Reinforcement as a Hindrance in the Disentanglement of Unknotted Chains

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Synopsis

Observation of many tangles supports a loop mechanism of entanglement in macroscopic systems. The untangling of an unknotted tangled cord gives curves resembling the behavior under constant stress of an uncrosslinked elastomer. Reinforcement as a function of filler loading has been calculated for a model system consisting of uniform spherical particles in an unknotted tangled matrix. These calculated curves show the maxima found in real systems. Reinforcement also increases with decreasing particle size. The effect on the entanglement of porous particles and particles forming surface attachments with the polymer have been considered. The maximum in the calculated reinforcement curve shifts toward higher filler loading with increasing surface activity. This shift is independent of particle size and suggests a method for assessing the relative effectiveness of different coupling agents.

INTRODUCTION

Polymer chains have properties of flexibility and continuity similar to many frequently tangled objects. Because entanglement is basic to polymer properties, an understanding of the process of entanglement and the nature of the tangled network in macroscopic systems may lead to useful insights into polymer behavior. This article presents a new model of entanglement based on observations of macroscopic tangles and their untangling and discusses the effect of inelastic spherical particles on this model.

Observation of many tangles, both intentional and inadvertent, suggests that systems of flexible strands that tangle by random processes not acting specifically on the ends are largely unknotted and that the entire length of the strand participates actively in the entanglement. In most of the previous work on polymer entanglement, the entanglements are explicitly[1,2] or implicitly[3–5] assumed to be knotted, with the ends being the active part.

ENTANGLEMENT IN MACROSCOPIC SYSTEMS

Many tangles containing up to 260 crossings were studied. Accidental tangles were also observed as the opportunity arose. Entanglement was observed in all of these to occur by means of loops.

An investigation into the untangling of one system showed behavior similar to the creep behavior of an uncrosslinked elastomer. Both ends of a length of cord were fastened to prevent knotting, and the loop was tangled to the desired degree. The tangle was suspended and measured. Using the weight of the cord as the extensive force, the tangle was kept in random motion manually for a period of time, after which the length to the lowest point was measured. This was

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repeated until the snarl was completely untangled. The plots of length vs. time, shown in Figure 1, show a surprising resemblance to the creep curves characteristic of uncrosslinked elastomers.

LOOP MODEL OF ENTANGLEMENT

Knotted and Unknotted Tangles

Since the concept of an unknotted tangle is central to this model of entanglement, short definitions of knotted and unknotted tangles are given here. Extend the ends of the cord to infinity or join them outside the tangle. The

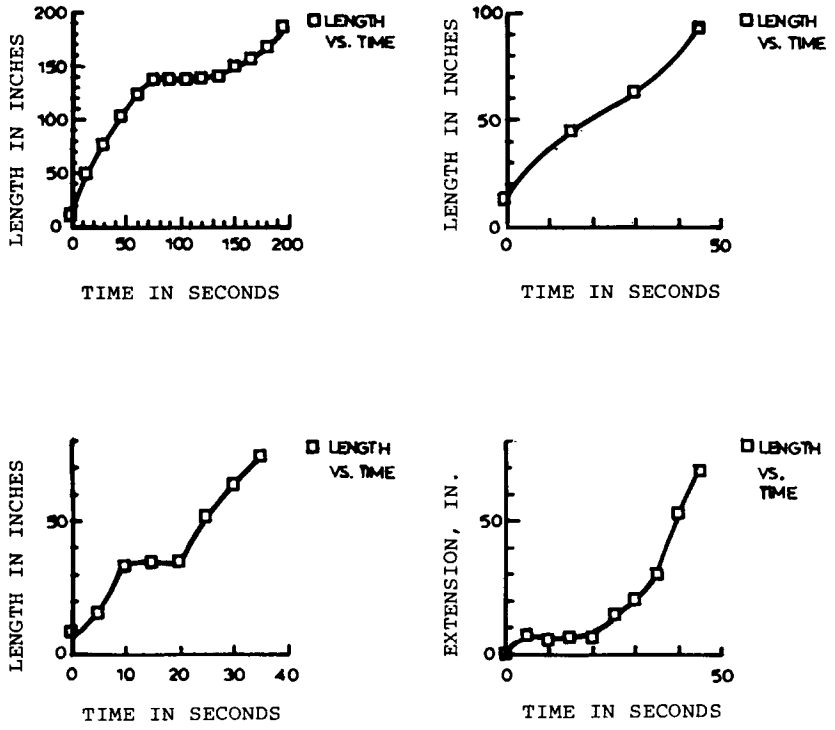
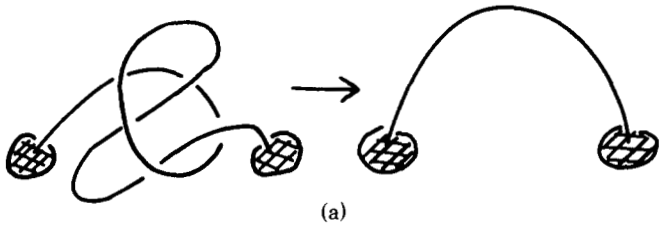


