

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Optimized Preparation Techniques for PVC-Green Coconut Fiber Composites

Robson L. Ferreira^a; Cristina R. G. Furtado^a; Leila L. Y. Visconte^b; Jean L. Leblanc^c

^a Instituto de Química/Universidade do Estado do Rio de Janeiro, Rio de Janeiro, RJ, Brazil ^b Instituto de Macromoléculas Professora Eloisa Mano/Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil ^c Université Pierre & Marie Curie (Paris 6), Polymer Rheology and Processing, Vitry-sur-Seine, France

To cite this Article Ferreira, Robson L. , Furtado, Cristina R. G. , Visconte, Leila L. Y. and Leblanc, Jean L.(2006) 'Optimized Preparation Techniques for PVC-Green Coconut Fiber Composites', International Journal of Polymeric Materials, 55: 12, 1055 – 1064

To link to this Article: DOI: 10.1080/00986440600642991

URL: <http://dx.doi.org/10.1080/00986440600642991>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Optimized Preparation Techniques for PVC–Green Coconut Fiber Composites

Robson L. Ferreira
Cristina R. G. Furtado

Instituto de Química/Universidade do Estado do Rio de Janeiro,
Rio de Janeiro, RJ, Brazil

Leila L. Y. Visconte

Instituto de Macromoléculas Professora Eloisa Mano/Universidade
Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

Jean L. Leblanc

Université Pierre & Marie Curie (Paris 6), Polymer Rheology and
Processing, Vitry-sur-Seine, France

Composites of poly(vinyl chloride) (PVC) and green coconut fibers were prepared by two techniques: dry blending + extrusion and dry blending + mixing. The degree of homogeneity of the mixes was evaluated through dynamic modulus measurements in both the molten and the solid states. Dry blending + mixing was found to be most appropriate in the preparation of laboratory scale composites. In addition, results suggest that no physico-chemical interactions occur between the matrix and the fibers.

Keywords: dynamic mechanical analysis, green coconut fiber, PVC, rubber processing analyzer

Received 4 February 2006; in final form 13 February 2006.

The work was performed within the frame of a project sponsored by CAPES-COFE-CUB. The authors express their thanks to Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA) for providing the coconut fibers, and to PIBIC/CNPq for financial support.

Address correspondence to Leila L. Y. Visconte, Instituto de Macromoléculas Professora Eloisa Mano/Universidade Federal do Rio de Janeiro, CP. 68525, Rio de Janeiro, RJ, Brazil. E-mail: lyv@ima.ufrj.br

INTRODUCTION

Fibers possess high Young modulus as compared to thermoplastics and show good reinforcement capability when properly combined to polymer matrixes. Improvement in the Young modulus of the composites depends on a number of factors such as fibers concentration, orientation, size and distribution, and their interaction and adhesion to the polymer matrix [1].

The use of coconut, sugar cane bagasse, sisal, rami, and curaua natural fibers as alternative reinforcement in polymeric materials has been the focus of increasing interest of researchers and governmental organisms, especially in those countries where these fibers are abundant. Natural fibers have low density, when compared to synthetic ones, thus contributing to the preparation of lighter composites and, in addition, present low abrasiveness, which is advantageous when it comes to processing, as this minimizes equipments wearing [2–3].

The coconut fiber is a lignocellulosic material found as a 3 to 4 cm thick layer between the thin green outer shell and the central hard nut of the green coconut. The fiber from the mature fruit has already found application in agriculture and in the automotive industry [4]. The green coconut fiber, on the other hand, despite its potential, is still not widely used.

Green coconut water is a traditional drink in the coastal regions of Brazil that generates huge quantities of empty coconuts waste, that need up to 10 years to disappear from dumping fields through natural degradation [5]. After drying, the intermediate core of the coconut gives rise to brown fibers of up to 10 cm long.

