CHAPTER II

THEORY AND LITERATURE REVIEW

1 Composite Materials

The word "composite" in composite material signifies that two or more materials are combined on a macroscopic scale to form a useful material. The key is the macroscopic examination of a material. The advantage of composites is that they usually exhibit the best qualities of their constituents and often some qualities that neither constituent possesses. The properties that can be improved by forming a composite material include: strength, fatigue life, stiffness, temperature-dependent behavior, corrosion resistance, thermal insulation, wear resistance, thermal conductivity, attractiveness, acoustical insulation and weight. Naturally, not all of the above properties are improved at the same time nor is there usually any requirement to do so.

Composite materials have a long history of usage. Their beginnings are unknown, but all recorded history contains reference to some form of composite material. For example, straw was used by the ancient Egyptians when they realized that wood could be rearranged to achieve superior strength and resistance to thermal expansion as well as to swelling due to the presence of moisture. Medieval swords and armor were constructed with layers of different materials. More recently, fiber-reinforced resin composites that have high strength-to-weight and stiffness-to-weight ratios have become importance in weight-sensitive applications such as aircraft and space vehicles.

2.1.1 Properties

Composites typically are make up of the continuous matrix phase in hich fiber and additives are embedded: (1) a three-dimensional distribution of randomly oriented reinforcing elements, e.g., a particulate-filled composite; (2) a two-dimensional distribution of randomly oriented elements, e.g., a chopped fiber mat; (3) an ordered to-dimensional

structure of high symmetry in the plane of the structure, e.g., an impregnated cloth structure; or (4) a highly-aligned array of parallel fibrous randomly distribution normal to the fiber directions, e.g., a filament-wound structure, or a prepage sheet consisting of parallel rows of fiber impregnated with a matrix. Except in case (1), the properties of the composite structure viewed as a homogenous average material are more complex than are the more familiar isotropic materials which require two independent constants, such as the Young's modulus and the Poisson ratio, to specify their elastic response. The other types of composites (2,3 and 4) require at least four independent constants, such as two Young's moduli and two Poisson ratios, for the elastic response as affected by the orientation of the applied stress relative to that of the reinforcing fiber. These properties can be measured. Since composites in turn are often built up by laminating layers of composite sheets, these properties are needed to predict the overall reponse of the laminated structure. The fiber in each layer can be oriented differently from adjacent layers. If proper attention is not available, peculiar effects can occur, such as, a composite part twisting when a simple tensile load is applied. With an isotropic material, this would merely stretch the body. However, for purpose of designing optimum materials, it would be desirable to compute the properties of the constituent matrix and reinforcements. The present state of analytical skills allows such predictions to be made with reasonable confidence in specialized cases. However, for many other situations, only upper and lower property bounds can be stated.

Micro mechanics is the detailed study of the stresses and strains within a composite considered as a true heterogeneous system. This approach allows the effective average properties of the composite to be computed when the reinforcement has a simple geometric shape and is located in regular arrays. Such idealized models can be used to provide a semiquantitative framework for the behavior of real composite materials. Modeling of the properties of composites as a function of temperature, pressure, or other environments requires a corresponding knowledge of the behavior of the separate constituents plus of their interactions, such as, result from differences in thermal expansion.

2.1.2 Classification and Characteristics of Composite Materials

There are three commonly accepted types of composite materials:

1). Filled porous system composites which consist of porous materials penetrated by matrix

2). Particulate composites which are composed of particles in a matrix

3). Fibrous composites which are composed of fiber in a matrix

These types of composite material are described and discussed with many aspects in the following sections.

2.1.3 Filled Porous Systems

The properties of filled porous systems must, depend on several factors[7]:

1)the degree of porosity; 2)the nature of the porosity (size, degree of pore connectivity, shape, and distribution of sizes); 3)the properties of the polymeric filler, including its state; 4)the nature of the filler-matrix interface.

Rationalization and prediction behavior will depend on the classification above. If porosity is negligible, models in Section 2.1.4 may be appropriate.

2.1.3.1 Polymer-impregnate Wood

General case: wood + monomer -----------> composite product
such as: wood + phenolic resin
    wood + vinyl monomer

Polymerization characteristic has been considered the same as a general chain polymerization, i.e. comprising of initiation, propagation and termination.

$$R_p = K[R\ ]^{1/2}$$
$$R_p = K'[DR]^{1/2} = K''[I]^{1/2}$$

the gel effect and the nature of substrate will also play the roles.
Properties[8]: Dimensional Stability

     * good dimensional stabilities
     * low water uptake
  : Mechanical
     * compressive strength up to 1.5x
     * shear strength   up to 2x
     * hardness   up to 11x
     * abrasion resistance up to 8x

the prediction model can be obtained from following equation[9]:

$$E_c = E_w v_w + E_p v_p \qquad \text{----------(2.1)}$$

where

    E = elastic moduli,
    v = volume fraction,
    w,p = refers to wood and polymer, respectively.

It can be assumed that $E_w = E_g/v_w$, E_g = the modulus of elasticity of gross untreated wood.

2.1.3.2 Polymer Impregnated Cements, Mortars, and Concretes

     Both tensile and compressive strength can be increased b a factor 3 to 5. The resistance to freeze-thaw cycling, to water permeation, and to degradation by inorganic acid, water or sulfate ions is considerably increased[10]. Polymer cements may be corporated in three ways:

     1) by adding polymerizable monomer to a concrete or mortar mix, and then curing both concrete and polymer,

     2) by adding a latex or an aqueous solution of a polymer to a mortar, or concrete, and then curing the composition in the presence of the polymer,

     3) by impregnating a cured mortar or concrete with a monomer, and then polymerizing the monomer using thermal or radiation catalysis.

Generally (1) and (2) are called "PCC", and (3) called "PIC". In general, PIC gives the best properties.

a) Monomer-Impregnated Cement Mixes

The incorporation of a latex into a cement mix makes it possible to achieve both an intimate blend of the polymer particles with the cement gel and an acceptable degree of hydration. Parasitic reactions between a monomer and cement constituents are thus avoided.

c) Polymer-Impregnated Cements and Concretes

This system is less inherently porous than the latex-concrete mixture. Use of irradiation initiation accomplished more mechanical properties than the thermal initiation. PIC's behaves much more like a classical elastic solid than an unimpregnated concrete. Due to the polymer strengthens the sand-matrix bond, the porosity is reduced, especially in the case of impregnation, and micro cracks result from shrinkage during curing.

