Complex Adhesion Effects of Inorganic Nanofillers *vs* Microfillers in Polymer Composites

V. Kovačević, M. Leskovac, S. Lučić Blagojević, D. Vrsaljko*

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, 10000 Zagreb, Croatia
Fax: + 385 1 4597 260; E-mail: vkovac@fkit.hr

Summary: The adhesion parameters of fillers in composites, coefficient of wetting, interfacial free energy and work of adhesion, were calculated in order to evaluate the difference between the effects of selected microfillers *vs* nanofillers in polyacrylate (PA) and poly (vinyl acetate)(PVAc) matrix. The results showed that the improved fundamental adhesion, i.e. higher work of adhesion in nanocomposites resulted in the improved practical adhesion i.e. higher mechanical properties. The interfacial region was additionally modified by the controlled pre-treatment of calcium carbonate micro- and nanofillers by sodium stearate that lowered the interactions with PVAc matrix. The composite morphological and mechanical properties changed accordingly. The lowered coefficient of interactions explained the pronounced composite failure at the interphase by dewetting and finally lead to the composite weakening. The conclusion about the complex relationship between the composite properties and engineering the interphase was confirmed.

Keywords: adhesion; failure, micro and nanofillers; nanocomposites; surface parameters

Introduction

Adhesion science might be applied in investigation of composites, as the materials where the three-dimensional area between matrix and filler, i.e. interphase, has a crucial role in determination of composite properties.[1] The interest in adhesion science is a result of its applicability to solution the engineering problems such as bounded components in adhesive joint but also in composite materials.[2] Of the key importance in adhesion is generally wetting and setting.[3] We found that the adhesion parameters in particulate filled composites, such as coefficient of wetting (S), interfacial free energy ($\gamma_{\text{filler/matrix}}$) and work of adhesion ($W_{\text{filler/matrix}}$) (eqs.1-3), could explain the composite behaviour.[4]

 DOI: 10.1002/masy.200550302

$$S_{\text{filler/matrix}} = \gamma_{\text{filler}} - \gamma_{\text{matrix}} - \gamma_{\text{filler/matrix}} \quad (1)$$

$$\gamma_{\text{filler/matrix}} = \gamma_{\text{filler}} + \gamma_{\text{matrix}} - 2(\gamma_{\text{filler}}\,\gamma_{\text{matrix}})^{1/2} \quad (2)$$

$$W_{\text{filler/matrix}} = \gamma_{\text{filler}} + \gamma_{\text{matrix}} - \gamma_{\text{filler/matrix}} \quad (3)$$

In equation (2) the Good - Girifalco interaction parameter is taken as unity, when the individual polar and dispersion components of the composite components appear not to be available.[5]

An increasing understanding of adhesion science enables engineers to develop the ways in which interfacial region can be modified.[2] By modifying the interface and by controlling the adhesion in composites, adhesive joints and/or multi-layers the resulting properties could be changed accordingly.[3]

The characteristics of filler particles that have the significant influence on the composite properties are shape and size, specific surface area, packing and surface activity, distribution and interactions with matrix.[6] On the other hand the polymer matrix characteristics that are relevant are flexibility/rigidity of polymer chains, crystallisation ability and also surface activity.[7]

The difference between the effects of nanofillers in nanocomposites *vs.* microfillers in the conventional microcomposites exists in the dimension of dispersion of the two components, organic polymer matrix and inorganic filler.

In the nanocomposite a great amount of matrix is affected by ultra-fine phase of nanofillers, that create the special 'constrained' matrix structure[8] with the restricted mobility of polymer chains.[9]

The modification of matrix/filler adhesion, by lowering the filler size to nano-dimensions *vs.* micro-dimensions and/or by changing the filler surface characteristics by the controlled filler surface pre-treatment, has been the subject of investigations in this paper.

The aim is to investigate the change in adhesion at the interphase and the resulted morphological and mechanical properties in poly(vinyl acetate) (PVAc) and polyacrylate (PA) composites, as a consequence of the effects of nanofillers *vs.* microfillers and the selected pre-treatment of the nanofiller surface.