It came to attention recently that interesting composites with thermoplastic polymers could be prepared with dried green coconut fibers (GCF), provided the right preparation technique was developed to yield homogeneous material with reproducible rheological and mechanical properties.

One of the most serious drawbacks related to the achievement of good performance of natural fiber reinforced composites is due to polarity differences of the fiber and the polymeric matrix, which result in weak interactions, low compatibility, and make dispersion of hydrophilic cellulosic fibers into hydrophobic polymeric matrix difficult [6]. To overcome these differences, several approaches have been envisaged [7–14]. The surface pre-treatment or the incorporation of coupling agents during processing have been tried and proved to be capable to promote better dispersion, attributed to a reduction in the fiber–fiber interaction.

The aims of this report are to investigate the most appropriate preparation procedures for PCV–GCF composites, named VCF, at the laboratory level. The adequacy of the preparation techniques will be documented through dynamic modulus measurements in both the molten and the solid states.

EXPERIMENTAL

Test Materials

Green coconut fibers (GCF) supplied by EMBRAPA (Empresa Brasileira de Pesquisa Agropecuária), Rio de Janeiro, Brazil, result from a complex process, which involves drying, grinding, and sorting of fibers from green coconut shells. Samples used in this study consist of a mixture of a fine brown powder with dispersed yellow-orange single fibers of up to 3–4 mm length; specific gravity is 1.20 g/cm³. The pH measurements were estimated from a suspension in water (1 g fiber in 10 cm³ water), according to ASTM D 1512; an average value of 4.81 was obtained. A standard suspension grade poly(vinyl chloride) (PVC) in powder form, Norvic SP 1100HP, was supplied by Triken-Organização Odebrecht; specific gravity is 1.39 g/cm³.

One PVC reference formulation and two PVC–GCF composites were prepared by first dry blending the ingredients, which were then melt mixed in a Haake Rheocord 900, fixed either with a 3 cm diameter screw extruder or a 85 cm³ mixing chamber with roller rotors. Immediately after melt mixing, around 2 mm thick plaques were prepared by compression molding at 160°C. Formulations and preparation conditions are given in Table 1. Note that the plasticizer (DOP) and the stabilizer (barium–zinc salt; UBZ-790[®]) were always 10 and 4 wt%, respectively, compared to the polymer.

Modulus in Molten State; Strain Sweep Experiments

Modulus at 160°C was measured on all samples with a Rubber Process Analyzer, RPA 2000[®] (Alpha Technologies), using strain sweep protocols Table 2. With respect to its measuring principle, the RPA cavity must be loaded with a slight volume excess of test material. With respect to the cavity volume (3280 mm³), a volume excess of 5% was considered, and optimized sample loadings were, respectively, 4.33, 4.27, and 4.23 g for VCF00, VCF80, and VCF70 samples. Samples for RPA testing were consequently prepared by die cutting disks of appropriate diameter out of molded plaques and, if necessary, adjusting their weight in order to maintain it within the optimized

TABLE 1 PVC-GCF Composites: Formulation and Preparation Procedures

Sample:	VCF00ex	VCF80ex	VCF70ex	VC00mi	VCF80mi	VCF70mi
PVC (%w)	87.72	71.94	63.75	87.72	71.94	63.75
GCF (%w)	—	17.99	27.32	—	17.99	27.32
DOP ^a (%w)	8.77	7.19	6.38	8.77	7.19	6.38
UBZ ^b (%w)	3.51	2.88	2.55	3.51	2.88	2.55
Φ_{fiber}	—	0.162	0.225	—	0.162	0.225
Preparation Conditions	dry blend + laboratory extruder (ex)					
	Temperature settings: Starting temperature: 130°C					
	(hopper) 130, 140, 150, (die) 160°C					
	Screw rotation: 60 RPM					
	Slit die: 30 × 2 mm					
	dry blend + laboratory mixer (mi)					
	Starting temperature: 130°C					
	Fill factor: 0.70					
	Roller rotors speed: 50 RPM					
	Final torque: 17–19 Nm.min					
	Dump temperature: 158–160°C					

^adi-octyl phthalate, spec. grav.: 0.98 g/cm³.^bUBZ-790; stabilizer; spec. grav.: 0.96 g/cm³.