2.1.3.3 Models for Mechanical Behavior

Porosity acts to reduce the amount of load-bearing material in any plane subjected to stress. This effective shear in the system, slippage occurs at lower stress than in a corresponding fully dense body. Porousness also serves to concentrate stress, a generally deleterious effect, which depends on the nature of the pores. At the same time, pores may also serve to interact with cracks in the matrix, and in some case to effectively obstruct further growth of cracks.

Auskern[11] has developed simple empirical models that combined effects of porosity and effects of a filler, which in this case is a polymer.

$$S_c = S_1 v_1 + f(S_2 v_2) \qquad \text{----------(2.2)}$$

where

    S = strength of composite,

    v = volume fraction,

    1,2 = cement and polymer, respectively,

In ideal case : $f(S_2v_2) = S_2v_2$, by assuming that cement strength is related to porosity by the following expression:

$$S_1 = S_{1,0}f(P) \qquad \text{----------(2.3)}$$

where

p = porosity,
$S_{1,0}$ = ideal pore free,
$f(P)$ = some function (exponential),

$$f(P) = (1-P)^n \qquad \text{----------(2.4)}$$

where

n = depends on nature of the material.

2.1.4 Particle- and Fiber-Reinforced Plastics

The modulus of a two-phase system is some kind of an average of the moduli of the individual components. One may consider fillers is two main groups, particle and fibrous. Particulate phases are usually called fillers, or if the interphase adhesion is high, reinforcing fillers. Fibrous phases are usually referred to as reinforcing. In general the behavior of the composite depends on size, shape, and state of agglomeration of the minor components, and the degree of adhesion between the filler and the matrix.

2.1.4.1 Particulate Phase

a) Mechanical Behavior at Small Strains

A polymeric matrix is strengthened or stiffened by a particulate second phase in a very complex manner. The particles appear to restrict the mobility and deformability of the matrix by introducing a mechanical restraint, the degree of restraint depending on the particulate spacing and on the properties of the particle and matrix. In the simplest possible case, two bounds have been predicted for the composite modulus E_c[12].

upper bound:

$$E_c = v_p E_p + v_f E_f \quad \text{(case of equal strain)} \quad \text{------------(2.5)}$$

lower bound:

$$E_c = E_p E_f / (v_p E_p + v_f E_f) \text{ (case of equal stress)} \quad \text{-----------(2.6)}$$

Equations 2.5 and 2.6 are derived from a parallel and a series model as shown in Figure 2.1a and b respectively.
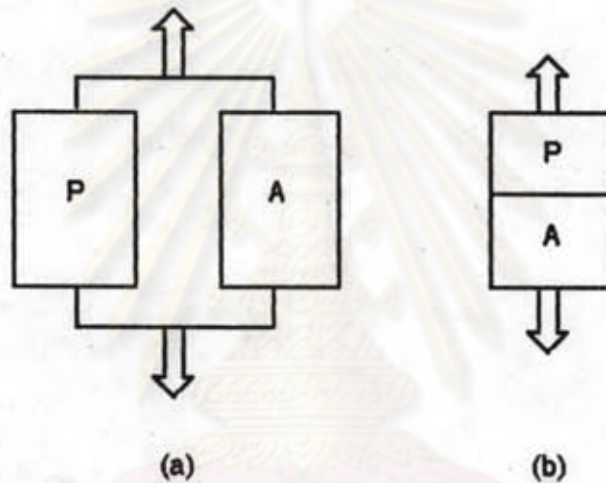

(a)   (b)

Figure 2.1 The parallel (a) and series (b) model, P an A refer to as
polymer and additive, respectively.

The predictation of the moduli of composites of a spherical filler randomly dispersed in a glassy matrix is[13]

$$E_c/E_p = \frac{G_f v_f / [(7-5v)G_p + (8-10v)G_f] + v_p/[15(1-v)]}{G_p v_f / [(7-5v)G_p + (8-10v)G_f] + v_p/[15(1-v)]} \quad \text{-----------(2.7)}$$

where

G = shear modulus,

v = Poisson ratio.

In general, lamella or fibrous fillers raise the modulus to a greater extent than do spherical fillers[14].

$$G_c = G_p v_p + AG_f v_f \qquad \text{----------(2.8)}$$

A = an empirical term to give a measure of the filler-matrix adhesion.

This equation, under some conditions, is approximately equivalent to Kerner's lower-bound type relationship.

The modified Kenner's equation[15]

$$G_c/G_p = (1 + ABv_f)/(1 - B\psi v_f) \qquad \text{----------(2.9)}$$

where

$A = (7 - 5v)/(8 - 10v)$,

$B = (G_f/G_p - 1)/(G_f/G_p + A)$,

$\psi v_f = 1 - \exp[-v_f/(1-(v_f/\phi_m))]$,

or $\psi = 1 + [(1- \phi_m)/ \phi_m^2]v_f$,

ϕ_m = maximum packing fraction.

This equation is best fit of a rigid plastic matrix. The Eilers equation has been frequently used to describe the behavior of such filled elastomeric systems.[16]

$$G_c/G_p = [(1 + 1.25v_f)/(1 - v_f/\phi_m)]^2 \qquad \text{----------(2.10)}$$

Mooney equation giving a slight increase in modulus is[17]

$$\ln(G_c/G_p) = K_E v_f/[(1 - v_f/\phi_m)] \qquad \text{----------(2.11)}$$

K_E = Einstein coefficient

A low filler content, one uses Guth - Smallwood relationship[18];

$$G_c = G_p(1 + 2.5v_f + 14.1v_f^2) \qquad \text{----------(2.12)}$$

In addition to the expressions mentioned for predicting moduli in the elastic state, blending equations developed by Ninomoya and Maekawa[19] have been adapted to predict frequency-dependent moduli

of filler-polymer system. Compliances were considered to be additive, and the following relations for relative moduli (D_p/D_c) were

$$D_c'(w) = f(v_f)Dp'(w\lambda2) \quad\quad \text{-----------(2.13)}$$

$$D_c''(w) = f(v_f)Dp''(w\lambda2) \quad\quad \text{----------(2.14)}$$

where

D', D'' = the tensile storage and loss compliances at frequency w,

$f(v_f)$ = the function of the volume fraction of filler v_f,

λ_2 = the effect of the filler on the matrix relaxation time.

