

The Elastic Modulus of Filled Polymer Composites

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SYNOPSIS

The elastic modulus of polyepichlorohydrin (PECH) filled with glass beads and wollastonite was studied. It was found that the elastic modulus of the composites depends not only on the volume fraction of the fillers but also on their size. Percolation theory was used to explain the experimental results. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The elastic modulus of a composite is a very important characterizing parameter. According to classical theory, it depends on the elastic modulus and Poisson's ratios of the filler and the polymer and the volume fraction of filler only. It does not depend on the morphology of the dispersed phase.¹ The assumptions in the classical theory are that the matrix phase is isotropic and homogeneous and the dispersed phase is spherical.¹

In the past few years, many new experimental results different from the classical theory have been reported.¹⁻⁵ In these reports, the particle size of the filler played an important role and the explanations are still speculative.

In the present paper, the effects of the volume fraction of filler and the effect of the filler particle size on the elastic modulus of filled polyepichlorohydrin were studied. Percolation theory was used to explain the results.

EXPERIMENTAL

Materials

The polymer used in the experiment was polyepichlorohydrin (PECH). Its molecular weight was 1.04×10^5 measured by GPC. The density of PECH is 1.36 g/cm^3 . The diameter of the glass beads was

about 300 mesh. The wollastonites were industrial products; their particle sizes were 200 mesh and 325 mesh.

Sample Preparation and Tests

The polymer and all fillers were predried at 70°C in a vacuum oven for 8 h. After each component was weighed to the given weight, the polymer and the glass beads were mixed in tetrahydrofuran (THF) and the mixture was stirred for a few hours. The same kind of glass bead was pretreated with coupling agent L570, stirred for 3 h, then centrifuged to obtain a sediment of glass beads. The sediment was washed with THF and dried in the vacuum oven for 6 h at 60°C. Then, it was also mixed with PECH. The mixture was poured onto a large glass plate and heated by infrared light to evaporate solvent for 4 h, then dried at 60°C in the vacuum oven for a few days. The polymer and the wollastonite were mixed in a Brabender internal mixer. The samples obtained were molded in all cases into plates. Tensile bars were machined from these plates. The tensile tests were performed on an Instron Tensile Tester with strain rates of 200 and 10 mm/min at about 20°C.

RESULTS AND DISCUSSION

The experimentally determined elastic moduli of the different composites are plotted as a function of the volume fraction of the filler in Figures 1-3. In these figures, we can see that the elastic modulus of the composites increases with the volume fraction of the

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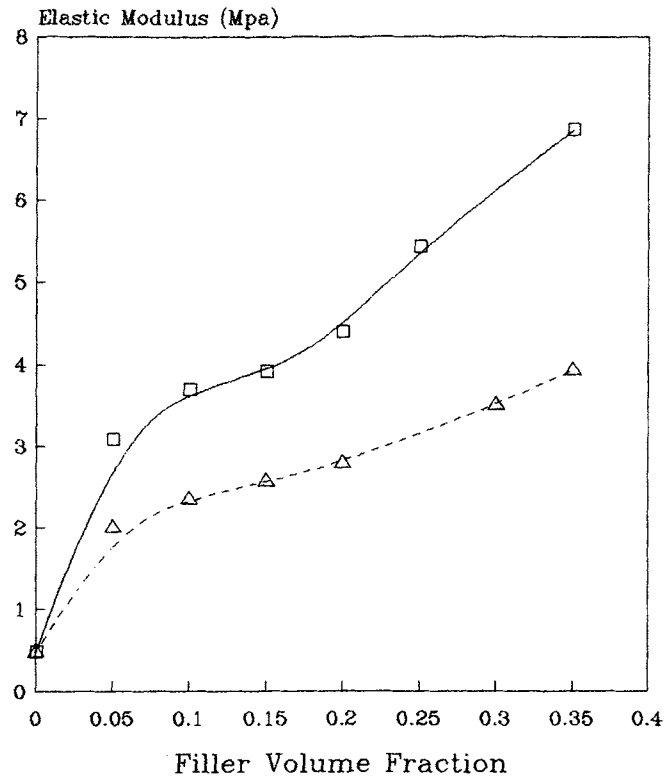


Figure 1 Elastic modulus of PECH filled with glass beads of about 300 mesh size as a function of the filler volume fraction; the strain rate is 200 mm/min: (△) pretreated glass beads; (□) normal glass beads.

