Acid–Base Interactions on Interfacial Adhesion and Mechanical Responses for Glass-Fiber-Reinforced Low-Density Polyethylene

S. H. PAK, C. CAZE

Laboratoire de Génie et Matériaux Textiles, Ecole Nationale Supérieure des Arts et Industries Textiles, 2 place des Martyrs de la Résistance, 59100 Roubaix, France

ABSTRACT: The relationship between interfacial adhesion and mechanical response in discontinuous glass-fiber-reinforced thermoplastics (GFTP) was investigated using low-density polyethylene (LDPE) as a matrix. It was found that the presence of acid groups in the matrix enhances the mechanical strength as well as the interfacial adhesion, to a great extent, especially with the glass fibers (GF) treated with basic coupling agents. However, some degradation in mechanical properties of the GFTP resulted when excessive interfacial adhesion was achieved with large amounts of the acid groups. The results of diverse characterization suggest the existence of an interphase of bound polymers at the GF surface, whose physical entanglement with the matrix plays a critical role in the mechanical response of the GFTP. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 143–153, 1997

Key words: composite; polyethylene; glass fiber; interface; acid–base interaction

INTRODUCTION

The importance of glass fiber–matrix interfacial adhesion on mechanical performances of glass-fiber-reinforced thermoplastics (GFTP) was recognized in the early days of the composites; therefore it merited the attention of plastics engineers.[1] The interfacial strength plays a major role in the composite properties when other factors such as fiber strength, fiber orientation, fiber aspect ratio, volume fractions, and the stress sensitivity of the matrix material are the same.[2] Different from thermosetting glass fiber (GF) composites, the interfacial adhesion is usually not strong enough in GFTP for lack of chemical bonds or specific interactions across the interface of the relatively immiscible components. One of the most common approaches to overcome this defect consists of introducing acid molecules as pendant functional groups in polymer backbone or side chains to allow interactions with polar groups on filler surface.

The acid–base interactions may be important in improving the interfacial adhesion of GFTP and effective, especially for apolar polymer matrices, such as polyolefins.[3,4] It has been reported from many researchers that a variety of acidic functionalities, including acrylic acid, methacrylic acid, crotonic acid, maleic acid, citraconic acid, itaconic acid, and their anhydrides in a polyethylene (PE) or polypropylene (PP) matrix were to enhance adhesion to the GF treated with aminosilane coupling agents.[5–8] In previous studies, however, the polymers containing only very low concentrations of the functionalities, hardly exceeding 1 wt %, were used as a matrix; and the stronger interfacial adhesion obtained by the more functionalities was reported to be bound to result in the better mechanical strength as far as the range of the acid concentration was concerned.

Studies addressing the interrelationships between the degree of matrix functionalization and the mechanical properties of GFTP with highly functionalized matrices are still incomplete. Literature on the subject is hardly found up to this day, but with a few exceptions.[9] Understanding of the interphase structure for the GFTP possessing strong interfacial adhesion is also not complete.

The primary objective of this study is to identify and measure the effects of acid–base interactions on interfacial adhesion and to correlate them with the physical properties of the discontinuous GF-reinforced low-density polyethylene (LDPE) containing acrylic acid groups in the matrix over 10 wt %. Of particular interest are the variations in mechanical responses expressed in stress–strain behavior as a function of the interfacial adhesion. Therefore, the material configurations investigated in this study are specifically chosen to allow the comparison of the mechanical responses and properties as the interfacial characteristics are changed. Further, the experimental results are employed to evaluate the degrees of interfacial adhesion using existing theories that predict the composite properties from the interfacial strength along with constituent properties. Finally, a correlation between mechanical response and interfacial adhesion is made in an attempt to elucidate a probable interphase structure of the GFTP around the GF surface.

EXPERIMENTAL

Materials

The matrix materials chosen to produce different degrees of interfacial adhesion in this study were four kinds of LDPE containing the following different levels of acrylic acid molecules as comonomer: 0, 6.2, 9.0, and 11.0% by weight (PE00, PE06, PE09, and PE11, respectively, hereafter). The PE00 was Lacqtene 1070MN18 from Elf Atochem; and PE06, PE09, and PE11 were Escor 5000, 5050, and 5100, respectively, from Exxon Chemical. Their specific gravities were around 0.93, and all of them had nearly the same melt flow rate at 190°C under ASTM D1238 testing condition.

The GF treated with aminopropyltriethoxysilane coupling agents (GF.A hereafter) were used as cointeracting GF with an acidic polymer matrix; and the GF treated with octyltriethoxysilane (GF.B hereafter) were also used to serve as non-interacting, control formulations. Both of them were noncommercial products of European Owens Corning Fiberglass treated purely with 0.2 wt % of the respective coupling agents, excluding size or other auxiliary additives. They were provided as 6 mm chopped strand with a diameter of 10 μm, and the E-glass reportedly have a bulk specific gravity of 2.54.