In addition to the prediction of moduli as a function of filler concentration, it is of interest to consider the relationships between modulus and viscosity. For example, it may be useful to predict the modulus of the composite that may be exerted to result from the solidification or curing of a given filled polymeric liquid whose viscosity can be determined. It is usually assumed that the viscosity η_c and shear modulus G_c of the composite are related as follows[20].

$$\eta_c/\eta_p = G_c/G_p \quad\quad \text{----------(2.15)}$$

(1) Stress Relaxation and Creep

The prediction of stress relaxation was carried with the WLF equation. The WLF shift factor was essentially independent of the type of filler used and of the mode of loading. All solid fillers increased the modulus of the system, the fibrous being more effective than the spheres. The rubber as expected decreases the modulus. The presence of a filler did in fact reduce the creep, the relative effect being nearly independent of the applied stress

In general, the creep elongation could be estimated in terms of the shear moduli alone as follows:

$$\varepsilon_p(t)/\varepsilon_c(t) = G_c/G_p \quad\quad \text{----------(2.16)}$$

where

$\varepsilon(t)$ = the elongation at time t.

(2) Damping

Often, a filler which increases the relative damping, specially of the matrix is rubbery. The logarithmic decrement Δ, was found to exceed the value due to polymer only[21].

$$\Delta_c = \Delta_p v_p \qquad \text{-----------(2.17)}$$
$$\Delta = \ln(A_1/A_2) \qquad \text{---------(2.18)}$$

where

A_1, A_2 = the amplitudes of successive oscillation.

The high damping capacity of filled viscoelastic polymers makes them useful as a vibration-damping material; damping is not only increased, but high damping exists over a wider range of temperatures than an unfilled system.

b) Mechanical Behavior at Large Strains

(1) Large vs. Small Strains

Young's modulus of a filled rubber decreases with increasing strain, approaching that of the unfilled rubber. This effect which may be to some extent reversible, is usually attributed to a dewetting of the filler particles or to a breakdown of a filler agglomeration. Dewetting behavior is clearly dependent on the filler and its surface characteristics. The stronger the filler-resin interaction, the greater the number of primary chemical bonds which must be broken, and the larger the strain required for dewetting.

(2) Stress Relaxation

The modulus E varied by as much as 40% when the strain was varied from 0.1 to 0.3 the data could be fitted by the following empirical function[22].

$$[E_{c\varepsilon}(t)]_2/[E_{c\varepsilon}(t)]_1 = [1 + (\varepsilon_p)_1]/[1 + (\varepsilon_p)_2] \quad \text{-----(2.19)}$$

where

$\varepsilon = \ln(L/L_0)$,

$\varepsilon_c = \varepsilon_p + (1 - Kv_f^{1/3})$.

$E_{c\varepsilon}(t)$ = the moduli for the composite measured at time t and strain ε

The stress relaxation curves for a filled polymer at different strainsε_c could be shifted along the modulus axis to give a master curve at the reference strain. The corresponding modulus function becomes as the following equation[22].

$$E_c(t) = [1 + \varepsilon_c/(1-v_f^{1/3})]E_{c\varepsilon}(t) = (1+ \varepsilon_p)E_{c\varepsilon}(t) \quad \text{---------(2.20)}$$

(3) Yield and Strength Phenomena

Nielson[23] has sought to extent of additivity predictions to include stress-strain behavior as a function of filler concentration for the cases of:

(a) perfect adhesion between polymer and filler,
(b) no adhesion between them.

Assuming perfect adhesion, the equations are[23]

$$\varepsilon_p/\varepsilon_c = 1/(1-v_f^{1/3}) \quad \text{---------(2.21)}$$
$$\varepsilon_B(\text{filled})/\varepsilon_B(\text{unfilled}) = 1 - v_f^{1/3} \quad \text{---------(2.22)}$$

and assuming that the polymer in the composite at the same elongation behaves as the unfilled polymer. The higher in filler content the greater the elongation.

In the case of no adhesion to the matrix, the effective porosity was introduced[23].

$$\sigma_{Bc}/\sigma_{Bp} = (1-K'v_f^{2/3})S' \quad \text{---------(2.23)}$$

where

$K' = 1$

S' = stress concentration factor = 0.5

Leidner and Woodhams[24] have developed the more elaborate approach to the effect of filler content on strength of the composite:

* For a case of high v_f and interfacial adhesion:

$$\sigma_{Bc} = (\sigma_a + 0.83\tau p)v_f + \sigma_a S'(1-v_f) \qquad \text{----------(2.24)}$$

* For a case of low v_f or interfacial adhesion:

$$\sigma_{Bc} = 0.83p\alpha v_f + K\sigma_p(1-v_f) \qquad \text{----------(2.25)}$$

where

σ_a, σ_p = the ultimate tensile strengths of the interfacial
           bond and the matrix, respectively,
τ_p = the shear strength of the polymer matrix,
S' = the stress concentration factor,
K' = a parameter dependent on particle diameter,
p = the y component of the pressure exerted by the matrix
        on a sphere,
α = the coefficient of friction.

With poor matrix-filler adhesion, yielding was always observed as in the pure matrix; on the other hand, with good adhesion, specimens fail before yielding.

Sahu and Broutman[25] reported decreases in flexural and tensile strengths for systems exhibiting good adhesion. But sometime the presence of a filler may not decrease ductility as mentioned above, but may increase it instead, depending on the type of matrix and the degree of adhesion. Such behavior may well be complicated by ewetting or cavitation, which depends strongly on interfacial characteristics.

The compressive yield stress of filled system was a linear function of the logarithm of the strain rate with slope being independent of filler concentration and so was tensile strength.

Nicolas and Narkis[26] stated that the yield stress was a function of strain rate which was temperature and filler dependent.

$$\sigma_{yc}/(1-1.2v_f^{2/3}) = A + B\ln(\varepsilon a_T) \qquad \text{----------(2.26)}$$

where

σ_{yc} = the yield stress of the composite,
a_T = the shift factor of the WLF equation,
A,B = a constant,
ε = strain rate.