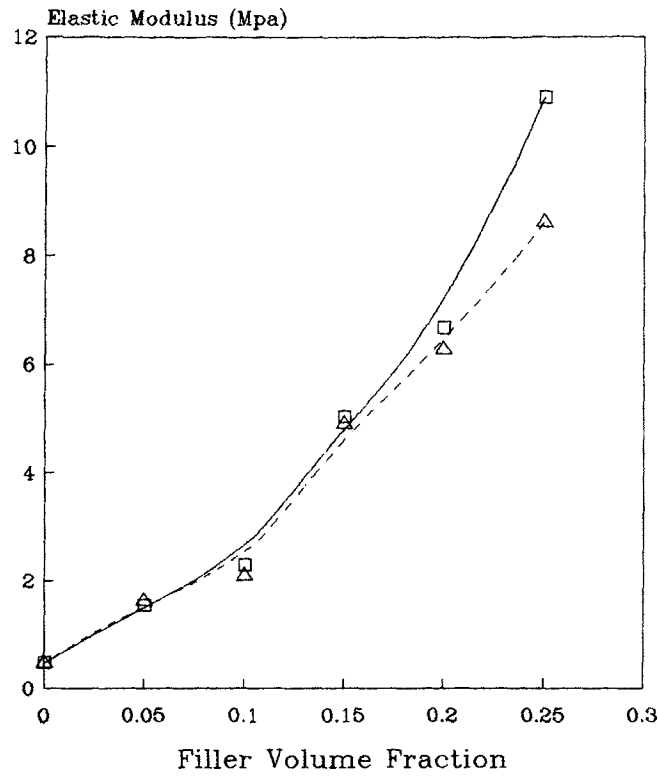


Figure 2 Elastic modulus of PECH filled with wollastonite filler of 200 mesh size and 325 mesh size as a function of filler volume fraction; the strain rate is 200 mm/min: (□) 325 mesh size; (△) 200 mesh size.

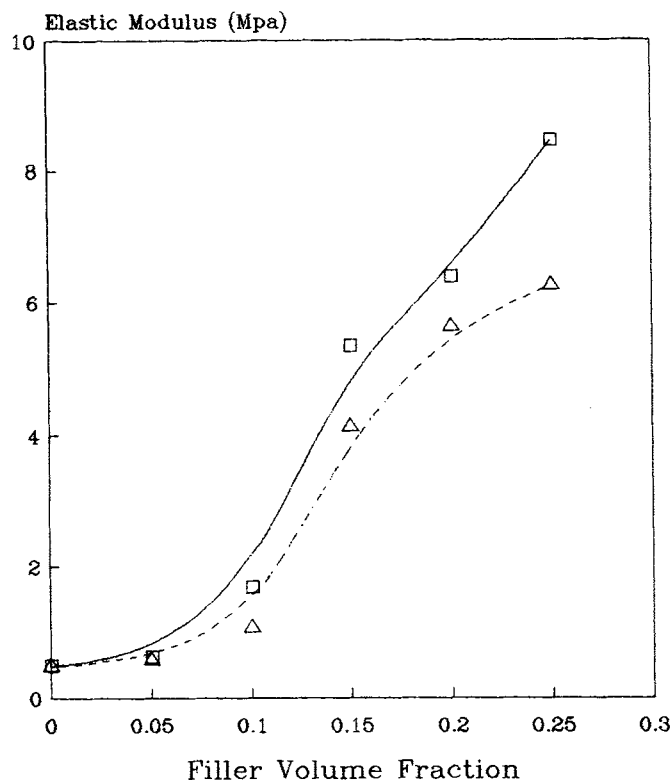


Figure 3 Elastic modulus of PECH filled with wollastonite filler of 200 mesh size and 325 mesh size as a function of filler content; the strain rate is 10 mm/min: (□) 325 mesh size; (Δ) 200 mesh size.

filler. When the volume fraction of the filler is greater than a critical value, the modulus increases very fast and the modulus also changes with the particle size of the filler, just as in the experimental results reported by Heikens et al.^{2,4,5}

Possible causes for these results have been discussed in several papers including those by Heikens et al. In the following discussion, we will apply percolation theory to explain these experimental results.

Percolation theory is an effective mathematical method to deal with highly disordered systems. It considers the connectivity of the dispersed phase in the matrix. Wu has used it to explain the tough-brittle transition of polymer blends.⁶⁻⁹

Many experimental results have been published that prove that filler particles disperse in the matrix randomly.⁸ The interparticle distance (T) is also random. In the tensile process, there will be stress concentration around the filler particles, and this causes the plane strain-plane stress transition in the matrix that forms shells around the filler particles. The thickness of the shell is $T_c/2$. If the interparticle distance (T) is less than the critical value

T_c , there will be shear stress between two nearest-neighboring particles and the shear stress regions will connect to each other and form percolation pathways.

When the size of the filler does not change, it is obvious that the interparticle distance between two nearest-neighboring particles (T) will decrease with the volume fraction of the filler and the number of percolation pathways formed by the shear stress region will increase very fast, as will the elastic modulus.