Experimental

The characteristics of matrices and fillers presented in Table 1 are determined previously.[4,10-12] The general aim was to compare the effects of kaolin filler with the great surface area due to layered structure [12] and thus well suited to create nanocomposites *vs.* diatom microfiller in the same PA matrix. The other example presented in Table 1 is nano-sized (<100nm) calcium carbonate ($CaCO_3$) filler *vs.* microsized $CaCO_3$ in PVAc matrix. The investigations are made on the thin films of composites (thickness ≈0.2 mm), prepared by pouring the composition on polyethylene foil and drying to the constant weight. The composite samples were prepared by simple mixing with necessary additives and different filler volume fraction (ϕ_f = 3,6,9,12 %). The details of the preparation of microcomposites and nanocomposites used in this paper are described elsewhere.[10,11]

Table 1. Structure and properties of matrices and nanofillers (N) *vs.* microfillers (M).

Sample	Characteristics			
Matrix	PA		PVAc	
[1] Structure	*		**	
[2] T_g(°C)	20.4		18.1	
[3] γ (mJm^{-2})	54.8		37	
[4] Filler	Kaolin (N)	Diatom (M)	$CaCO_3$ (N)	$CaCO_3$ (M)
[3] γ (mJm^{-2})	72.4	60.5	72.9	58
[5] x_{50} (nm)	600	1300	80	520
[6] S_{BET}(m^2g^{-1})	11.63	2.61	12	0.96

[1]* Polyacrylate (PA): Styrene-co-butylacrylate-ethylbenzene-acrylamide-formaldehide water dispersion (50 wt%) (BASF, Germany).
** Poly(vinyl acetate)(PVAc): water emulsion (55wt%) (Karbon, Croatia).
[2] DSC method [11,12].
[3] Surface energy measured by methods: contact angle, IGC, capillary [4,10].
[4] $CaCO_3$ (M): Calcite (Industrochem, Croatia);$CaCO_3$ (N): Precipitated $CaCO_3$ (Solvay, Germany); Diatom Opal C [11], (Solvay, Germany); Kaolin China clay [12] (ECC International, UK).
[5] Amount of 50% particles with sizes lower than the value given (suppliers data).
[6] Specific surface area [11, 12].

A JEOL JSM-330 scanning electron microscope was used for investigation the composite surface structure. In order to evaluate the initial morphology of nanocomposites *vs.*

microcomposites and the changes in morphology after failure, the composite films were observed before and after fracture was produced.

Tensile properties of the composite films were determined with a Zwick 1445 Universal testing Machine, with a crosshead speed of 50 mm/min and 50 mm gauge length.

The controlled surface pre-treatment of nanofiller calcium carbonate samples by adding the increasing amount of sodium stearate to change the filler surface activity, was carried out. This is described in a previous paper.[10]

Results and Discussion

The relevant factors for the composite study are the adhesion phenomena at the interphase (Table 2).

Table 2. Adhesion effects of nanofillers (N) *vs.* microfillers (M) at the interphase in composites.

Samples		Interphase in composites (mJm^{-2})		
Matrix	Filler	[1] S_{fm}	[2] γ_{fm}	[3] W_{fm}
PA	Kaolin (N)	16.4	1.2	139.0
	Diatom (M)	-5.3	0.2	118.5
PVAc	$CaCO_3$ (N)	29.9	6.06	104.0
	$CaCO_3$ (M)	18.6	2.36	92.4

[1] Equation (1); [2] Equation (2); [3] Equation (3).

Results of studies on the effective adhesion for a given system indicate some conditions as optimal, i.e. work of adhesion as maximal (optimal), interfacial free energy as minimal (tends to null) and coefficient of wetting as a positive value.[3]

It should be stressed that the improved fundamental adhesion might result in the improved practical adhesion.[3] For example, the work of adhesion is a term, which has a strong, but indirect influence on practical adhesion. We found that although the work of adhesion levels are low (of order of mJm^{-2}) compared with fracture energies (often several kJm^{-2}), that the small absolute increases in the work of adhesion lead to large absolute increases in fracture energy.[10] The increase in interfacial strength between filler and matrix and thus in

work of adhesion (W_{fm}) enables more bulk energy dissipation to occur, for example through plastic energy losses.[13] The results in Table 2 show that a higher value of work of adhesion would be achieved with the nanofillers. Of the great importance for the improvement of the composite properties is a good filler dispersion in the polymer matrix, which depend on the process of composite preparation, wetting ability and strength of interactions between filler and matrix.