Composite Preparation

Melt compounding was carried out in a Brabender Plasticorder PL2000 equipped with a 50 CC mixing chamber at the rotor speed of 60 rpm. Pre-weighed quantities of the polymeric ingredients were melted down at 200°C through sequential feeding over 10 min, followed by adding 30 wt % of GF in a single portion to continue the compounding another 5 min at the temperature. The size of each lot was deliberately adjusted to attain 80% of the mixing chamber in volume in an attempt to assure of a good dispersion and collect reasonable torque values. All the parameters, including the temperature, rotor speed, and mixing time, were precisely controlled by a built-in computer program; and the torque moment necessary to turn the mixer blades was continuously recorded during the compounding.

The melt compounded materials were then transformed into sheets of 1.5 mm thick by compression molding at 200°C under 50 kN. The materials were preheated for 5 min in the mold before applying pressure for 1 min, followed by water cooling to ambient temperature maintaining the pressure upon the mold. The specimens for the measurements of mechanical properties and swelling were cut from the obtained sheets using a die punch cutter. The sheets were kept at 100°C for three minutes in an oven just prior to the specimen cutting in order to attenuate their brittleness.

Testing Procedures

Uniaxial tensile tests were conducted at room temperature with a constant crosshead extension rate of 5 mm min^{-1} (strain rate $\approx 2.8 \times 10^{-4}$ s^{-1}) using dog bone specimens on a Zwick 1456 universal mechanical testing machine equipped with Z1005 version software. Tensile strength was the yield peak stress, which was the fracture stress, at the same time in some cases.

Flexural tests were carried out on the same machine as the tensile tests using a span distance

of 30 mm with a constant flexural rate of 20 mm min^{-1}. The maximum stress attained either at yield or at fracture was taken as flexural strength.

In performing the rheological study, a Brabender Plasticorder was considered as two adjacent coaxial cylinder viscometers in which the viscosity (η) meets a relationship, $\eta = C\,M/N$, (C, M, and N are the coefficients related to mixer, measured torque moment, and rotor speed, respectively).[10] The relative viscosity (η_r) was defined as the ratio of the composite viscosity (η_c) to the viscosity of its matrix (η_m), $\eta_r = \eta_c/\eta_m$; and this can be directly obtained by substituting the corresponding torque values in place of the viscosities when the rotor speed is identical. The torque moments just prior to complete the melt compounding were taken for the calculation of the η_r.

Stress relaxation tests were realized using the same machine and specimens as the tensile tests. The dog bone specimen was subjected to 1% strain with a strain rate of $2.8\ 10^{-4}\ \mathrm{s}^{-1}$, and the stress change was followed to the calculated percentage of residual stresses as a function of time. The measurement of residual stresses for predetermined time intervals was continued until the stress reached 50% of its initial stress within the limit of 200 min.

Swelling studies were made to estimate the compactness of the interface using n-hexane as solvent. Specimens of $10 \times 10 \times 1.5$ mm (≈ 170 mg) in dimension were immersed in 20 mL of the solvent and left at the ambience for 48 h to reach an equilibrium. The degree of swelling was determined from the weight increase of the specimen, as it is a generally accepted method for semicrystalline polymers.[11] The composite swelling (s_c) was calculated for the matrix component excluding the nonswellable GF fraction using the relationship $s_c = (m_e - m_o)/m_o(1 - W_f)$, where m_e, m_o, and W_f stand for the weights after and before swelling, and the weight fraction of the GF, respectively. The percentage of relative swelling (s_r) was the ratio of the s_c to that of the pure polymer (s_0) that the matrix was constituted, as defined $s_r = (s_c/s_0) \times 100$.

Morphological studies were also conducted by observing the fractured surface of the composites on a scanning electron microscope (SEM) of Jeol 120CX equipped with ASID 4D unit. The specimens were broken in liquid nitrogen in order to obtain undeformed surface followed by gold coating on a cathod pulverization under reduced pressure in argon atmosphere.
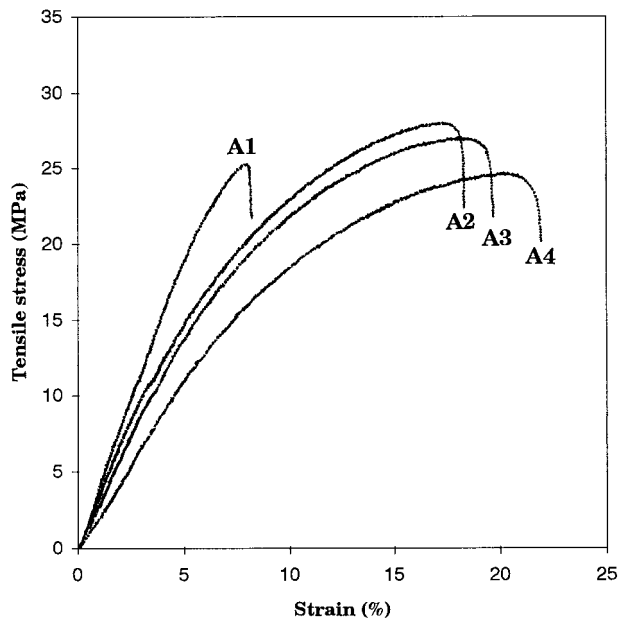

Figure 1   Stress–strain curves of LDPE/GF.A (30%): A1, PE00; A2, PE06; A3, PE09; and A4, PE11.