In Figures 4 and 5, we show schematics of the randomly dispersed sphere of stress volume and its structure, where d denotes the diameter of the filler particle; S , the size of the stress-volume sphere; and L , the center-to-center distance of the two nearest-neighbor stress-volume sphere:

$$S = d + T_c \quad (1)$$

$$L = d + T \quad (2)$$

When T is equal to or less than T_c , there will be interaction between the nearest-neighboring stress-

volume spheres. We define the stress-volume fraction as

$$\begin{aligned} v_s &= (S/d)^3 v_f \\ &= (1 + T_c/d)^3 v_f \end{aligned} \quad (3)$$

where v_f is the volume fraction of the filler. When the size of the filler is a constant, S is independent of the volume fraction of the filler, and $v_s \propto v_f$. It can be seen that v_s will increase with v_f . According to Wu's formulae,^{7,10} the number of stress-volume spheres that interact with each other increase with v_s . These spheres will form some percolation clusters, and at the critical value of the volume fraction of the filler, v_{sc} , there will be a percolation pathway of the interacted stress-volume spheres, which makes the modulus of the composite increase very fast. The effect of the volume fraction of the filler has been demonstrated experimentally.

When several kinds of fillers of different sizes are used, the size effects must be taken into account to explain the experimental results.³⁻⁵ According to the conclusions of Vollenberg and Heikens' paper^{4,5} using the interphase concept, the hypothesis of interphase is still speculative and further research is necessary.

As stated in eq. (3),

$$v_s = (1 + T_c/d)^3 v_f$$

If v_f is a constant,

$$v_s \propto d^{-3} \quad (4)$$

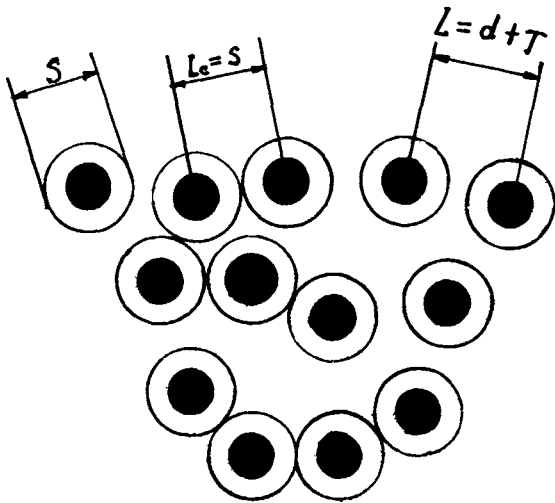


Figure 4 Schematics of filler particles and polymer matrix ligament.

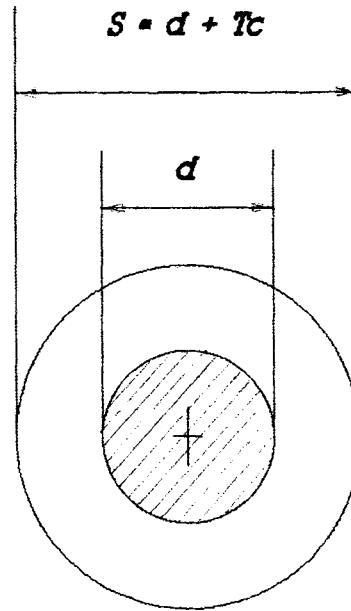


Figure 5 Schematics of stress volume around a filler particle. The filler particle is shaded.

Obviously, when the filler's size d decreases, the stress-volume fraction of the filler, v_s , will increase very fast to approach the critical point v_{sc} . This means that the first percolation pathway forms earlier in the sample with smaller filler particles than that with larger filler particles, so that the elastic modulus will also be higher when the volume fraction of the filler is constant.

If we take the contribution of the interphase into account, we will come to the same conclusion: In Vollenberg and Heikens' papers, the solidification of the matrix is locally activated at a free filler particle surface and the filler particle will be surrounded by a high-modulus layer and a lower-modulus layer. These effects make the effective volume fraction of the filler increase, and the effective value of T_c increases as well.

We can find in Figure 1 that the pretreatment affects the elastic modulus, just as in Vollenberg and Heikens' reports. The reason is not known and further investigation is necessary.

CONCLUSION

The elastic modulus of untreated glass bead and wollastonite-filled polymers were studied. It was found that the elastic modulus of the composites are dependent on the volume fraction of the filler and its size. Percolation theory was used to explain the

experimental results, the problem of filler size effect, and its content in Vollenberg and Heikens' papers was solved, but the reason why the pretreatment has an effect on the elastic modulus is not known yet and further investigation is necessary.

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