A double shift with respect to both temperature and filler content is performed as in the case of stress relaxation. It can be mentioned from master curves that the shift factors are functions of temperature, stress, and composition.

In addition to the empirical measurements, an attempt was made to calculate stress-strain curves from the strain-independent relaxation moduli by integrating the following equation[27]:

$$f(t) = \varepsilon \int_{-\infty}^{\ln(t)} tE(t)d\ln t \qquad \text{----------(2.27)}$$

where

f = force,
ε = strain.

(4) Fracture Toughness

The effect of the particulate filler in a plastic on fracture properties is complex. Although there are exceptions, the energy required to induce and propagate crack at normal temperatures is often reduced by the presence of a particulate filler. This is not surprising since fillers act as stress concentrators, and thus one should supply a composite with potential sites for crack growth, especially if debonding occurs between the filler and matrix. At the same time, in principle, rigid fillers may serve to divert cracks (and thus increase total surface area of fracture) or dissipate energy otherwise associate with crack growth.

The modulus itself contributes to the total energy and the stress required for fracture. The filled material was brittle at higher temperatures and lower strain rates than the unfilled polymer.

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The "fracture toughness" for characterizing brittleness provides a measure of the conditions required for catastrophic crack propagation in a material[28],

$$\gamma = G_c/2 = K_c^2[(1-v^2)/2E] \qquad \text{----------(2.28)}$$

where

γ = surface fracture energy,

K_c = critical stress intensity factor (near the crack tip).

The effects of several factors on fracture toughness are clearly of interest in terms of temperature, filler type, geometry, size, content, and interfacial bonding. When glass spheres were treated with silane coupling agents to promote adhesion, values of γ were decreased. But when fiber were so treated, the opposite effect was found.

If little additional transfer of stress can occur, improved adhesion will inhibit plastic flow at the filler surface and thus decreases the γ.

The study of the effect of filler on the area under a stress-strain curve and on impact strength found that both the areas under the stress-strain curves and unnotched impact strength were reduced in proportion to the volume fraction of filler.

2.1.4.2 Fiber-Reinforced Composites

a) Mechanical Properties

The filler stiffens the composite to a greater extent, and begins to carry increasing fractions of the load. With short discontinuous fiber of a high modulus material, the mechanical load is shared between the matrix and the filler, and most mechanical properties of the composites are improved to greater or lesser extents i composition of the matrix. With continuous fiber, on the other hand, the fiber carry most of the mechanical load, while the matrix serves to transfer stress to the load-bearing fiber and to protect them against damage.

For use of materials in aerospace technology, the weight of material must be kept to a minimum, and considerable attention was given to achieve high strength-to-weight and high modulus-to-weight ratios.

ratios. Table 2.1 shows that, for example, composites based on epoxy resins reinforced with boron or graphite fiber have specific strengths (per unit weight) and moduli far surpassing values for aluminium, titanium, or high-strength steel.

Table 2.1 Properties of Oriented Polymeric Chain Structures and
Related Engineering Materials[30]

Material	$E_{11}^{*} \times 10^{-6}$ psi	$E_{22}^{*} \times 10^{-6}$ psi	$E_{iso}^{*} \times 10^{-6}$ psi	Tensile strength ksi	Density lb/in^3
Steel and iron (cast and alloy)	-	-	28-30	13-300	0.25-0.29
Titanium	-	-	19	60-240	0.16
Poly(vinyl alcohol)	36.2	1.54	14.4	~100	0.05
Polyethylene	34	0.7	13.6	~100	0.05
Boron/epoxy	30	2.7	11.89	83	0.07
Aluminum	-	-	10	22-90	0.10
Polytetrafluoro-ethylene	22.2	-	-	-	0.05
HTS-graphite/epoxy	21	1.7	10	62	0.05
Cellulose I	18.5	-	7.6	50	0.05
E-glass/epoxy	5.6	1.2	2.85	47	0.06
Polypropylene	6.0	0.42	2.5	-	0.05
Poly(ethylene oxide)	1.42	0.56	0.88	-	0.05

* E_{11} and E_{22} refer to measurements parallel to and transverse to, respectively, the direction of orientation;
E_{iso} refers to isotropic orientation.

b) Modulus and Tensile Strength

A matrix can transfer a major portion of an applied stress to fibrous elements only if the ratio of length l to diameter d exceeds a critical value l.

$$l_c/d \quad = \quad \sigma_f/2\tau \qquad \text{----------(2.29)}$$

where

σ_f = the maximum stress in the fiber,

τ = the matrix or interface shear strength.

The reason is that the fiber ends do not carry load; as the fiber length increases, the relatively ineffective portions of the fiber decrease. The average stress in a fiber σ_f is given by[29]

$$\sigma_f = \sigma_f(1-l_c/2l) \qquad \text{----------(2.30)}$$

Since as a matter of practice, l/d ratios are typically in the range of 150-5000, it is clear that such a fiber resembles a

continuous fiber in its ability to carry load transferred from the complex, good adhesion appears to generally lower the value of l_c/d[31].

Thus, in contrast to at least some of nonfibrous reinforcements, both tensile moduli and strengths are increased simultaneously by even relatively short fibrous reinforcements (Figure 2.2)[32].
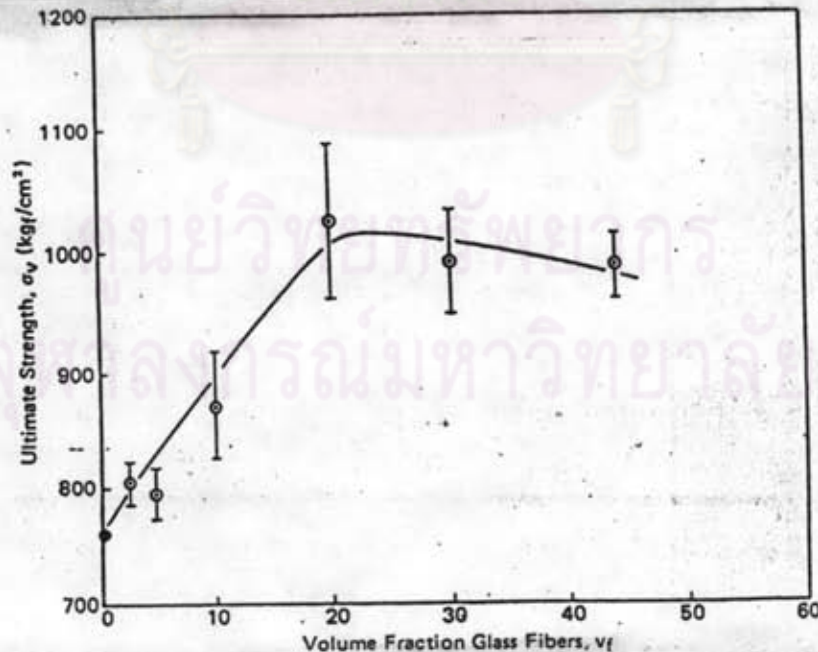