RESULTS

Tensile Strength

Some typical stress–strain curves for the composites of LDPE/GF.A (system A) and LDPE/GF.B (system B) made of different matrices are shown in Figures 1 and 2. A comparison of each curve with its counterpart across the systems may reveal useful information about the difference in their interfacial states, while direct comparison between the curves within a system cannot be made due to the different natures of their matrices.

It was noted at a glance that the specimens of system A produced significantly higher strengths and moduli being fractured without noticeable stress whitening, while those of system B were cold-drawn after yielding at low strengths. The ultimate strength of GFTP is a direct measure of the interfacial adhesive strength as the applied stress being transferred more efficiently across a strong interface.[12] The superior tensile strengths of A2, A3, and A4, to B2, B3, and B4, respectively, could be attributed to the strong interfacial adhesion exerted by the acid–base interactions between aminopropyl functional groups on the GF.A surface and acrylic acid groups of the matrix polymers. These interactions might have stiffened the polymer chains to resist against deformation and to fail at the end without yielding. A2, A3, and
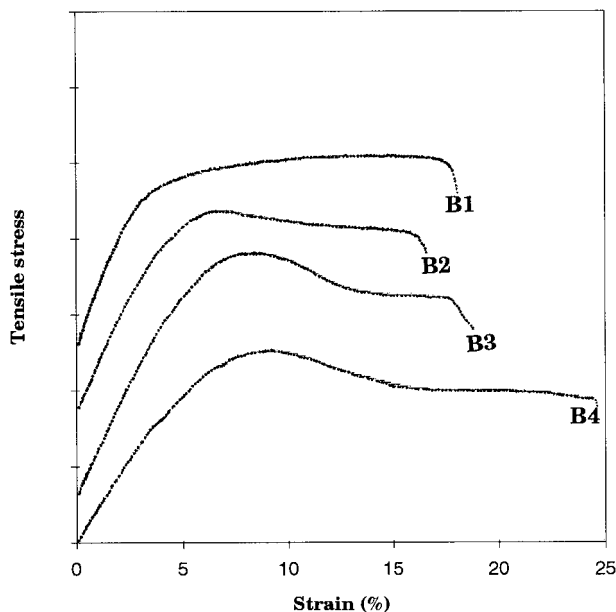
Figure 2 Stress−strain curves of LDPE/GF.B (30%): B1, PE00; B2, PE06; B3, PE09; and B4, PE11. The *y*-axis is on the same scale as in Figure 1. B1, B2, and B3 were vertically shifted for a clear view.

A4 were improved to great extents in comparison with A1 in the elongations at fracture as well as the tensile strengths; while those of B2, B3, and B4 fell around B1. These also can serve as a proof of the functioning of the acid−base interactions to bring about a stronger interfacial adhesion from which improved miscibility is to be resulted in between the two phases.

On the other hand, the stress−strain behaviors of the A1−B1 pair were unexpected results. The functional groups of GF.B and the branches of the matrix PE00, *n*-octyl, and PE, respectively, being similar in their chemical natures, might have resulted in a good interfacial adhesion as a result of interdiffusion at the interface.[13] One of the most plausible explanations for this discrepancy can be found in the works of Hartlein,[14] who reported that the GF treated with propyltrimethoxysilane had resulted in poorer mechanical strengths than those treated with aminosilane coupling agents in a polypropylene (PP) matrix. The author concluded that the mechanical strength of the coupling agents layer, as well as its degree of affinity toward the matrix, are important to produce reinforcement in GFTP. Another possibility concurrent with the previous one is the plastification effect of the LDPE matrix near the interface by the segments of coupling agents from the outermost layer of the GF surface.[15] The octylsilane

segments are believed to have induced a far higher degree of plastification than aminosilane due to the better solubility in polyolefins.