Fig. 1. Untangling of a randomly tangled unknotted cord.

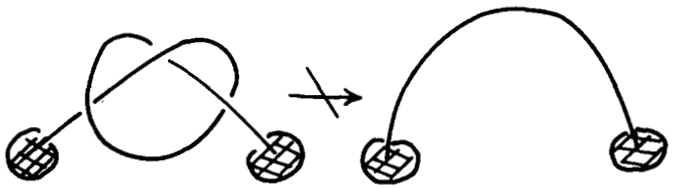
tangle is unknotted if it can be untangled without cutting the cord. A knotted tangle can not be untangled without cutting the cord or involving an end. The tangle shown in Figure 2(a) is unknotted, and that in Figure 2(b) is an overhand knot.

Loop Interactions

The interaction of separate loops will be considered first. For simplicity in these diagrams, the loops are short, regularly shaped, and rather narrow. The ends are assumed to be fixed in the matrix and to be unavailable. Although these conditions will not necessarily be found in a real tangle, the interaction between



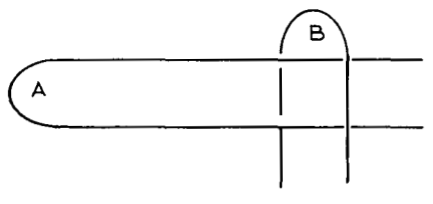
(a)



(b)

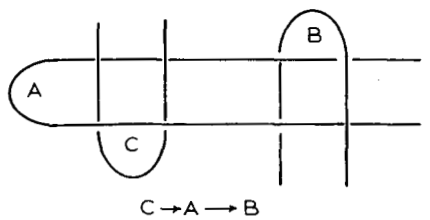
Fig. 2. Unknotted (a) and knotted (b) tangles.

loops remains unchanged. The following convention will be used to describe the interactions of the loops. Each loop is represented by a letter; when one loop passes through another loop, an arrow is drawn from the first letter to the second. Define the order of a loop to be the number of loops which must be successively withdrawn before the loop is free. The order of the tangle is that of the highest



A → B

(a)



C → A → B

(b)

Fig. 3. Basic loop interactions in entanglement. In (a) loop A passes through loop B forming a first order tangle. In (b) loop C passes through loop A making the tangle second order.

order loop in the tangle. Figure 3(a) shows the simplest case of entanglement in an unknotted system and illustrates the process by which such systems tangle. Loop B cannot be withdrawn in the direction of the arrow until loop A is removed. Loop A is free. Figure 3(a) is a first-order tangle. Loop A is zero-order and loop B is first-order. If another loop, C, is inserted through loop A, as shown in Figure 3(b), the tangle becomes second-order and the order of each of the loops A and B increases by one. Loop C is zero-order.