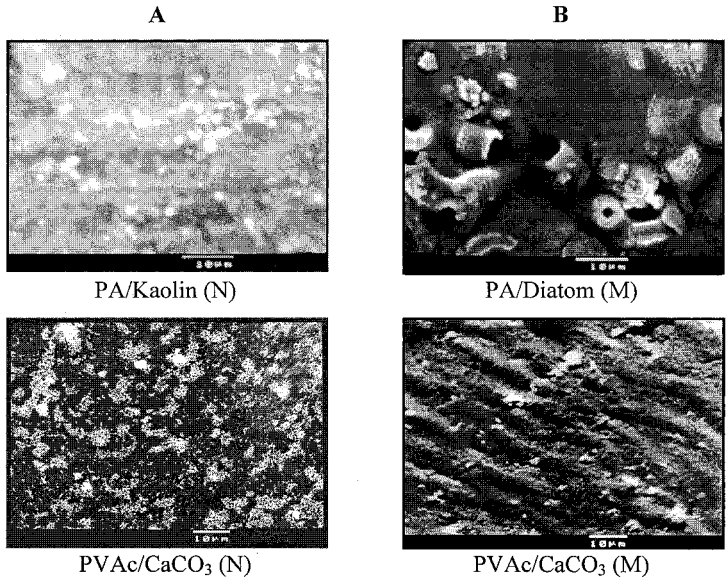

Fig. 1. Morphology of composites filled with nanofillers (A) and microfillers (B) ($\phi_f = 0.12$).

The morphologies of nanocomposites *vs.* microcomposites are illustrated by the 'net-like' structure of nanofiller particles (Figure 1A), in comparison to the micro-particles and their agglomerates dispersed as isolated 'islands' in the matrix (Figure 1B). The specific structure of nanocomposites with significant volume of organic phase affected by nanofiller, is described in literature as similarity with ionomers structure, where the strong interactions determined the phase heterogeneity and specific properties of the system.[9]

The polymer matrix introduction into the nanofiller three-dimensional 'net-like' structure results in a matrix 'constrained' structure.[8,14] The kaolin filler, which is supposed as a

nanofiller due to its layered structure and high specific surface area (Table 1),[12] showed the same "net-like" effect on the composite morphology as we noticed with $CaCO_3$ nano-sized filler particles (Figure 1A). The similar effects on composite morphology were illustrated in literature for poly (methyl methacrylate) composites filled with the same volume fraction of aluminium hydroxide of coarse and/or fine filler particles.[7]

The strong interactions are expected to change the locus of failure. In adhesion study, the locus of failure, or separation between phases is also very important, i.e. cohesive in matrix *vs.* adhesive failure at the interphase.[12]

In the case of evenly distributed filler particles the high specific surface area of nanofillers could assure the increased amount of the interphase between matrix and filler and thus the significant changes in the nanocomposite properties. It is necessary to stress the importance of the successful dispersion of nanofillers in the matrix.

The interphase has a crucial role as a 'heart' in composites[15] due to its importance in transferring the stresses.

Failure in the material is taking place at the weak points in structure, where the product EG, in equation (4), i.e. composite modulus times fracture energy in the known Griffith-Irwing theory of fracture, has the lowest value.[6]

$$\sigma_F = k\,(EG / l)^{1/2} \qquad (4)$$

where σ_F is a fracture stress, k is a constant and l is the length of critical crack.

Mechanisms of failure in composites could take place in polymer matrix by shear yielding and/or crazing, inside the aggregates of filler particles and/or at the interface that depending on the 'weak' points where the product EG has the lowest value. In Figure 2B it is visible that in microcomposites the failure is taking place at the interphase by dewetting. On the other hand in the case of small radius of particles (R) of nanofillers, the stress at dewetting, σ^D, is enough high to transfer the failure from the interphase to the matrix (Figure 2A), because of the high work of adhesion between filler and matrix, W_{fm} in equation (5):

$$\sigma^D = - C_1\,\sigma^T + (C_2\,W_{fm} / R)^{1/2} \qquad (5)$$

σ^T is the thermal stress that, in our isothermally prepared composites, should be close to zero. *C1* and *C2* are constants.

