force balance along the tensile direction of the model, due to the stress concentration, the stress at an arbitrary section of the matrix cannot arrive at the limit at the same time, or the total load that the section sustains cannot be larger than that of the original uniformly deformed matrix.

In conclusion, the two-phase model lacks the ability to simulate the reinforcing mechanism of composite strength; on the other hand, the perfect adhesion between the particle and matrix is not enough for preserving the strengthening of the materials.

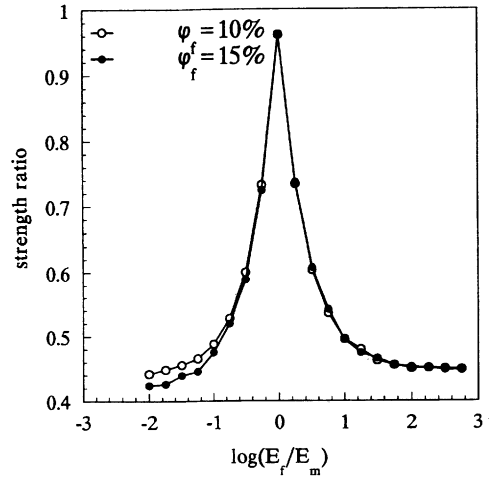

Figure 3. The composite strength cannot surpass that of the original matrix material if only two phases are considered.

But in engineering practice, the fact is that the particulate polymeric composites can and do improve their strength at certain cases. Therefore, besides the interfacial bond, there must be a not-well-understood mechanism that works.

3. MICROSCOPIC OBSERVATION: THE INFLUENCE ZONE

Material property is strongly related to the internal structures. As far as the sizes of commercial fillers are considered (most are in the diameter of 1–100 μm), the interactions between the fillers and polymeric matrix in its aggregate phase play a great role in improving the composite strength. These interactions are mainly controlled by the manufacturing environment, cure temperature, cooling speed, etc.

Taking the polyethylene for example, it has a strong contraction effect during the cure procedure. When it is used as a free (unfilled) matrix, the contraction does not bring any stress heterogeneity to the matrix material. However, when it is being filled with particles, the different thermal coefficient of the fillers brings stress distortion to the domain near the particles. This extra stress in the cure procedure will deduce the crystallization of polymers, so as to form a stress-induced "influence zone" mostly made of the extended molecular chains. Such an influence zone has different properties from the rest of the matrix.

The concept of influence zone is slightly different from the *mesophase* used by Theocaris (1992): when the polymeric matrix is cast around the inclusions, due to the physi-sorption and chemi-sorption, the intermediate boundary layer creates between successive phases which was called the mesophase. The influence zone, however, has a more far-reaching radius than the mesophase. It is estimated in the dimension of micrometers, and is expected to be observed at ordinary optical microscopes.

The testing material was a mixture of HDPE (high density polyethylene) and glass beads. The glass beads which were chosen as the particulate fillers were 30 to 40 micrometers in diameter. The moulded specimens were supplied by Institute of Chemistry, Chinese Academy of Sciences.

A variety of testing material is examined according to the coupling agents used or the volume fraction of the fillers (see Table 1).

The size of moulded specimen is schematically shown in Figure 4.

A piece of squared plate (10 × 10 × 4) is cut from the specimen for microscopic observation. The square is polished carefully according to the parameters listed in Table 2.

When the observation square is polished, the average pressure acted on the tribo-surface is about 7.5×10^{-2} MPa, which is much lower than the yield stress of

Table 1. The material used in present study.

Material Code	Volume Fraction	Coupling Agents
J_0	—	—
J_1	10%	—
J_5	10%	Silane + Agent "C"