The order is independent of the number of separate strands involved. The loops participating in a given tangle may belong to the same strand or to different strands, and twisting of the loops does not affect the entanglement. The strands continue on to another loop of the same tangle, another tangle, or other random behavior. Note that in any of these tangles, untangling must begin with a zero-order loop and proceed in the direction of the arrows. No loop can be withdrawn until it has become zero-order by the removal of all loops passing through it. The addition of another zero-order loop increases the order of the tangle only if it locks a zero-order loop that determines the order of the tangle. The ends may be thought of as loops that are permanently zero-order. They may lock other loops but may not themselves be locked or extended. A small degree of knotting is introduced in this manner, but it is of low order and transient.

Stress can be transmitted to a loop only along the cord. When the stress is resolved into components acting parallel and perpendicular to the cord, only the cases shown in Figure 4 are effective in untangling. If the loop is zero-order, it

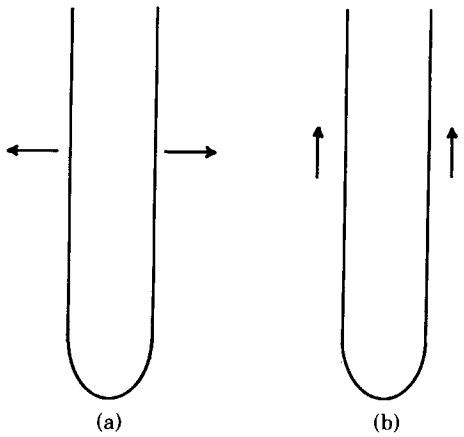


Fig. 4. Effect of stress on chain loops. Stress may be applied perpendicular (a) or parallel (b) to the axis of the loop.

responds to stress (a) by straightening out and is not available for further tangling. Its order is defined as 0*. When a zero-order loop responds to stress (b), it lowers the order of any tangle it is removed from; but, unless a stress of type (a) is also imposed, it is available for further tangling at its new location. Its order is unchanged. If either stress is applied to a loop that is not zero-order, the stress is transmitted to the loops trapped inside; but the order of the tangle is not changed by the motion of the first loop.

Entanglement in Polymers

In an elastomer above its glass transition, the chains are in constant random motion. Loops are constantly being thrust out and withdrawn. The order of a given loop will change on a time scale that depends on the segmental jump frequency. If the system is unstressed, the tangle reaches an equilibrium state where the tangling and untangling of the loops are balanced. When the system is extended along one axis some of the zero-order loops are straightened. These loops are effectively removed from the system, disturbing the equilibrium which then shifts in the direction of untangling.

Action of Crosslinks in This Model

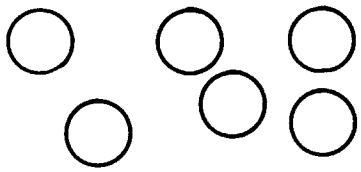
Filled elastomers are usually also crosslinked. The role of crosslinking in this model will be discussed briefly here since it differs from that usually assumed. In this model, the effect of crosslinks is to alter the probability of tangling and untangling so that the tangled network persists. Any section of the tangle dependent on a crosslinked loop cannot go below the order determined by that loop. The extension is controlled, not by the crosslinks, but by the tangle as hindered by the crosslinks. The creep behavior of crosslinked and uncrosslinked elastomers is similar through the plateau zone until the point where the uncrosslinked system begins to flow. The crosslinked system shows no sharp change in behavior but responds to an additional stress according to the superposition principle. This suggests strongly that the extension is controlled in the same manner in both crosslinked and uncrosslinked systems.

REINFORCEMENT AS HINDERED DISENTANGLEMENT

Model

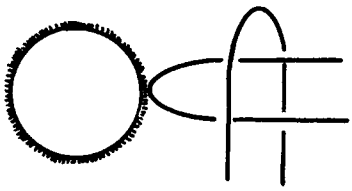
Reinforcement in this model arises from the interaction between inelastic filler particles and the tangled matrix. Since this interaction is affected by the filler surface, three different types of filler surface will be considered. The first type of particles are smooth spherical particles having no interaction with the polymer, as shown in Figure 5(a). The particles shown in Figure 5(b) are basically spherical but contain cavities or crevices into which sections of the polymer chain can enter. The particles shown in Figure 5(c) can form attachments with the neighboring polymer chains. These two surface modifications can occur separately or together. If both are present, their effect is additive.