Figure 2.2 Effect of filler content on glass-fiber-PPO composite tensile strength.

The orientation and configuration of the fiber are important. At the same concentration of the fiber, isotropic systems will exhibit a lower .degree of reinforcement than systems that have preferential alignment in the direction of stressing, while orthogonally oriented systems are less strong, but have good properties in both directions.

With random fiber in a plane a modified rule of mixtures has been proposed by Nielsen[33] and Nielsen and Chen[34] to predict the modulus:

$$E_c = KE_f v_f + E_m(1-v_f) \quad\text{----------(2.31)}$$

where

K = an empirical fiber efficiency parameter which depends on the volume fraction of fiber v_f and on the ratio of the fiber to the matrix modulus, E_f/E_m (generally about 0.15-0.56).

If the fiber is long and oriented in the direction of applied stress, higher levels of reinforcement occur, and the following rule of mixtures is found to hold in terms of moduli of the constituents:

$$E_{c//} = E_f v_f + E_m v_m \quad\text{----------(2.32)}$$

where

$//$ = the fiber orientation is parallel to the stress direction.

This equation corresponds to an upper bound of a composite modulus predicted by equation 2.5. Thus, particulate fillers tend to yield lower bound values, equation 2.6, or as predicted by Kerner's[35], while long, oriented fiber tend to yield upper-bound values of modulus. Short, randomly oriented fiber tend to yield intermediate behavior.

With long fiber, the advantage gained in the direction of stress is offset by a compensation reduction in the transverse direction as indicated in the following equation[36]:

$$E_{c\perp}=2[1- v_f+(v_f\text{-} v_m)v_m] - \frac{[M_f(2M_m+G_m)\text{-}G_m(M_f\text{-}M_m)v_m]}{[(2M_m+G_m)+2(M_f\text{-}M_m)v_m]} \quad\text{---(2.33)}$$

where

      $E_{c\perp}$ = the transverse Young's modulus of the composite,

      M   = the area modulus, $M = E/(2-2v)$,

      v   = Poisson's ratio.

In any case, the effects of high stress concentration localized at the tip of fiber are extremely important. Several investigators have measured such stress as a function of the following parameters: critical aspect ratio l_c/d, spacing between fiber ends and between fiber, eccentricity of fiber, and overlap of fiber ends. For example, Maclaughlin[37]reviewed earlier studies and presented results of a study of this problem by photoelastic techniques. Glass fiber was used in an epoxy matrix, the fiber to matrix modulus was 40. Maximum shear stress in the fiber was found to occur for critical aspect ratios of 40-80, with the smaller value for the closer lateral spacing. Maximum shear stress in the matrix was observed, as expected, at fiber ends; especially high values were observed near fiber ends that were close together. Carrara and McGarry[38]analyzed matrix and interface stresses as a function of geometry of fiber ends, and showed that a tapered tip should have the lowest stress concentration.

C) Fatigue Behavior

Fatigue has been studied for several viewpoints, such as effects of aspect ratio, frequency, modes of failure and crack propagation. Lavengood and Gultransen[39], worked with short boron fiber embedded in an epoxy resin, and determined the number of cycles required for a 20% deflection at a rate of 3 Hz which was low enough to minimized heating by hysteresis. A significant increase in fatigue life was observed when the aspect ratio equaled 200. Further improvements in fatigue life were small for values of $l/d > 200$.

At higher frequencies, a substantial degree of hysteretic heating may occur. Thus, at frequencies up to 40 Hz, Dally and Broutman[40] observed the generation of surface temperatures up to $130^\circ C$ for fiber-glass-roving-resin systems. The heat generated per unit volume per

second, q, depends on the frequency f and tensile strength , and is given by

$$q = H\sigma^2 f/2E \qquad \text{----------(2.34)}$$

where

E = Young's modulus,

H = constant (depending on the loss modulus, E").

The number of cycles to failure was somewhat reduced by increasing the frequency, with the greater effect the lower the stress level and the greater for the isotropic material. It was suggested that the increased temperature lowered the modulus, which in turn effectively increased ineffective fiber length and thus lowered the ability to withstand stressing.

2.1.4.3 Role of the matrix and Interface

While it is true that in fibrous composites the fiber bear the major fraction of the load, the matrix and the nature of the fiber-matrix adhesion are often excludingly important. In fact, the matrix is the strength-limiting variable in the following cases: aligned continuous fiber, tested off-axis; cross-plied continuous fiber, test at all angles; and incompletely dispersed random-in-a-plane discontinuous fiber, test at all angles. Thus, in many common cases, matrix strength is desired- a combination is not often achieved. While the incorporation of rubbery materials in a brittle matrix can increase toughness substantially, the modulus tends are reduced to some extent. Possibly better approaches to achieve both a high modulus and improved toughness might include the addition of small glass spheres, especially if interfacial adhesion is minimized; the use of ductile or crack-stopping filler; the use of high-modulus organic fiber; the structural modification of epoxy and other resins; and the use of other matrixes altogether.

In all cases, the nature of the interface must be carefully controlled. For example, in contrast to the case of particulate composites, good adhesion between a ductile matrix and short glass fiber may enhance crazing and hence energy dissipation at the fiber tips[41].