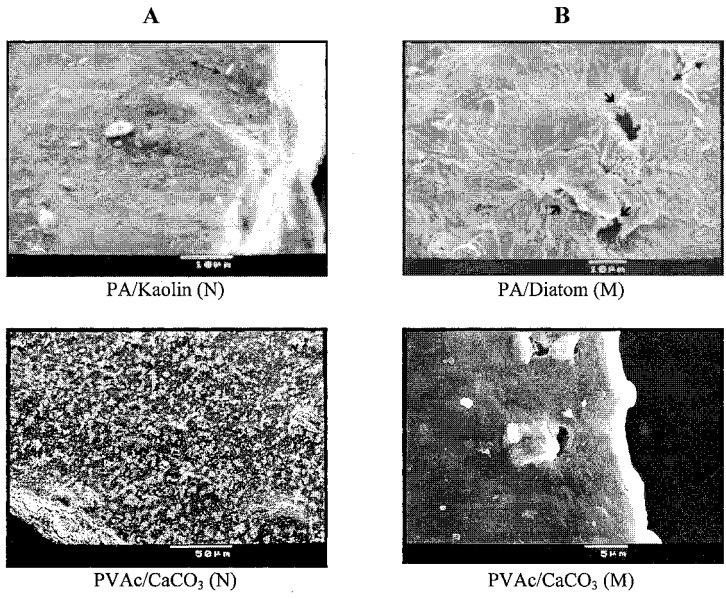

Fig. 2. Failure in nanocomposites (A) and microcomposites (B) ($\phi_f = 0.12$).

The examples from literature illustrate cohesive failure in matrix due to strong interactions and dewetting at the interphase due to low interactions.[16] The conclusion could be drawn that the stress need to initiate the failure in composite increased with decreasing radius of filler particles. In that case the interphase is not any more the weak point in a composite.

We found the improved fundamental adhesion resulted in the improved practical adhesion.[12] The higher work of adhesion and improved wetting in nanocomposites *vs.* microcomposites in Table 2 with no signs of dewetting (Figure 2), should thus result in the improved mechanical properties i.e. composite reinforcing (Figure 3).

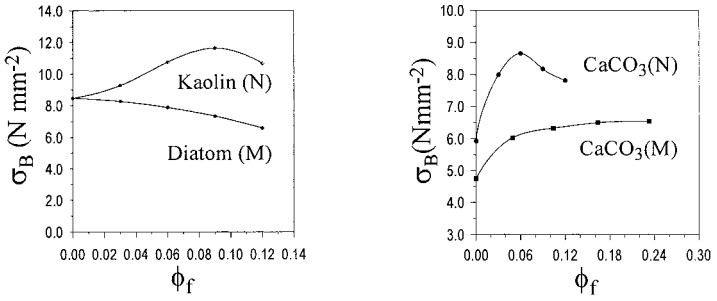

Fig. 3. Effect of fillers on the composite strength at break (σ_B) with increased filler vol. fraction (ϕ_f); N= nanoparticles, M= microparticles.

The results in Table 2 showed that the adhesion parameters at the interphase changed as a consequence of the effects of nanofillers *vs.* microfillers.

After the $CaCO_3$ nanofiller pre-treatment, the results in Table 3, i.e. the negative wettability, the increased interfacial free energy along with the lowering in the work of adhesion illustrate that a relationship exists between the thermodynamic parameters, which characterize the polymer-filler interactions at the interphase.

Table 3. Interfacial adhesion parameters before and after the $CaCO_3$ filler pre-treatment with sodium stearate.

Composite	[1] Interphase (mJm^{-2})		
	S_{fm}	γ_{fm}	W_{fm}
PVAc/$CaCO_3$ (M)	18.6	2.36	92.4
[2] PVAc/$CaCO_3$ (MS)	17.2	2.00	91.2
[3] PVAc/$CaCO_3$ (N)	29.86	6.06	103.9
PVAc/$CaCO_3$ (NS_1)	22.09	3.29	96.1
PVAc/$CaCO_3$ (NS_2)	-9.64	0.63	64.4
PVAc/$CaCO_3$ (NS_3)	-18.28	2.26	55.7
PVAc/$CaCO_3$ (NS_4)	-25.30	4.33	48.7

[1] Table 2; [2] Commercial treatment; [3] Filler surface coverage [10] : N (0%); NS_1 (16%); NS_2(47%); NS_3(78%); NS_4(< 100%) calculated using 0.21 nm^2 as the 'cross-sectional area' for stearate.[17]

The changes of the adhesion parameters in composites by the interface engineering as a consequence of the controlled filler surface pre-treatment (Table 3) are expected to reflect in the changes of the composite properties (Figure 4).