TABLE 2 RPA Strain Sweep Test Protocols

Test Protocol SSweep_1Hz_A		Test Protocol SSweep_1Hz_B	
RPA test conditions Temperature (°C): 160 Frequency: 1 Hz		RPA test conditions Temperature (°C): 160 Frequency: 1 Hz	
Sample conditioning: Preheating: 3 min, at rest Fixing: 30 s; 1 Hz; 0.20° Preheating: 2 min, at rest		Sample conditioning: Preheating: 3 min, at rest Fixing: 30 s; 1 Hz; 0.20° Preheating: 2 min, at rest	
Strain sweep (run 1) Strain (°)	Dwell time	Strain sweep (run 2) Strain (°)	Dwell time
0.5		0.6	
1.0		1.5	
2.5		3.5	
5.0		6.7	
8.5	2 min, at rest	10.0	2 min, at rest
12.0		14.5	
17.0		20.0	
22.5		25.0	
27.5		30.0	
31.5		33.0	
			Strain sweep (run 2) Strain (°)
			0.5
			1.0
			2.5
			5.0
			8.5
			12.0
			17.0
			22.5
			27.5
			31.5

loading ± 0.2 g. To ensure an easy filling of the RPA cavity, samples were disposed for 2–3 min on the lower die at the test temperature (160°C) before closing the chamber.

Strain sweep tests were performed with the RPA, according to protocols that consist in two subsequent runs separated by a resting period of 2 min. At least two samples of the same material were tested, using protocols such that, through inversion of the strain sequences (i.e., run 1 and run 2), sample fatigue effects would be detected, if any. Each experiment lasted some 23 min. The strain range was documented by 20 experimental points and any differences between runs 1 and 2 would indicate that the tested material was sensitive to strain amplitude. This experimental procedure was designed in order to obtain the maximum number of data in the shortest test time (less than one hour), while documenting test repeatability and material homogeneity.

Modulus in the Solid State; Temperature Sweep Experiments

A Perkin-Elmer Dynamic Mechanical Analyzer DMA7e was used to assess the elastic modulus and the $\tan \delta$, between 20 and 150°C, using a three points bending test mode. Frequency was 1 Hz, with 10 μm maximum strain amplitude on $19 \times 12.5 \times$ plate thickness samples. Temperature scan rate was 5°/min. Static stress was 1 MPa, whereas dynamic stress was 0.8 MPa. Samples were prepared using a small circular saw and edges were polished with a very fine grain sand paper. Two specimens were tested for each composition.

RESULTS

Dynamic Modulus at 160°C

Dynamic modulus results from strain sweep experiments at 160°C, on two samples of the same test material do not superimpose well when dry blending + extrusion is used, in contrast with dry blending + mixing whose results show an excellent homogeneity. To further document the poor sample homogeneity when simple extrusion is used, additional tests were made with more samples. A large scatter was observed that clearly demonstrates that dry blending + extrusion does not lead to good sample homogeneity. When using internal mixing, samples are homogeneous as reflected by the excellent superposition of data when testing two samples.

The lack of sample homogeneity when using extrusion is also observed with the unfilled PVC composition. This of course suggests

that it is rather a defect in PVC plasticization than in fibers dispersion that is responsible for the observed experimental scatter.

In the case of the unfilled PVC composition, G^* vs. γ curves yield the most familiar picture of a plateau region at low strain, which correspond to the linear viscoelastic region, then a typical strain dependence. Here, G^* is the complex modulus and γ is the strain. There is a significant difference between data gathered through runs 1 and 2, which suggests that the material is somewhat sensitive to strain history. Note however the large experimental scatter given by the samples prepared by extrusion.