As with particulate fillers, then, the fracture energy of a fiber-reinforced composite is a complex function of the properties of the reinforcement, the matrix, and the interface. Several modes of dissipation (Figure 2.3) may be involved as follows:

1) Debonding of the fiber from the matrix as a crack impinges upon a fiber. Such a debonding may occur when the fracture strain of the fiber is greater than the fracture strain of the matrix.

2) Pulling of broken filaments out of the matrix following fracture.

3) Redistribution of strain energy from fiber to the matrix after fracture of the fiber.

4) Fracture of the fiber and matrix themselves.

Clearly, all these modes may participate in determining the overall toughness of a composite, though to degrees dependent on the system. Broutman and Agareval[42] have critically analyzed this question, and developed more or less generalized treatments of the overall work required for fracture. Such analysis based on fracture mechanics concepts should be of reasonable level of toughness without sacrificing strengths of the order predicted by the rule of mixtures. In general, an intermediate value of the interfacial bond strength is desired to optimize toughness, an optimum fiber length also exists, the value depending on the nature of the fiber.

The interface may also be "tailored" to obtain a gradation in modulus from the fiber to the matrix, and hence a more efficient transfer of stress; such a tailoring was effective with annealed graphite and glass-fiber-reinforced polycarbonate.

2.1.5 Matrix and Interface Behavior

It is appropriate to discuss specific molecular effects of rigid inclusions (particulate or fibrous) on a matrix, in order to demonstrate continuity between all types of reinforcements.

Table 2.2 Factors Contribution to the Work of Fracture

Type of work	Symbol	Origin	Form of energy dissipation
Fiber internal work	γ_{fb}	Fiber brittle fracture	Stored elastic energy
	γ_{fs}	Fiber bending during pullout	Plastic flow during bending
	γ_{fd}	Fiber ductile fracture	Plastic flow and necking
Interface work in matrix	γ_{mf}	Difference in tensile strains across interface	Frictional sliding or plastic shear
	γ_{fp}	Fiber pullout	Frictional sliding or plastic shear in matrix
Interface and matrix work	γ_{ms}	Splitting of matrix parallel to fibers	Matrix surface energy and fiber-matrix bond energy
Matrix internal work	γ_{m}	Matrix fracture	Matrix surface energy and plastic flow

Figure 2.3 Effect of glass-polymer interface on advancing crack. (A) adhesive strength of bond equals cohesive strength of matrix. (B) Adhesive of bond is much less than cohesive strength of matrix

2.1.5.1 Molecular Effects of Rigid Inclusions

It is generally recognized that this simple statement below is inadequate, and that, probably in general, the interface between an adhesive and adherent or substrate (matrix and reinforce-ment) should be considered not as a singularity but as a layer or "interphase". As shown in Figure 2.4, a filler-matrix system may be considered to possess a region at the interphase whose properties differ from those of the bulk matrix. One may envisage several phenomena which may be involved in generation of a interphase: roughness or porosity of the substrate surface, such that the adhesive (or matrix) penetrates beyond the outer bounds of the surface; changes in composition at the interface, as may occur due to selective adsorption of one component, e.g., an amine in an epoxy system; other influences of the substrate on the curing of thermosetting resins; morphological changes induced at an interphase with a crystalline polymer during solidification; the presence of a coupling agent or adhesion promoter, such as silane, on the substrate; and ordering effects of various kinds, possibly due to annealing effects or thermal stress. Other effects may also be observed or postulated, such as incomplete wetting, air voids, and softening due to residue stress. Force fields at short distance (up to 20 A) are certainly operative and long range effects up to 10^3 A or more have been postulated.
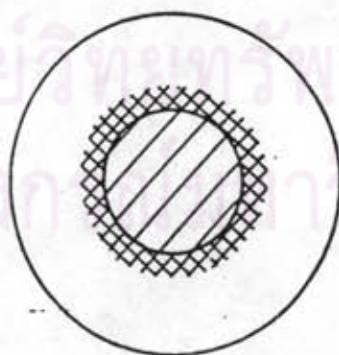
Figure 2.4 Scheme showing filler particle embedded in a matrix resin. Note crosshatched "interphase region between bulk matrix and outer bound bound of filler surface. Also note that filler surface may be porous or rough, so that interphase bounds may include filler asperities, and that interphase boundary is not sharp.

2.1.5.2 Effects of Fillers on Relaxation Behavior and Other Transitions

T_g is an extremely important parameter for determining appropriate temperatures for use. T_g can be determined by the curve of modulus as a function of temperature. As shown in Figure 2.5, the result of mechanical reinforcement is to raise the modulus throughout from glassy to rubbery states. In such a case, no change in relaxation behavior of the matrix is involved. If the relaxation behavior is changed by the filler, some degree of horizontal shift or at least a change in slope at the transition would be observed.

A number of studies of high-surface-area fillers (surface area 100 m^2/g) reveal detectable increases in T_g or other changes in relaxation behavior.

While T_g of a matrix resin appears to be often increased by the presence of a filler, the magnitude of the effect does appear to depend on the nature of the surface. Surface treatments are also important. Treatment of silica to reduce adhesion eliminates any elevation of T_g in several polymer matrices[43].

Secondary transitions may also be affected by fillers. Glass beads in an epoxy resin tend to slightly owner the temperature of the low-lying β transition (at about -60°C) corresponding to the motion of the glycidyl group.[44-46] A similar lowering was observed in the cases of Al powder[47] and carbon and graphite[48]. Jenness[49] reported a tendency for a peak to shift to higher temperatures as the volume fraction of filler was increased. In the presence of absorbed water, at least one new peak was observed in the glass-bead system (Figure 2.6) just mentioned[46]. New peaks have also been observed in some cases by Yim et al.[43] and attributed to the existence of an observed polymer component (Figure 2.7).