The interfacial adhesive strengths were evaluated using Suetsugu−Sakairi equation,[16] which successfully correlated the tensile strength and the interfacial adhesion in GFTP, excluding most of the tedious parameters in theoretical equations,

$$\sigma_c = K\Phi\chi V_f + \sigma_m(1 - V_f) \qquad (1)$$

where σ_c, σ_m, Φ, χ, and V_f represent the composite strength, matrix strength, interfacial adhesion parameter, GF aspect ratio, and volume fraction of the GF, respectively; and K is a coefficient reflecting the orientation and the length distribution of the GF. Equation (1) can be rewritten as eq. (2) in terms of $\Phi = f(\sigma_c, \sigma_m)$ for our composite system substituting 0.14 for V_f and assuming identical K and χ values for every lot. This should be a valid approximation considering that the matrices have the same melt flow rate and all the lots were exposed to the same processing condition.

$$\Phi = K'(\sigma_c - 0.86\sigma_m) \qquad (2)$$

The interfacial adhesion of system A, according to eq. (2), was evaluated to be much higher than that of system B, regardless of the matrix; and the acid−base interactions improved it even further, as shown in Figure 3. A gradual decrease in the adhesive strength for the matrices of higher acid contents indicates that sufficient level of the interfacial adhesion, from the viewpoint of stress transfer efficiency, could be attained at an acid
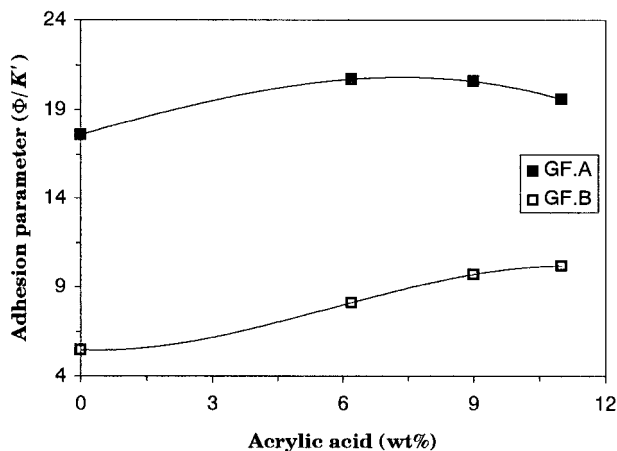

Figure 3 Interfacial adhesion of LDPE/GF (30%) as a function of the acrylic acid content in the matrix (I).
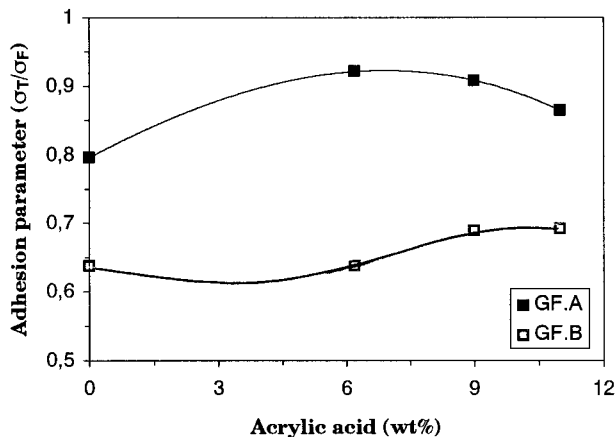
Figure 4 Interfacial adhesion of LDPE/GF (30%) as a function of the acrylic acid content in the matrix (II).

content well lower than 6.2%. It was also noted that the matrices with acid groups have improved interfacial adhesions with GF.B as well, suggesting that acrylic acid–silanol interactions were taken place at the lateral surfaces of the GF.

Flexural Strength

The flexural strength is a combination of compressive and tensile strength components.[17] Due to the partial compressive nature in flexural deformation, the flexural strength becomes less dependent upon the degree of interfacial adhesion than the tensile strength does in a composite. Consequently, the proportion of tensile strength to flexural strength, σ_T/σ_F, can serve as a parameter for the interfacial adhesive strength of GFTP.[18,19]

The variations of the interfacial adhesion expressed in this parameter as a function of acrylic acid content in the matrix are shown in Figure 4. The coincidence of these curves to those of Figure 3 reconfirms the observations made from the tensile strengths.

Viscosimetry

The relative viscosities of the composites are shown as a function of the matrix acid content in Figure 5. These may reveal more reliable information about the GF–matrix interfacial interactions than the ultimate strengths in the sense that a completely amorphous state of the polymers in the melt should allow a physically, as well as chemically, homogeneous matrix. In addition, a dynamically dispersed state of the GF under con-

stant shear force might have allowed every lot to have the same fashion of GF orientation.

The curve patterns, which are similar to those of Figures 3 and 4, suggest that the acid–base and the acid–silanol interactions take place at the interface to affect the interfacial adhesion. Interactions or chemical bonds at the phase boundary are known to reduce the interfacial voids and the chain mobility, hence inducing an increase of the viscosity of multiphase flow.[20] The viscosity increase observed in the presence of the acid–base interactions confirms the observations of Boluk and Schreiber for rutile–PE composites.[21] A more persuasive theoretical explanation, however, can be found from those of Favis and Willis, who observed immobile interface in the polymer blends of polyamide and acid-modified PE.[22] It is supposed that the acid–base interactions between the GF and the matrix form an immobile interface to resist against matrix melt flow around the GF, while a mobile interface of the noninteracting composites leave the melt flow freely producing interlayer slip at the interface. A slightly higher η_r of GF.A than GF.B, even in the nonpolar matrix, seems to be the result of the filler–filler interactions for GF.A as a characteristics of polar surface.