In an unfilled elastomer under tension, the forces are extensive in the direction of the stress and compressive perpendicular to the stress. The forces are uniform throughout the sample except at the surface. When inelastic filler particles are present, the distribution of forces is much more complex. When the sample is extended, the tangle between adjacent filler particles in the plane perpendicular to the extension is compressed. The untangling in this region is repressed and further hinders the untangling in neighboring regions because some loops are "locked in" by the loops of the compressed regions. This mechanism does not depend on any surface interaction between polymer and filler and may explain the reinforcing effect of filler particles of the type shown in Figure 5(a).



(a)

(b)



(c)

Fig. 5. Types of filler particles considered. The surface of a filler particle may be smooth and inert (a), pitted (b), or able to form attachments to the polymer chains (c).

If the filler particles contain crevices, such as those shown in Figure 5(b), sections of the tangle may enter. The sections of the tangle inside the filler particle are not only unstressed, except at the mouth of the crevice, but are also constrained by the walls of the cavity. They will tend to remain there and will lock any loops that they are entangled with, thus increasing the reinforcing effect of the filler. In Figure 6, loops A, B, and C are inside a cavity in the filler particle. Loops D and E cannot be freed until the entire section inside the cavity is removed.

Attractive forces between the surface of the filler and the polymer reduce the mobility of the loops adjacent to the filler suface and hinder untangling. Even weak attachments between polymer and filler inhibit the motion of the loops involved, thus preventing or greatly slowing their untangling. It is apparent with this model that the increase in strength in such a system is not directly dependent on the strength of these attachments in relation to the stress. To be effective, the attachments need only overcome the random motion of the polymer chain. The attachments will be effective to the extent that they inhibit the motion of the adsorbed loops. The response is controlled by the entanglement, not by the polymer–filler attachments. This effect increases with the number of attachments up to the limit at which all loops in contact with the filler surface are

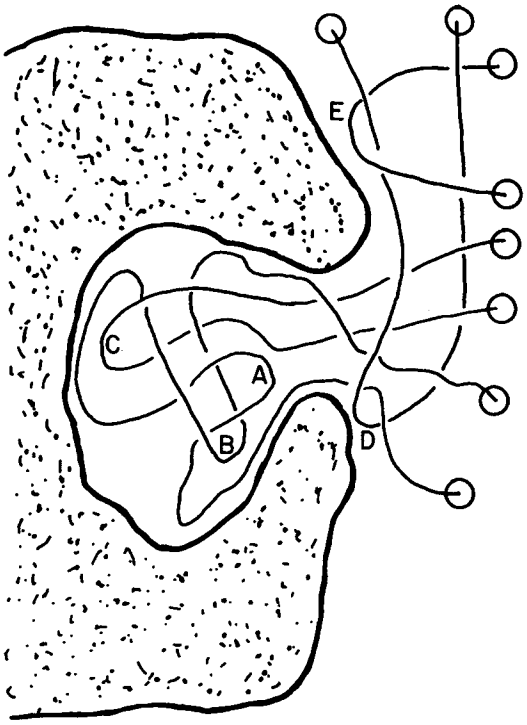


Fig. 6. Entanglements trapped in a surface cavity. Loops A, B, and C are inside a crevice in the surface of the filler particle. Loops D and E are hindered by the section of tangle inside the crevice.