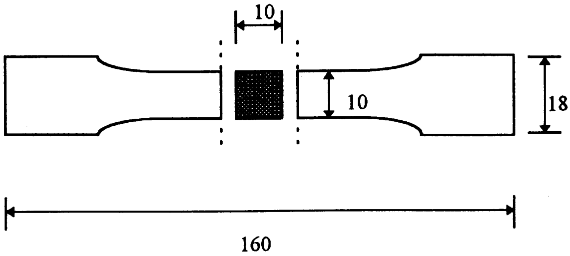

Figure 4. *The specimen used in present experiment.*

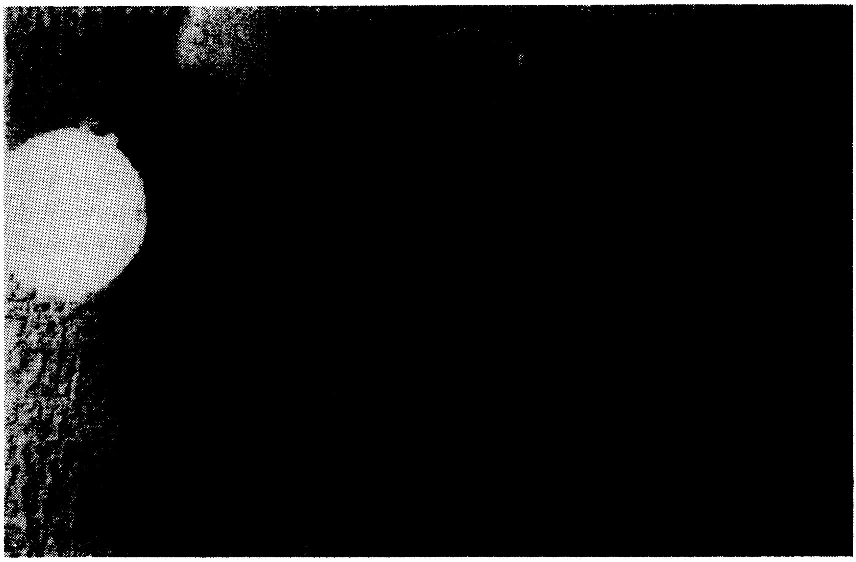

Figure 5. *An influence zone is observed around each glass bead.*

Table 2. The parameters for polishing.

Program	Sand Paper Code	Period	Liquid	Pressure
#1	220	30 Sec	Water	300N
#2	1000	4 Min	Water	150N
#3	2400	4 Min	Water	150N
#4	2.5 μ	—	Red	80N
#5	0.5 μ	—	Red	70N
#6	Fine	—	—	50N

HDPE (20 MPa). Therefore, the polishing treatment cannot bring plastic dent to the observation square.

The observation square is etched in the dimethylbenzene at 80°C for 24 hours, then washed by water and put into a dry box for 24 hours, and then examined under the Reichert Microscopes (Polyvar and Univar). To discern the cavities, protrusions and other rough regions of the surface, polarized green illumining light is adopted.

For three categories of the testing materials, an influence zone is observed around each particle (see Figure 5), including some pine-shaped fillers (Figure 6). The thickness of the influence zone is measured from 2 to 10 micrometers. It will

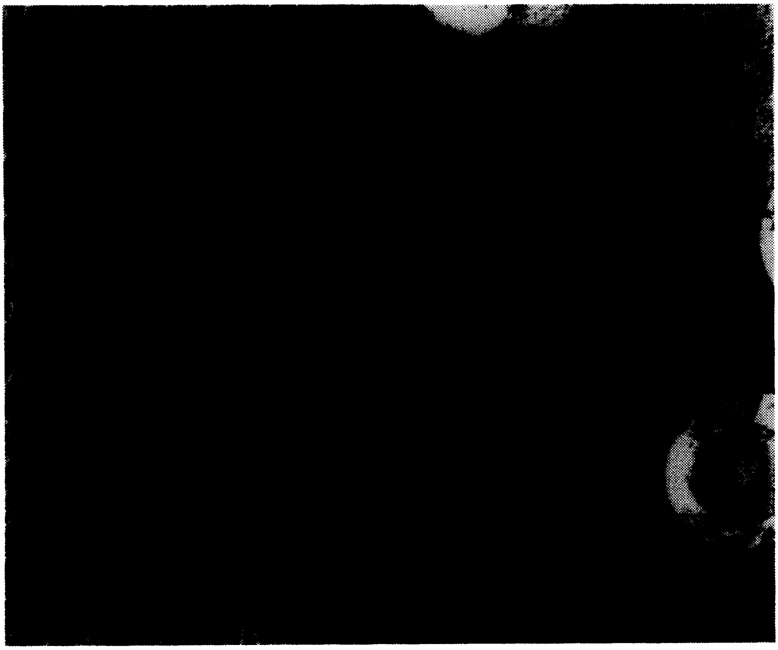

Figure 6. *The influence zone is also observed around the pine-shaped filler.*

be illustrated in section 4 that the influence zone instead of the interfacial bond plays a crucial role in reinforcing the strength of composites.