With reference to the mathematical form of the so-called Cross equation [15] for the shear viscosity function, such a behavior can be adequately modeled as shown in Eq. 1:

$$G^*(\gamma) = G_0^* \times \left[\frac{1}{1 + (A\gamma)^B} \right] \quad (1)$$

where G_0^* is the modulus in the linear region (in fact a modulus at “zero” strain), A the reverse of a critical strain marking the limit between the linear and nonlinear region, and B a parameter describing the strain sensitivity of the material.

Table 3 gives the parameters of Eq. 1 for all the materials tested; note that the reverse of parameter A is given. Three blocks of results are easily seen, with respect to fiber content. G_0^* increases with fiber fraction, with marginal effects of the preparation technique. The linear region reduces strongly with increasing fiber level as reflected by parameter $1/A$.

TABLE 3 Complex Dynamic Modulus at 160°C of PVC–GCF Composites: Fitting Parameters of Eq. 1

Sample	Run	G_0^*	$1/A$ (%)	B	r^2
VCF00ex	run1	314.17	139.7	1.44	0.9817
VCF00ex	run2	278.65	133.2	1.33	0.9958
VCF00mi	run1	302.08	140.6	1.48	0.9975
VCF00mi	run2	287.53	136.1	1.44	0.9978
VCF80ex	run1	571.85	38.0	0.88	0.9529
VCF80ex	run2	473.79	58.8	1.07	0.9977
VCF80mi	run1	534.97	59.5	1.10	0.9976
VCF80mi	run2	449.24	65.8	1.15	0.9997
VCF70ex	run1	1161.22	22.0	0.92	0.9869
VCF70ex	run2	704.70	35.9	0.98	0.9969
VCF70mi	run1	798.69	34.7	0.99	0.9991
VCF70mi	run2	619.59	39.9	1.02	0.9994

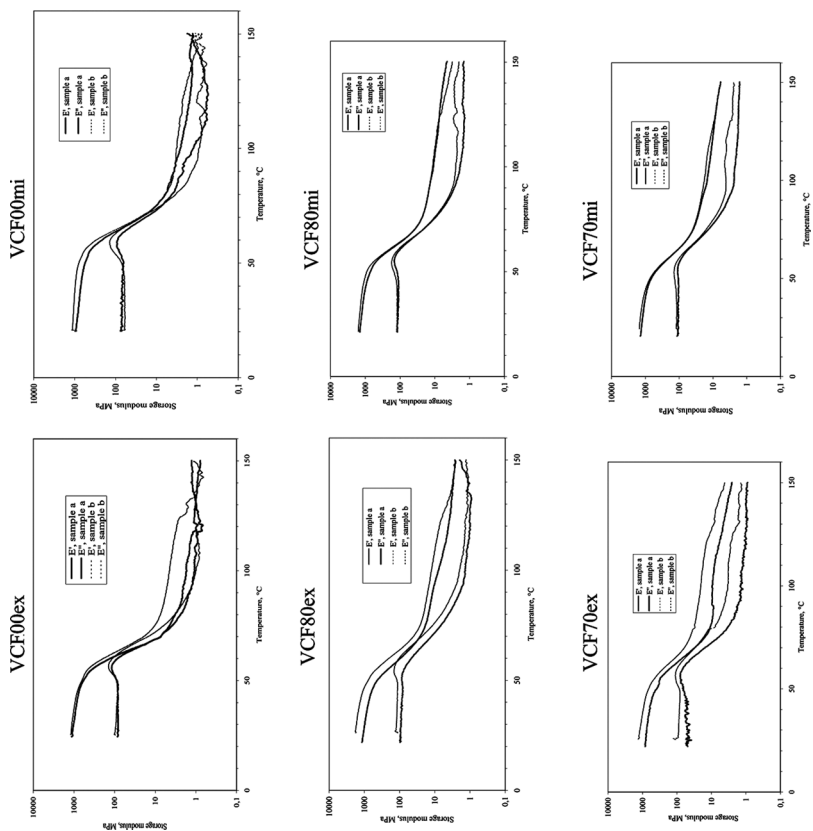


FIGURE 1 DMA curves for PVC-GCF composites.