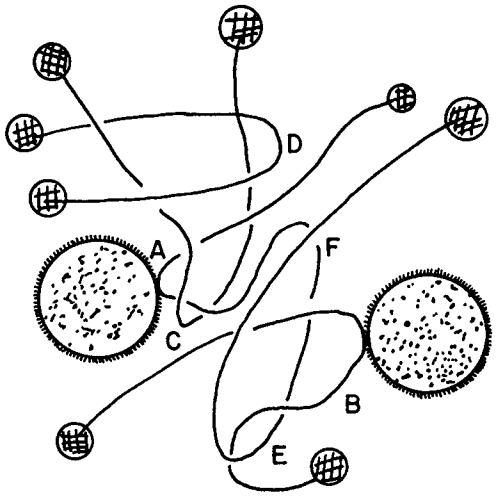


Fig. 7. Entanglement with some loops adsorbed on the filler surface. Loops A and B are adsorbed on the filler surface. Loops C and D hindered by loop A, loop E is hindered by loop B, and loop F is free.

hindered. In the case shown in Figure 7, loops A and B are adsorbed on the filler particles. Loops C, D, and E are "locked in." Loop F is free to respond to stress.

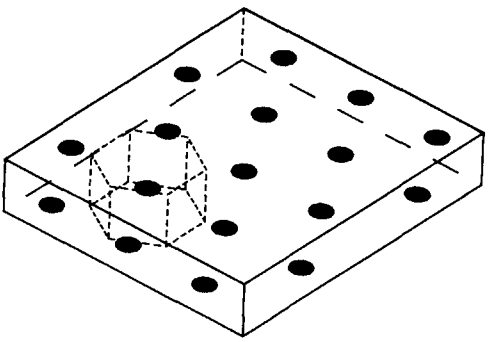


Fig. 8. Hexagonal packing model used in calculations.

Calculations

Consider a thin layer of polymer, perpendicular to the extensive force, containing uniform spherical filler particles in the packing shown in Figure 8. Assume that the untangling is hindered in a cylinder with its axis along the line joining the centers of the particles and a radius equal to one-half the radius of the particles. If d is the distance between the centers of the particles, the volume and surface area of each cylinder are given by

$$V_{cyl} = \pi(r - 2)^2(d - 2r)$$

$$S_{cyl} = \pi r(d - 2r)$$

The area of the surface of the sphere adjacent to each end of the hindered region is $r^2(2 - \sqrt{3})\pi$. The volume of unhindered tangle is equal to the total volume minus the volume of filler and hindered tangle. Reinforcement should be proportional to the ratio of the total hindered surface to the volume of unhindered tangle. If polymer–filler surface interactions of any type are present, part of the filler surface must be included in the total hindered surface. Let f be the ratio of the reinforcement due to the filler surface to that due to the hindered tangle per unit area. Then that fraction f of the filler surface adjacent to the unhindered regions must be added to the lateral surface of the hindered regions to determine the total hindered surface area.

For the hexagonal packing shown in Figure 8, the unit of volume is a hexagonal prism. The in-radius of the prism circumscribed about a sphere of radius r is r. The height is $2r$, and the edge of the hexagonal face is $(2\sqrt{3}/3)r$. The volume of the prism is $4\sqrt{3}r^3$, and the maximum loading for a unit volume is $1/4\sqrt{3}r^3$. The number of particles, n, present is given by $n = v/4\sqrt{3}r^3$, where v is the fraction of the maximum loading. The volume per particle at a loading v is $4\sqrt{3}r^3/v$. If the height of the prism and the distance between the centers of adjacent spheres is d then the volume is $(\sqrt{3}/2)d^3$, and

$$d = 2rv^{-1/3}$$

Each particle has six neighbors in the plane giving an average of three compressed

regions per sphere. The volume compressed per sphere is $3\pi(r/2)^2(2rv^{-1/3} - 2r)$. The total volume compressed for n spheres, V_h, is given by