4. A NEW MODEL FOR PREDICTING THE STRENGTH

To simplify the problem considered, we ignore the plastic or viscoplastic effects of the matrix materials. Only elastic case is considered in present paper.

4.1 Model

In accordance with the experimental observation in section 3, we introduce the influence zone into the computational model (Figure 7). The dimension of the influence zone is commensurable to that of the particles.

The physical properties of the influence zone, the local Young's modulus and tensile strength, are assumed to vary according to the distance apart from the particle:

$$E_I = \frac{r+\delta}{d} E_m \tag{1}$$

$$\sigma_I^b = \frac{r+\delta}{d} \sigma_m^b \tag{2}$$

The subscript I indicates the influence zone, and δ is the thickness of the zone. The Young's modulus of the fillers is specified as

$$E_f = 65E_m \tag{3}$$

The quarter-cell is subdivided into a finite element mesh shown in Figure 8.

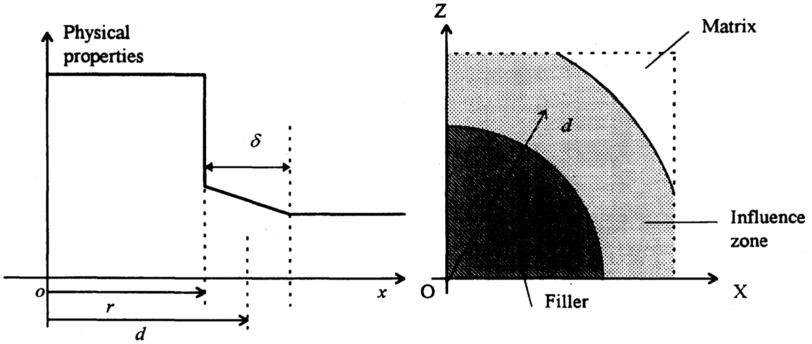

Figure 7. A new computational model for predicting the composite strength (influence zone considered).

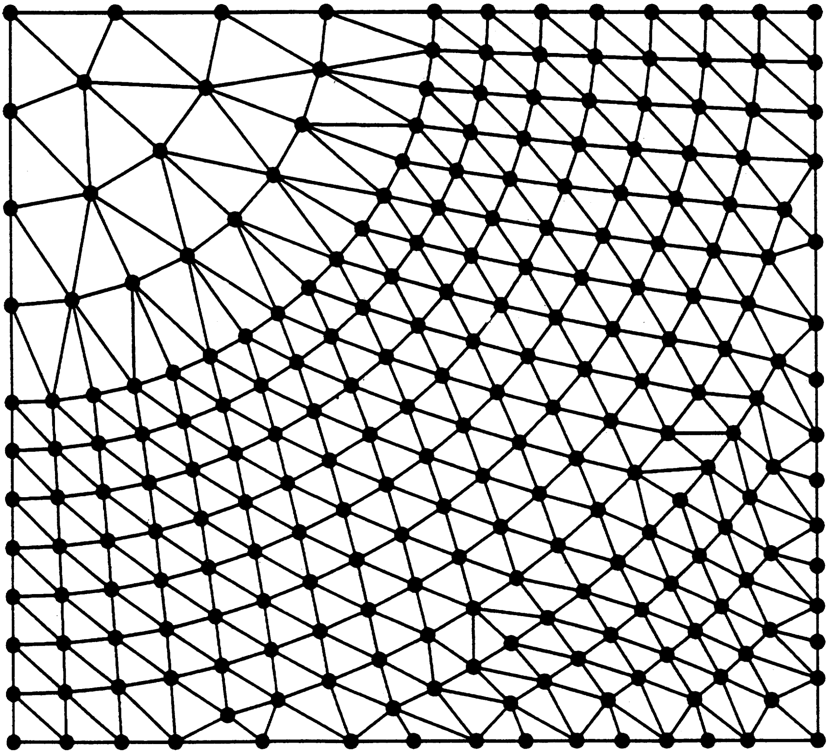

Figure 8. *A finite element subdivision of the quarter-cell (influence zone considered).*