The existence of maximum in η_r can be understood considering the mathematical balance for two kinds of dominating interactions, the intermolecular acid–base interactions between the GF and the matrix polymers, and the acid–acid interactions (dimerization) among the matrix polymer chains[23] involved in the system. The acid–base interactions are to increase the η_r, forming an immobile interface; while the acid–acid interactions are to decrease it, making the matrix itself vis-
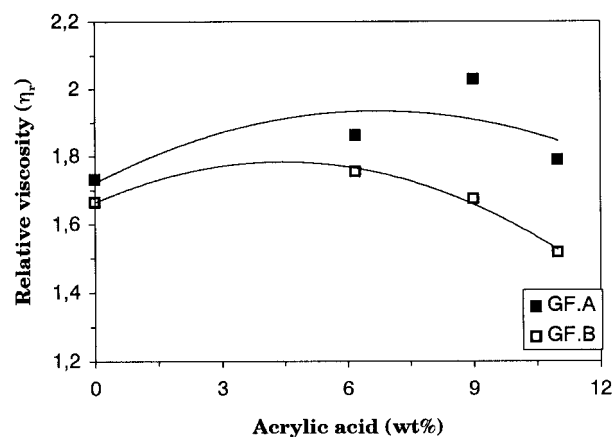

Figure 5 Relative viscosity of LDPE/GF (30%) as a function of the acrylic acid content in the matrix.
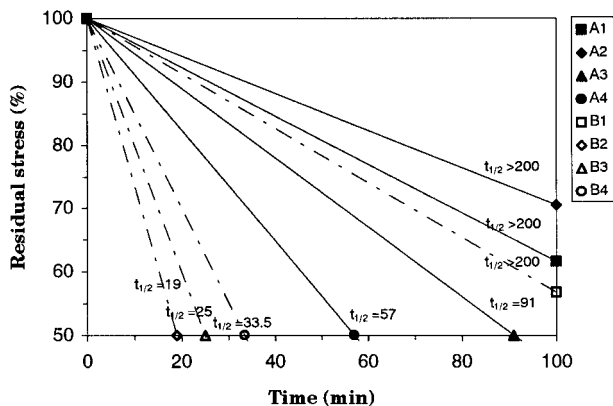
Figure 6 Simplified stress relaxation curves of LDPE/GF (30%). Designations are the same as in Figures 1 and 2.

cous. Denoting the concentrations of the acid groups in the matrix, and the base groups on the GF surface for a system as [A] and [B] respectively, [B] is constant as long as the fraction of the GF remains unchanged; while [A] varies according to the acrylic acid content in the matrix polymers. The positively contributing acid–base interactions term becomes roughly proportional to [A][B]; while the negatively contributing acid–acid interactions term becomes proportional to $[A]^2$, thus reaching a maximum at a certain acid concentration.

Stress Relaxation

Simplified stress relaxation curves expressed as straight lines passing the origin and the half-relaxation points are shown in Figure 6. Considering the small strain within the range of the matrix elastic deformation and the small stresses subsequently applied, the principal mechanisms involved in the relaxation process must be interfacial debonding and microfailure at a poorly bonded region around the GF–matrix interface.[24] The relaxation behavior under this condition, being free from noninterfacial failures, is expected to describe the interface region of the composite more accurately than the concerned parameters calculated from their ultimate strengths.

It was noticed that the stress relaxation behaviors of A2, A3, and A4 form a striking contrast to those of B2, B3, and B4. The obvious decrease of system A composites in half-relaxation time ($t_{1/2}$) as a function of matrix acid content, in spite of the interfacial acid–base crosslinks to retard the relaxation process, suggests that the relaxation

did not occur through the GF–matrix interfacial debonding. This can be true, supposing that the polymer matrices of higher acid contents would not form less interfacial crosslinks; and no doubt exists about this plain assumption, as the swelling tests will prove. Occurrence of GFTP failure at the matrix phase very near to the interface is a characteristic of strong interfaces achieved by either chemical[25] or physical[26] adhesion; and these are probable for A2, A3, and A4. For all these considerations, the question about the adverse effect of excessive acid–base interfacial crosslinks on the adhesive strength of the composite around the interface remains unexplained. We were interested in this fact and will examine it further in the following discussion section in conjunction with the physiochemical structure of the interface area.

For B2, B3, and B4, $t_{1/2}$ was extremely short, and only trivial differences were found among them, indicating the undergoing debonding at the interface in the absence of acid–base crosslinks. On the other hand, the stress relaxation curves of A1 and B1, which do not match to their interfacial states, could be attributed to the different relaxation nature of the homopolymer PE00 from the copolymers PE06, PE09, and PE11.