$$V_h = \frac{\pi\sqrt{3}}{8}(v^{2/3} - v)$$

The total lateral surface area of the compressed regions, S_h, is

$$S_h = \frac{\pi\sqrt{3}}{2r}(v^{2/3} - v)$$

The total surface of the spheres not adjacent to the hindered regions, S_f, is

$$S_f = \frac{v(9 - 4\sqrt{3})}{6r}$$

For a filler surface efficiency f, the total hindered surface S_t is

$$S_t = S_h + S_f \cdot f$$

$$S_t = \frac{\pi}{6r}\{3\sqrt{v}^{2/3} + [(9 - 4\sqrt{3})f - 3\sqrt{3}]v\}$$

Let $p = (9 - 4\sqrt{3})f - 3\sqrt{3}$; then

$$S_t = \frac{\pi}{6r}(3\sqrt{3}v^{2/3} + pv)$$

The unhindered volume is

$$V_f = 1 - \frac{\pi\sqrt{3}}{8}v^{2/3} + \frac{\pi\sqrt{3}}{72}v$$

The ratio of total hindered surface to unhindered volume is

$$R = \frac{3\sqrt{3}v^{2/3} + pv}{r\left(\frac{6}{\pi} - \frac{3\sqrt{3}}{4}v + \frac{\sqrt{3}}{12}v\right)}$$

where $p = (9 - 4\sqrt{3})f - 3\sqrt{3}$.

Figure 9 shows the curves obtained by plotting reinforcement as a function of the fraction of the maximum loading for several values of the radius when the

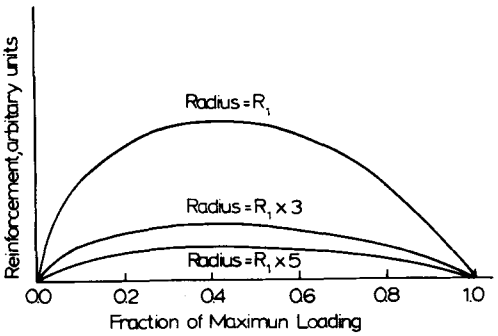


Fig. 9. Reinforcement as function of filler loading. Effect of particle size for a surface efficiency ratio of 0.

surface efficiency ratio of the particles is 0.0. Figure 10 shows the curves obtained for values of the surface efficiency ratio ranging from 0 to 1 for a radius of 0.01.

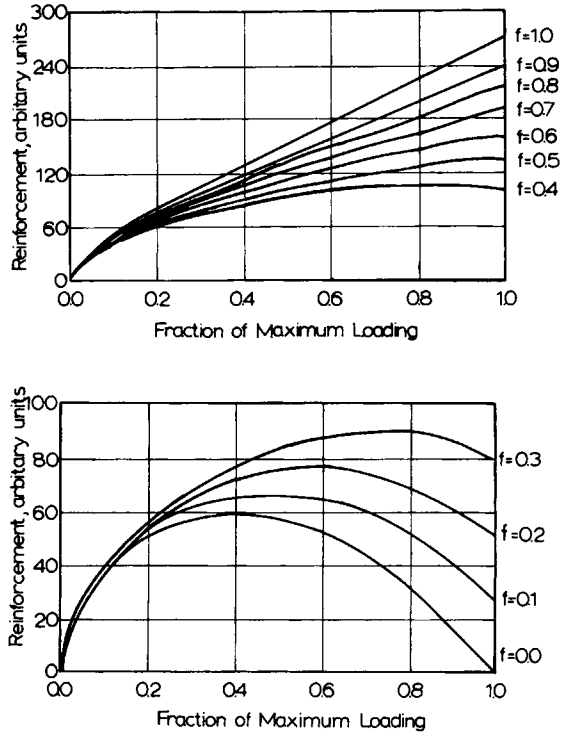


Fig. 10. Reinforcement as function of filler loading. Effect of surface efficiency ratio.

Agreement with Observed Properties

Decreasing particle size increases the reinforcement in this model. The curves obtained by plotting reinforcement as a function of filler loading show the maxima characteristically obtained in real systems. Increasing the surface activity ratio increases the reinforcement and also shifts the maximum reinforcement toward higher filler loadings. Beyond a critical value of the surface activity ratio, the curves showed no maximum as shown in Figure 10. The surface activity ratios actually attained in real systems are probably well below this critical level. The shift in the maximum is independent of particle size, at least for uniform spherical particles. For hexagonal packing, the plots of reinforcement as a function of loading show a maximum up to a surface efficiency ratio of 0.43. Figure 11 shows the filler loading at maximum reinforcement as a function of the surface efficiency ratio.