4.2 Computational Results

1. Compared to the experimental results (Figure 1), the new model is able to simulate the relationship between the composite strength vs. the filler volume fraction (Figure 9). According to the experimental measurement in section 3 (the thickness of influence zone: 2–10 micrometers; the radius of glass beads: 10–50 micrometers), the relative scale of the influence zone to commercial fillers is about 0.2–0.4. For such composite systems, as shown in Figure 9, the tendency of the overall strength is predicted generally decreasing with the volume fraction, but having a "spring-back" at 20–30%. This happens to coincide with the phenomena shown in Figure 1.
2. The new model is also able to simulate the size effects of fillers (see Figure 10). It is obviously reproduced in Figure 10 that for a large span of volume fraction of the fillers, as their radii decreases, the composite strength increases monotonously.

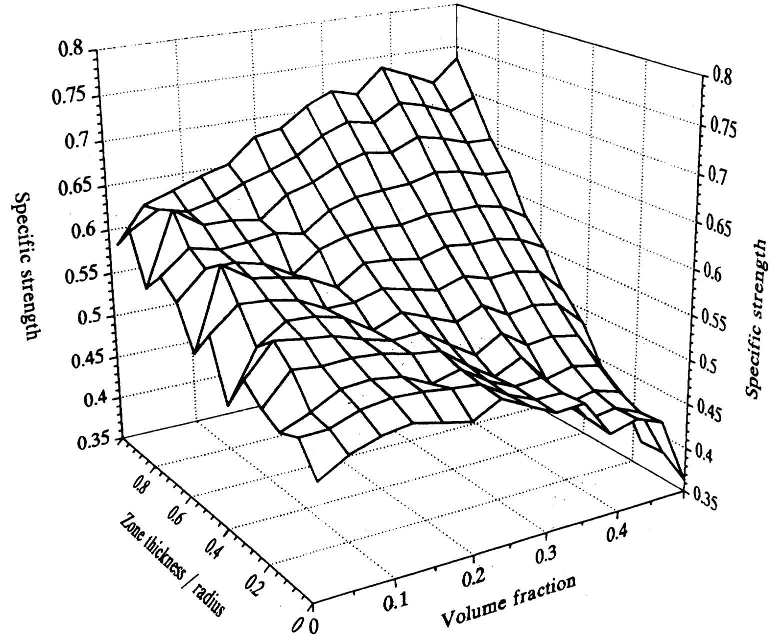

Figure 9. *The predicted composite strength varies with the volume fraction of the fillers.*

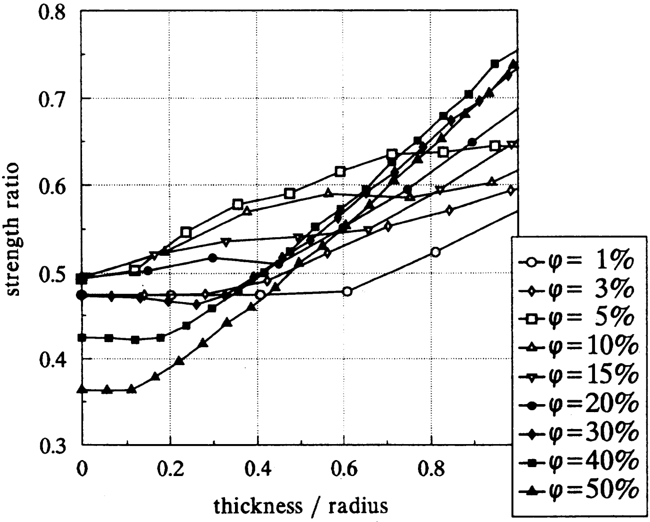

Figure 10. *The predicted composite strength can reproduce the size effects of the fillers.*