Swelling

The relative swelling of the system A composites continued to decrease as the matrix acid content increased, as shown in Figure 7. The existence of chemical crosslinks at the filler–matrix interface were known to decrease the solvent swelling of
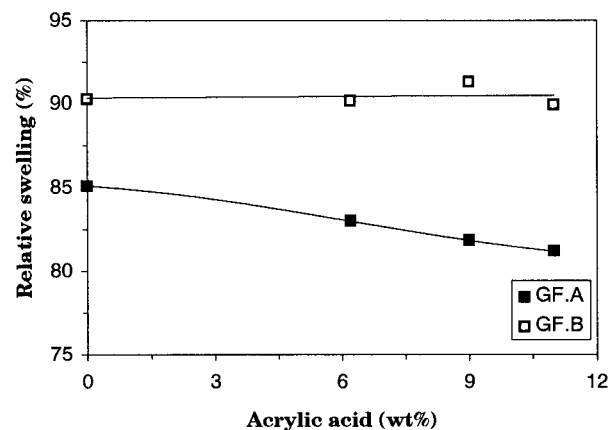

Figure 7 Relative degree of matrix swelling in LDPE/GF (30%) as a function of the acrylic acid content (n-hexane; 48 h).

composites,[27] increasing the number of active network chains of the Flory–Rehner equation,[28] as well as reducing the void volume at the interface. The acid–base crosslinks involved in system A composites are supposed to be rigid under the swelling condition due to the hydrocarbon nature of the solvent that will not compete with either of the functional groups in the existing acid–base crosslinks. The continual decrease of relative swelling in the matrices of higher acid contents suggests that the achieved degrees of interfacial acid–base crosslinking were directly proportional to the matrix acid content, as is the general case for the filler–matrix specific interactions.[29] The high relative swelling of system B composites regardless of their matrix could be attributed partially to the solvation effect of the matrix induced by the coupling agents segments at the interface, as mentioned in the tensile strength. The fact that the relative swellings of the composites were smaller than the unit (100%) suggests that the presence of the GF restricts, more or less, the mobility of the matrix polymer chains regardless of their interfacial natures.

Morphology

System A composites were found to consist of fewer empty holes along with shorter GF than system B composites in their fractured surfaces, as shown in Figure 8. This implies that the GF were broken near the fracture surface for system A composites, while the GF were easily pulled out to the bottom from either of the sides for system B composites when the specimens were subjected to the fracture. A strong interface was reported to promote crack propagation across the fibers, while a weak interface would promote failure by fiber debonding and pull out.[30] The morphologies of A2 and A4 made remarkable differences from that of A1; while those of B2, B4, and B1 did not make any difference among them. A significant decrease in the length of projected GF, as well as the number of the empty holes, was observed only in A2 and A4, indicating that the acidic polymer matrices could enhance the interfacial adhesion, provided that basic GF were matched. It could be revealed from a close examination of the SEM photographs that many of the projected GF possessed rough and coarse surfaces in A2 and A4, while those were smooth without exception in the others. In addition to that, the diameters of the projected GF also appeared larger in A2 and A4,

affording firm proof that the coat of the projected GF in A2 and A4 were the matrix components torn out from the matrix phases. The fracture surfaces of the polymer matrices, where the bumpy ones for A2 and A4 in contrast with the flat ones for the others were observed, also imply the different status in interfacial adhesion. Strong filler–matrix adhesion is known to result in a bumpy surface through matrix failure, while weak adhesion brings to a flat surface as a result of interfacial failure.[31] Putting these morphological observations together, the failures were believed to occurred at the matrix phases near to the GF–matrix interface in the presence of the acid–base interfacial crosslinks, leaving a layer of strongly attached matrix polymers on the GF surfaces.

DISCUSSION

It may be necessary first of all to outline the interface and the relevant phases to which our attention will be focused. Three easily distinguishable layers and two consequent interfaces are found in GFTP between the bulk glass phase and the matrix polymer phase, as they are GF phase, GF-coupling agents interface, coupling agents layer, coupling agents–matrix interface, and matrix phase. The GF surface and the coupling agents layer were known to form an interface physically and chemically stable under the favor of siloxane bonds, where the bond energy (Si—O; 88.2 kcal/mol) is even higher than C—C bond (83.1 kcal/mol)[32]; failure at this interface is unlike that for GFTP, but like that for hydrolysis.[33] For the reason of simplicity, we will regard the coupling agents layer, as well as the GF-coupling agents interface, as the outermost part of the GF. Thus, our attention about the GFTP interfacial adhesion will be centered around the coupling agents–matrix interface where we manipulated the adhesive strength by means of acid–base interactions. The acid–base crosslinks formed across the interface are believed to be diamine salt bonds with a minor amount of possible covalent amide bonds.[34]