Since the filler surface efficiency ratio f is the ratio of the effectiveness of the filler surface to that of the surface of the hindered cylinder, it can be changed either by altering the filler surface or, if the filler surface is not inert, by changing the molecular weight of the polymer and thus altering the extent of entanglement and the effectiveness of the hindered cylinder.

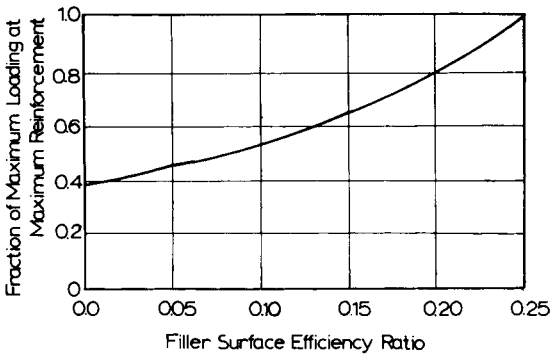


Fig. 11. Filler loading at maximum reinforcement as function of the surface ratio.

Brabender plasticity as a function of filler loading for poly(dimethylsiloxanes) of varying molecular weights and degrees of branching was measured by Schatz and Svehla.[6] The filler used was Aerosil 200. Viscosity of polymer melts of sufficiently high molecular weight varies as molecular weight to the 3.4 power. This strong dependence of viscosity on molecular weight is thought to be a direct manifestation of chain entanglements. If the branched polymers are assumed to be divided into segments of equal length by the branching points, a quantity E proportional to the entanglement can be calculated. E is taken to be the sum of the 3.4 powers of all continuous paths, adjusted so that each section is counted only once.

Table I gives the assumed configuration and the formula by which E was calculated for chains having 0, 1, and 2 branching points. Table II lists the filler

TABLE I
Degree of Branching and Calculated Entanglement

Degree of branching	Configuration assumed	E
0	——	$M^{3.4}$
1	Y	$\frac{1}{2}\left[3\left(\frac{2M}{3}\right)^{3.4}\right]$
2	><	$\frac{1}{2}\left[2\left(\frac{3M}{5}\right)^{3.4}+2\left(\frac{2M}{5}\right)^{3.4}\right]$

TABLE II
Calculated Entanglement and Location of Maximum

Polymer	Loading at max.	$M \times 10^{-4}$	B	E
A	4	61	0	110
B	8	45	0	42
E	8	61	1	44
C	11	39	0	26
F	11	61	2	26
D	14	21	0	3.1

loading at the maximum, the molecular weight, and the degree of branching as reported by Schatz and Svehla and the calculated value of E. As the entanglement decreases and f increases, the maximum occurs at higher loading. Branched and linear polymers having similar entanglement have similar loading at the maximum.

DISCUSSION

This model uses a fundamentally different mechanism of entanglement that requires reexamination of many of the commonly held concepts of polymer science. The entanglements in this model are unknotted, and entanglement is a result not of single crossings but of a number of crossings working jointly. Polymer entanglement by this model is a dynamic equilibrium process actively involving the entire strand. There are no "points of entanglement," and the term "distance between entanglements" is meaningless because the entire chain is involved in the entanglement process. The quantity determining the properties of a system is not the number of entanglements per unit volume but the degree of entanglement. Slow relaxations are the result of a number of loop relocations that must occur in sequence, and no point on the chain moves through a large distance during tangling or untangling. The effect of inelastic spherical particles on an entanglement of this type agrees qualitatively with the observed behavior of elastomer–filler systems.

Reinforcement was calculated for a very simple model system. As the filler loading is increased, the reinforcement first increases, then goes though a maximum, and decreases. The effect of the activity (of unspecified type) of the filler surface was also calculated. The loading at the maximum in these curves seems to reflect the relative effectiveness of the entanglement and the filler surface. It does not depend on particle size and will probably be less sensitive to changes in other variables than the value of a physical property at the maximum. Thus, the filler loading at the maximum should be a useful measure for assessing filler surface activity and comparing the relative effectiveness of different coupling agents since it depends only on the filler surface activity ratio. Its use for this purpose should be investigated further.

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