Thus it appears that, as long as good bonding can be obtained between a filler and a matrix, relation behavior can be significantly affected. A filler may increase damping in the matrix for filled epoxy resin[12] and polyethylene[20]. In general, damping is normally greater when the matrix is in the rubbery state, regardless of the degree of adhesion, perhaps due to the occurrence of frictional effects at the
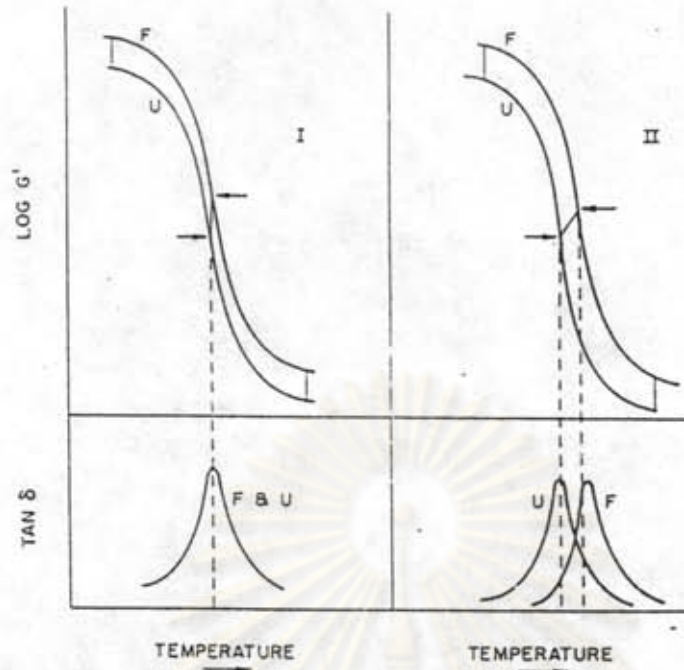
Figure 2.5   Scheme showing storage modulus G' and dissipation factor tan δ   as
a function of temperature for two case of filler-matrix system: I, case
of simple volume replacement and stiffening by filler, with no effect on
on relaxation behavior of filled polymer F; II, case of volume replacement
and stiffening with an effect of filler on relaxation behavior. (No attempt has
been made to illustrate specific effects such as transition broadening, enhanced
stiffening in the rubbery region, or additional peaks due to bound resin.)
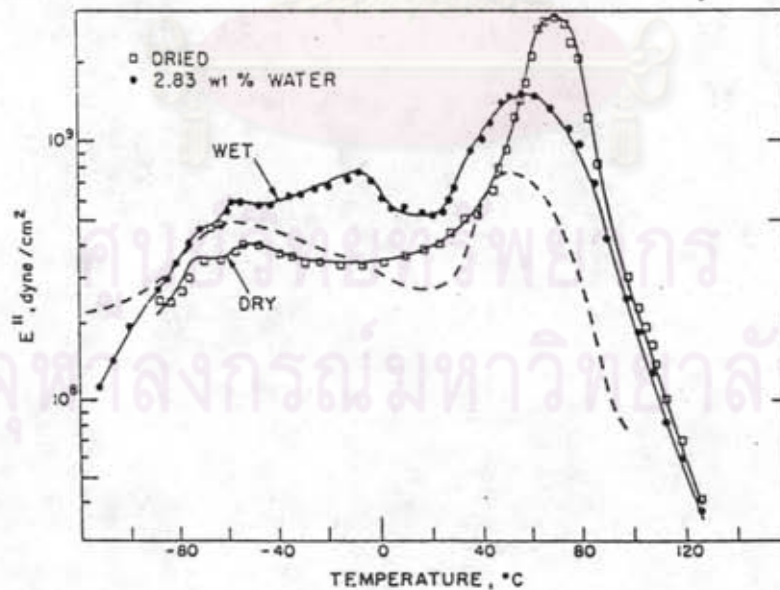
Figure 2.6   Effect of water (2.83 wt%) on damping in glass bead-epoxy systems (Vf = 0.3).
Note the appearance of a new peak at 0 °C in the presence of water: a shoulder
also has developed on the peak near 60 °C. Dashed line represents unfilled
polymer (wet)

interface(50-51). In the glassy state, a filler may increase damping associated with the transition(48-49), perhaps due to the presence of either excess resin or a separate gel phase at the interface. Generally, lower, damping tends to be reduced for glassy matrices, as observed in TiO_2 filled poly(vinyl acetate)(54), in silica- and carbon black-filled SBR(50), in Carbon-filled epoxy resin for transition(48). This tendency is certainly consistent with the existence of some kind of interphase due to constraint by the filler.
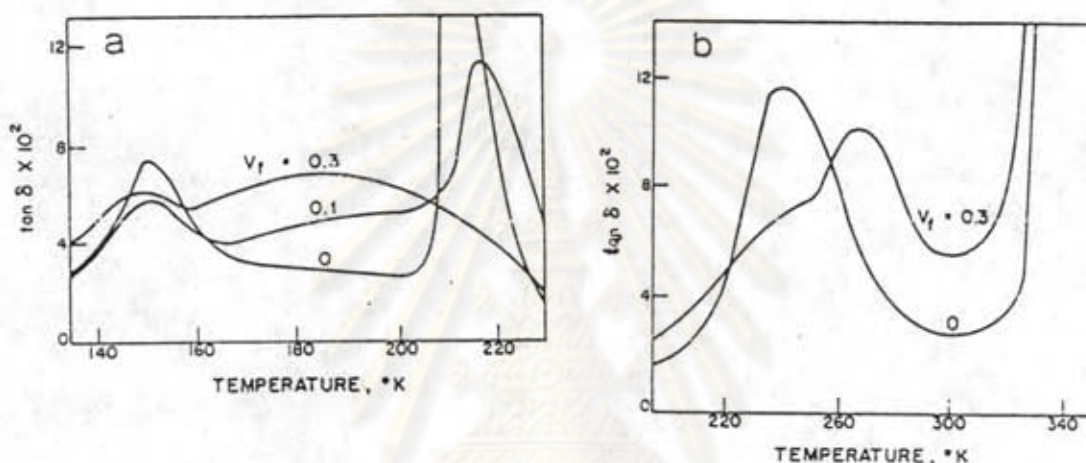

Figure 2.7 Effect of "active" silica filler (Vf is volume fraction) on Tg and tan δ of (a) a siloxane resin and (b) poly(ethylene glycol). Note appearance of additional peaks in these in other cases, such peaks may not be resolved.

2.1.5.3 Sorption and Permeability

The sorption of the vapors or liquids by a polymer containing a nonsorbing filler will be reduced in proportion to the volume fraction of the filler. However, a significant interaction between the filler and matrix may cause lower a value of sorption than predicted. The incorporation of TiO_2 in poly(vinyl acetate) and epoxy resin is an example case that the ability of the matrix to sorb organic vapors was lowered than predicted on the basis of simple additive(55).