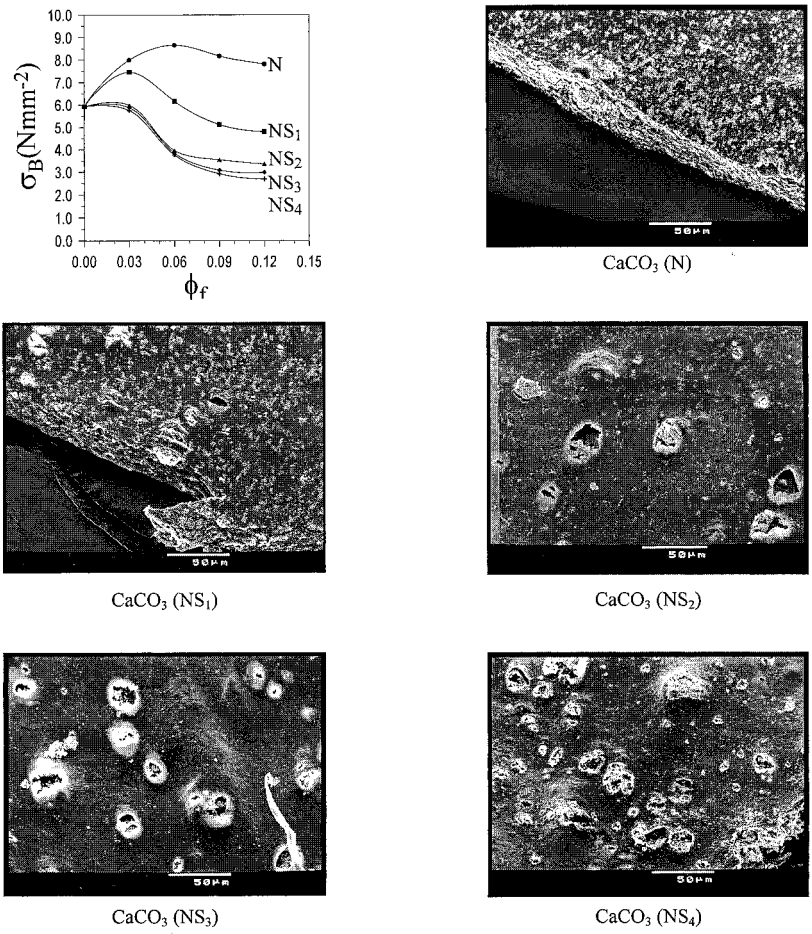

Fig. 4. Effect of the $CaCO_3$ nanofiller (N) increased pre-treatment (NS_1-NS_4) on the PVAc composite strength at break and the resulted morphology at failure.

The reinforcing effect in the composite PVAc/$CaCO_3$ (N) with the excellently adhering nanoparticles is followed by the high work of adhesion (Table 3) and thus no signs of dewetting at the interphase, while the failure is directed into the polymer where dissipation

of fracture energy (high local G in equation 4) leads to a higher fracture stress. On the other hand the opposite effects are found after the filler increased pre-treatment (NS_1 - NS_4) (Table 3 and Figure 4).

One can conclude that the relationship between the properties of composites and engineering the interfacial region by pre-treatment is very complex in a way that often the modification could improve one property but will have an adverse effect on another.

The quantitative calculations of the interactions by fitting the mechanical properties of filled composites to the theoretical and/or empirical equations might help in the prediction of the composite mechanical properties. The relationship between the ultimate strength and relative amount of particulate filler described by the exponential model proposed by Pukanszky[18] gives the interaction coefficient B:

$$B = (1 + LA_f \rho_f) \ln \sigma_{Ti} / \sigma_{To} \qquad (6)$$

where A_f and ρ_f = specific surface area and density of filler; L and σ_{Ti} = thickness and strength of the interphase; σ_{To} = true tensile strength of the polymer matrix.

Table 4. Comparison of the interactions between matrix and fillers.