5. CONCLUSION

The interface is crucial to the composite strength. Its importance can be put in this way that no strong interface between the fillers and matrix, no complete stress can pass through the phases. For this reason, in the past decades, chemists have paid much attention to the study of coupling agents. However, it does not seem to have solved all the problems. Examples given in present paper show that the "influence zone" formed around each particle in the cure procedure plays a more substantial role in determining the overall strength. To improve the strength, forming an influence zone which satisfies the following conditions seems more important:

1. The local strength of the influence zone is higher than the rest of the matrix.
2. The influence zone is thick enough to overlap each other so that a strong "network" of the influence zone is formed in the matrix. This is somewhat similar to the steel skeleton in constructions that bears the main force.
3. The volume fraction of the fillers must be specified at a proper value. If it is too low, then the neighboring particles becomes so far away that their influence zones cannot reach each other nor the "network" can be formed; if the fraction is too high, then the neighboring particles become so close that the influence zone becomes too thin to play a key role in reinforcing the composites.

Reviewing all the aspects above, it seems worthy to pay some attention to the influence zone around the fillers rather than the interface or coupling agent only.

Finally, it is noted here that all the conclusions drawn above are based on the assumption that the physical properties of the influence zone, especially the local strength, are superior to the rest of the matrix [see Equation (2)]. It is reasonable, but still waiting to be examined by careful experiments. This, however, is a next challenging work for the future.

ACKNOWLEDGEMENTS

The work was supported by the China Postdoctoral Science Foundation, the LNM Special Grant and partially by the National Natural Science Foundation of China. The authors are indebted to Professor Yi-Long Bai and Professor Xi-Nian Lu (S.-N. Lu) for their helpful suggestions and discussions.

REFERENCES

Eshelby. 1957. *Proc. Roy. Soc.*, A241:376–396.

Hashin. 1962. *J. Appl. Mech.*, 29(2):143.

Hashin and B. W. Rosen. 1964. *J. Appl. Mech.*, 31(3):223.

Jayaraman, K., K. L. Reifsnider and R. E. Swain. 1993a. "Elastic and Thermal Effects in the Interphase: Part I. Comments on Characterization Methods," *Journal of Composites Technology and Research*, 15(1):3–13.

Jayaraman, K., K. L. Reifsnider and R. E. Swain. 1993b. "Elastic and Thermal Effects in the Interphase: Part II. Comments on Modeling Studies," *Journal of Composites Technology and Research*, 15(1):14–22.

Katz, H. S. and J. V. Milewski. 1978. "Handbook of Fillers and Reinforcements for Plastics," 1st Ed., Van Nostrand Reinhold Company, New York.

Miller, James D., Hatsuo Ishida and Frans H. J. Maurer. 1989. "Interfacial Role and Properties in Model Composites: Fracture Surfaces by Scanning Electron Microscopy," *Journal of Materials Science*, 24:2555–2570.

Papanicolaou, G. C. and D. Bakos. 1992. "The Influence of the Adhesion Bond Between Matrix and Filler on the Tensile Strength of Particulate-Filled Polymers," *Journal of Reinforced Plastics and Composites*, 11:104–125.

Theocaris, P. S. 1985. "The Unfolding Model for the Representation of the Mesophase Layer in Composites," *Journal of Applied Polymer Science*, 30:621–645.

Theocaris, P. S. 1992. "The Elastic Modulus of the Mesophase as Defined by Diffusion Processes," *Journal of Reinforced Plastics and Composites*, 11:537–551.

Wu, Xin-Sen, Xian-Bao Chen and Huan-Cheng Song. 1987. "Effect of the Boundary Layer on the Strength of Composites," *Acta Materiae Compositae Sinica*, in Chinese, 4(4):18–23.

Yan Lin. 1990. "On the Mechanical Behavior and Microdamage Mechanism of Glass-Filled HDPE Materials," Master thesis, in Chinese, Institute of Mechanics, Chinese Academy of Sciences.

Zhang, R. and S. N. Lu. 1994. "Numerical Analysis of Stress Field Around the Second-Phase Particle in Polymeric Composite Materials," *Applied Composite Materials*, 1:115–124.