Observed values of permeability may be expected to deviate from predictions based on a simple two-component model of an impermeable, noninteraction filler embedded on a permeable matrix. If an interface exists, it may be more permeable than the matrix, as in some

pigment paint films[56], or less permeable in several other filler-polymer systems.

2.2 Literature Review of Natural Fiber as the Reinforcement in Polymer Composites

Last decade, the natural fiber as a reinforcement in polymer composites has been the matter of a large number of published papers. Recent works on the study of natural fiber-polymer composites in various applications are listed below.

Belmares, H. et al.[57] have showed that the natural fiber of the North American continent, lechuguilla(Agave lechuguilla), have good mechanical properties such as tenacity, percent elongation and initial modulus. Mechanical properties of lechuguilla are good enough to use in composite materials compared to glass fiber. Later Belmares, H. et al.[58] have introduced new composites from hard natural fiber consisting of sisal, henequen and palm fiber bases used with polyester resin as a matrix. The fiber were coated with poly(vinyl alcohol), PVAl, or poly(vinyl acetate), PVAc, to enhance tensile properties.

Guthrie, J.T.[59] has used cellulosic fiber, membranes and timber to make composites with polystyrene for various applications. Polyethylene was also used to make composites with wood fiber by a laminated technique but mechanical properties was dropped significantly in wet condition.[60] The decline in the flexural properties of paper-polyolefin laminates upon exposure to H_2O could be markedly reduced by acetylation or crosslinking with formaldehyde on pulp.[61] Roofing material systems consisting of bagasse-phenolic, bagasse-rubber, bugasse-thermoplastic and oriented bagasse-phenolic were successfully demonstrated on pilot roofs in 3 developing countries, Jamica, Ghana, and the Philippines reported by Usmani, A.M. et al..[62] The composites provided good alternative roofing primarily based on materials indigenous to these countries.
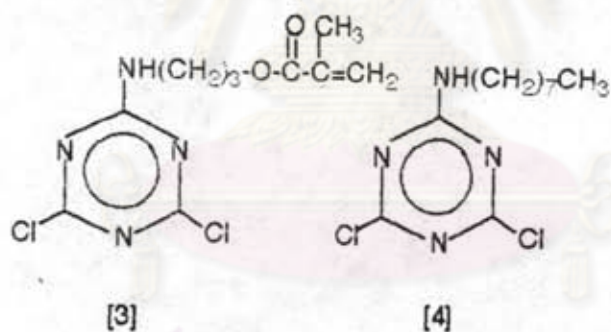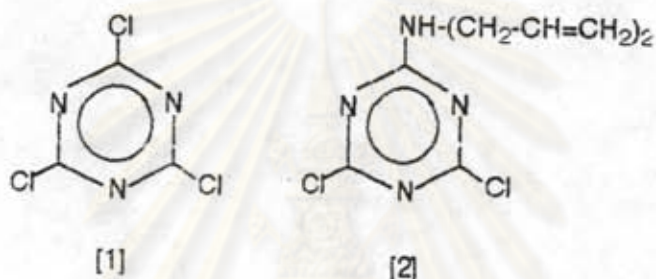
Jute fiber also acts as reinforcement in polymer composites presented by Murty, V.M. et al..[3] Carbon black and silica were introduced to the formulation of composite to promote adhesion between fiber and rubber. Polyester reinforced with jute fiber was introduced by

Wells, H. et al.[63]. The composites having good mechanical were prepared with high fiber content by compression of the mat containing nonwoven jute fiber of a maximum length of 10 cm before the matrix sets; the composition also contained mica flakes or powder. The specimens had mean flexural strength of 11.0×10^3 psi and mean flexural modulus of 0.85×10^6 psi.

Rubberized coconut hair, one of many utilizations, had the most significant use published by Freitag, F. et al.[64] which is a random mat coated with fire retardant additive and bound with synthetic and/or natural latex, used in packaging and upholstery industries. Modification of coir fiber surface to develop fire retardant and mechanical properties was successfully made by Pavithran, C.[65]. Firstly, coir fiber surface was treated with NaOH-HCOH/ammonical $AgNO_3$ solution to activate its surface. Cu was deposited on the activated surface of the coir fiber from Fehling-formaldehyde solution. Reinforcement of polyester with copper-coated coir fiber increases the tensile and flexural strength by about 25% as compared to polyester reinforced with plain coir fiber. Owolabi, O. et al.[2] have published the composites consist of coir fiber and thermosetting plastics. Coir fiber was treated by NaOH and/or gamma-preiradiation to improve its wettability to plastic matrix for better mechanical properties compared to plain coir fiber-reinforced thermosetting plastics.

Polyesteramide polyols (PEAP) was synthesized by melt condensation using a mixture of alkanolamines, polyethylene glycols, and dicarboxylic acids/anhydrides and used as interfacial agent in jute/epoxy and jute/polyester composites respectively, as reported by Mukherjea, R.N. et al.[66]. Mechanical properties and water resistance capacities of the composites were increased significantly. S-triazine derivatives were suggested by Zadorecki, P. et al.[4] to act as coupling agent of cellulosic fiber and polymer composites due to the good reactivity of trichloro-s-triazine[1] to cellulose[67]. 2-Dially-amino-4,6-dichloro-s-triazine[2] and methacrylic acid-3-((4,6-dichloro-s-triazine-2-yl)aminopropyl) ester[3] were synthesized and treated to cellulosic fiber(paper pulp), then the treated fiber was analyzed by Fourier-transform infrared spectroscopy (FTIR), elemental analysis and electron spectroscopy for chemical analyses(ESCA) to detect the chemical

reactions on the surface. The papers[68] on an ESCA study of the chemical reaction on the surface of cellulose fiber were published later to show importance of a concept of the coupling reaction. Zadorecki, P. et al.[4] again have studied the effect of cellulose fiber treatment on the performance of cellulose-polyester composites. They found that the coupling agents (2-octylamino-4,6-dichloro-s-triazine[4], [3] and [2]) had a significant impact to cause all types of fiber treatment to decreased water absorption and the reduction of mechanical properties in wet conditions.

[1]

[2]

[3]

[4]