Samples	[1)] B
PA/Diatom (M)	3.8
PA/Kaolin (N)	8.6
PVAc/$CaCO_3$ (M)	6.4
PVAc/$CaCO_3$ (MS)	5.3
PVAc/$CaCO_3$ (N)	9.9
PVAc/$CaCO_3$ (NS_1)	5.9
PVAc/$CaCO_3$ (NS_2)	2.3
PVAc/$CaCO_3$ (NS_3)	1.4
PVAc/$CaCO_3$ (NS_4)	0.9

[1)] Equation (6).

The quantification of interactions between filler and matrix at the interphase, helps in the evaluation and comparison of the composite mechanical and other properties (Table 4). It

is important to stress that the interactions coefficients should be used only for comparison purposes. Still we showed that the parameters from equations used for fitting the experimental data to various models are strong indicators of polymer-filler adhesion.[12] For example, the higher interaction coefficient in Table 4 means the higher work of adhesion at the interphase of composite (Table 3). On the other hand, the increased filler surface pre-treatment (NS_1 – NS_4) lowered the interactions and thus the coefficient *B* resulting in the composite weakening (Figure 4).

Conclusion

The possibilities of 'engineering the interphase' in composite by lowering the filler size to nanodimensions and increasing the active surface area or changing the adhesion parameters by surface pre-treatment, may alter the composite properties in the interfacial region and thus in the composite material as a whole.

Acknowledgements

We are grateful for support from the Ministry of Science and Technology of Croatia and Universities of Bath and Loughborough (UK) for facilitating the international collaboration.

Thanks are due to Dr. Ch. Nover (Solvay Alkali GmbH, Germany), for supporting us with samples and information, and Dr. D.E. Packham for advices given during the experiments.

[1] P.E. Packham, in: *Handbook of Adhesion*, D.E. Packham (Ed.), Longman Scientific & Technical, Harlow, Essex, **1992**, pp.78-79.
[2] D.E. Packham, *National Meeting of the American Institute of Chemical Engineers*, Proceedings of the Conference, Seattle, USA, August **1993**, 24a.
[3] K.L. Mittal, *Pure and Appl. Chem.* **1980**, 52, 1295-1305.
[4] V. Kovačević, M. Leskovac, S. Lučić Blagojević, *J. Adhesion Sci. Technol.,* **2002**, 16(14), 1915-1929.
[5] A.J. Kinloch, *Adhesion and Adhesives, Science and Technology*, Chapman & Hall, London, **1995**.
[6] D.E. Packham, *J. Adhesion*, **1995**, 54, 133-143.
[7] R. Rothon in: *Particulate-Filled Polymer Composites*, Longman, Harlow, UK, 1995, pp.31-39.
[8] H.L. Frisch, J.E. Mark, *Chem.Mater.*, **1996**, 8, 1735-1738.
[9] G. Tsagaropoulos, A. Eisenberg, *Macromolecules*, **1995**, 28, 396-398.
[10] S.Lučić, V. Kovačević, D.E. Packham, A. Bogner, A. Geržina in: *Polymer Surface Modification: Relevance to Adhesion*, K.L. Mittal (Ed.), VSP **2000**, Vol. 2, p.505-525.
[11] M. Leskovac, V. Kovačević, S. Lučić, H.R. Perrott, I. Šmit, *Mat.Res.Innov.*, **2002**, 6, 206-213.
[12] V. Kovačević, S.Lučić Blagojević, M. Leskovac, *J. Adhesion Sci. Technol.,* **2002**, 16(10), 1343 – 1365.
[13] D.E. Packham. in: *Mittal Festschrift on Adhesion Science and Technology*, W.J. van Ooij and H.R. Anderson, Jr.(Eds), VSP, Utrecht, 1998, p.81.
[14] T. Seagusa, *Macromol. Symp.* **1995**, 98, 719-729.
[15] M.R. Piggot, A. Sandi, P.S. Chua, D. Anderson, in: *Composite Interfaces*, H. Ishida & J.L. Koenig, North Holland, New York, **1996**.
[16] M.E. Dekkers, D. Heikens, *J. Materials. Sci.,* **1984**, 19, 3271-3275.
[17] E. Papirer, J. Schultz and C. Turchi, *Eur. Polym. J.* **1984**, 20, 1155-1158.
[18] B. Pukanszky, *Composites*, **1990**, 21, 255-262.