It could also be helpful to make preliminary conclusions from the present study about the interfacial phenomena of the undergoing LDPE–GF system before entering into an overall discussion. Some interesting points, among the results based on the independent characterization techniques, that may merit a discussion, could be drawn as follows.
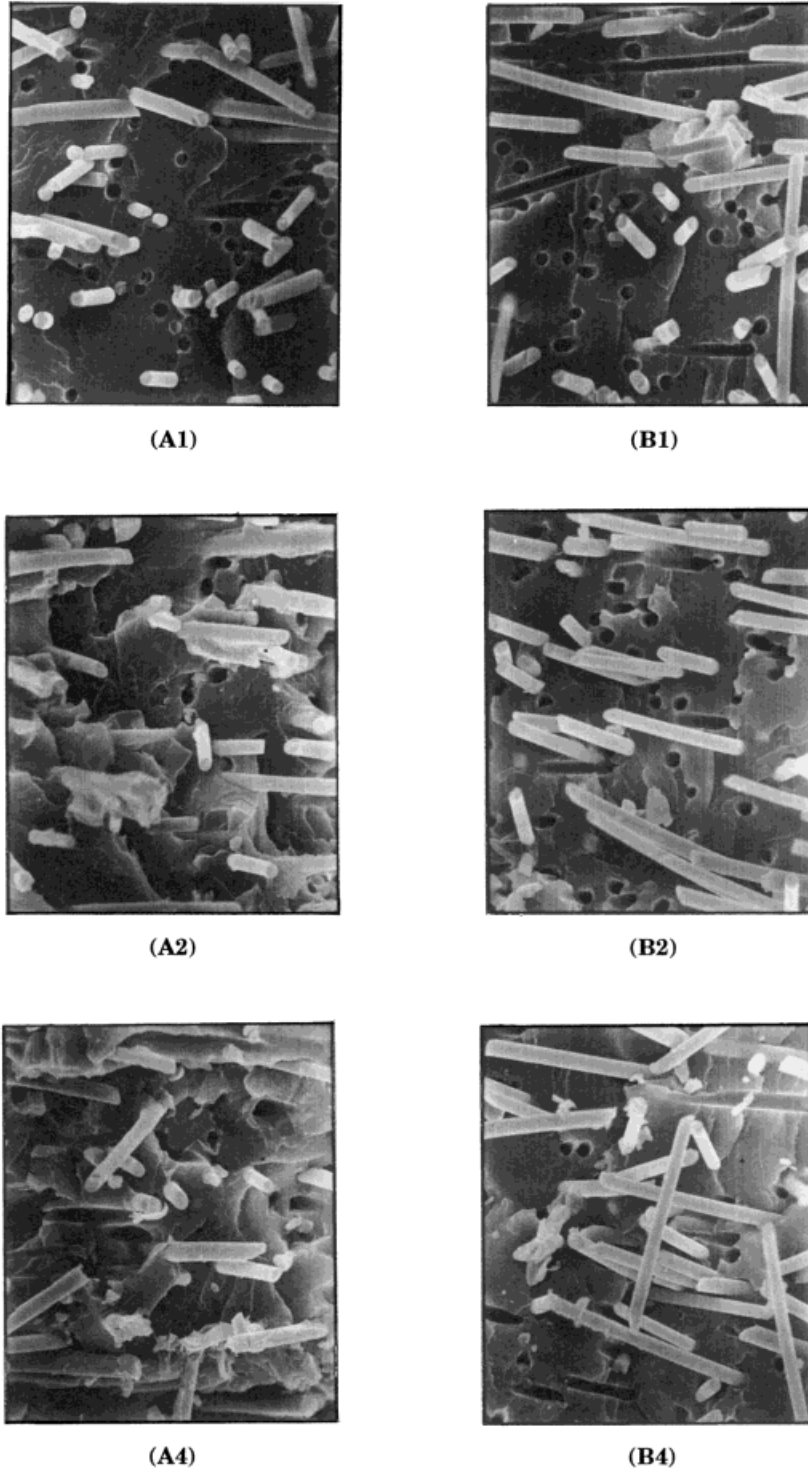
(A1)

(B1)

(A2)

(B2)

(A4)

(B4)

Figure 8 SEM photographs of the fractured surface of LDPE/GF (30%) at 300×
magnification. Designations are the same as in Figures 1 and 2.

1. The acid−base interactions across the GF−matrix interface enhance the interfacial adhesion as evidenced from viscosimetry.

2. The improved interfacial strength by the acid−base interactions was accompanied by gradual degradation as the concentration of the interacting site goes higher,
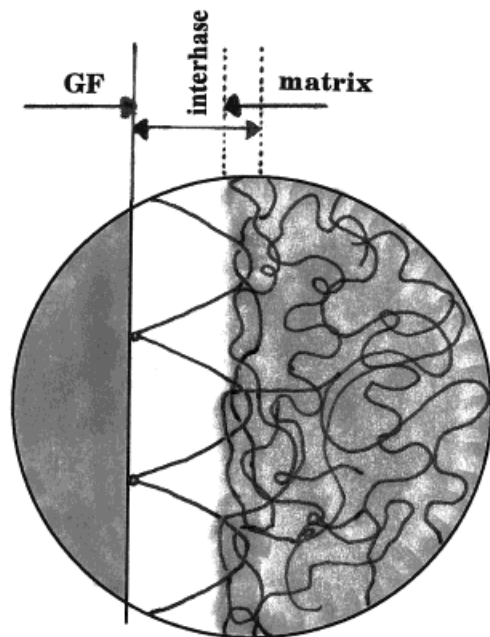
(a)
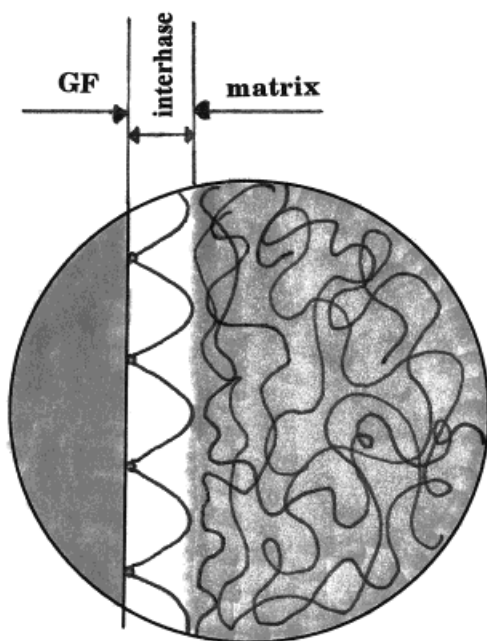
(b)

Figure 9 Schematic diagrams for (a) loose and (b) compact interphases.

judging from the ultimate strengths of the composite.

3. Stress relaxation behaviors of the composite also show the same trend as conclusion 2, resulting in easier relaxation for the interfaces of higher concentration of the interacting site.
4. However, the results of the swelling test assure that the degree of interfacial compactness is directly proportional to the concentration of the interacting site, showing a continual decrease of the relative matrix swelling as a function of the concentration.
5. The interfacial morphologies reveal that the failure occurred at the matrix phase near the interface in the presence of the interfacial acid–base interactions.

Conclusions 2 and 3, where more interfacial crosslinks did not produce better mechanical properties of the composite, can be partially understood considering conclusion 5, which may suggest no relationship between the interfacial strength and the composite ultimate strengths as long as the composites possess a strong interface enough to lead to a matrix failure. However, questions still remain to be answered for the degradation in reinforcement for the composites of high interfacial crosslinking density.

It seems reasonable to take the formation of an interphase of bound polymers[35] to the GF surface into account for the discussion in connection with the above questions. The interface and the interphase in GFTP are physically different in nature by definition. The former is the boundary at which the filler and the matrix meet; while the latter is a layer of matrix component around the interface, which has a different morphological structure from the bulk matrix.[36] The interactions between the filler surface and the matrix polymer chains may put the polymer molecules around the surface under restraint to form a polymer layer whose physical properties are distinguished from the molecules in the bulk matrix phase.[37] The interphase has lower density than the bulk matrix phase due to the unefficient packing around the filler surface caused by reduced chain mobility.[38] The interphase formations were known not to be unusual for GFTP possessing strong interfacial adhesion[39,40]; and the SEM photographs, as well as the nature of the involved interfaces, convince us that the acid–base interactive composites under this

study were the case. Therefore, with the newly made interphase–matrix interface being the most fragile part in the composite, failure is to occur along this interface. Considering the concentrations of the functional groups in the matrix polymer chains, the PE06 must have formed a loose and thick interphase in A1, while PE11 in A4 constructed a relatively compact and thin interphase. One of the probable interphase structures to satisfy all the requirements in our conclusions could be the models schematically represented in Figure 9.

It should be borne in mind before examining the models that the mechanical responses are the measures of physical entanglements as well as the chemical crosslinks, while the swelling is the exclusively the measure of the chemical crosslinks.[41] It is likely a loose interphase to allow more chain entanglements with the matrix polymer chains through interdiffusion, while these must be more difficult for a compact interphase due to its smaller loops with more restricted mobility as well as the structural closeness. In fact, a simple mathematical calculation permits PE06 to have a loop more than three times larger than PE11 in its area. The advantages in chain entanglements for the loose interphase could give an explanation for conclusions 2 and 3 because the more compact the interphase is, the weaker the interphase–matrix interface becomes. On the other hand, more crosslinks with less void volume in the compact interphase explain conclusion 4. The interphases formed by the interfacial acid–base interactions are supposed to have altered the occurring place of the failure from the GF–matrix interface to the matrix phase near to the interface, where the interphase is partially linked with the matrix phase through polymer chain entanglements.

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