TABLE 4 DMA Results for PVC-GCF Composites

Sample	Φ_{fiber}	Max $\tan \delta$		T_g , °C		G' at T_g , MPa	
VCF00ex,Test A	0	0.87	0.95 ± 0.11	66.5	68.2 ± 2.3	41	24 ± 24
VCF00ex,Test B	0	1.02		69.8		7	
VCF80ex,Test A	0.162	0.54	0.59 ± 0.06	64.0	64.5 ± 0.8	52	67 ± 20
VCF80ex,Test B	0.162	0.63		65.0		81	
VCF70ex,Test A	0.225	0.53	0.52 ± 0.01	66.6	67.1 ± 0.8	53	66 ± 19
VCF70ex,Test B	0.225	0.52		67.6		80	
VCF00mi,Test A	0	0.78	0.85 ± 0.09	71.6	70.4 ± 1.7	17	24 ± 10
VCF00mi,Test B	0	0.91		69.2		31	
VCF80mi,Test A	0.162	0.63	0.64 ± 0.01	65.2	65.4 ± 0.2	78	78 ± 0
VCF80mi,Test B	0.162	0.64		65.6		78	
VCF70mi,Test A	0.225	0.50	0.52 ± 0.03	65.6	65.3 ± 0.4	98	102 ± 6
VCF70mi,Test B	0.225	0.54		65.0		105	

Dynamic Modulus in Solid State

DMA curves (Figure 1), either G' , G'' , or $\tan \delta$, show the expected behavior in the region around the glass transition temperature of PVC. Again, an excellent superposition of traces is observed for composites prepared by dry blending + mixing, while a large scatter is seen with samples prepared by extrusion. DMA results are summarized in Table 4 in terms of maximum $\tan \delta$, glass transition temperature T_g (in fact the temperature at which the maximum $\tan \delta$ is observed) and the corresponding elastic modulus (at T_g). As can be seen, $\tan \delta$ at T_g tend to decrease with higher fiber content, whereas the elastic modulus increases. Mean values and deviation demonstrate again that materials prepared by extrusion are not homogeneous. Differences in T_g due to fiber content can be considered not significant, as would be expected when no physico-chemical interaction occurs between the matrix and the fibers.

CONCLUSIONS

Both series of measurements, either in the molten (i.e., RPA) or in the solid state (i.e., DMA) are consistent and clearly demonstrate that dry blending + extrusion is not a recommended preparation technique for this kind of composite (at least at laboratory level). Dry blending + mixing is the preferred technique, as an excellent homogeneity is obtained. Whatever the test method, dynamic modulus varies with the fiber volume fraction. The RPA test technique used (i.e., strain sweep) allows the strain effect to be easily modeled with a simple

equation that gives access to an extrapolated linear modulus (i.e., at “zero” strain). The effect of fiber volume fraction on this linear modulus can be compared with the well known Guth, Gold, and Simha model, which leads to the conclusion that no physico-chemical interaction occurs between the PVC matrix and the green coconut fiber. The observed reinforcing effect has thus essentially a single hydrodynamic origin (i.e., a mere volume effect). Solid state results tend to support this conclusion.

REFERENCES

- [1] Singleton, A. C. N., *Composites: Part B* **34**, 519 (2003).
- [2] Carvalho, L. H. (1997). Chemical modification of fibers for plastics reinforced composites. In *Lignocellulosic-Plastics Composites*. A. L. Leão, F. X. Carvalho, and Frollini, Eds., Universidade de São Paulo, Brazil, pp. 197–222.
- [3] d’Almeida, J. R. M. and Monteiro, S. N. (2003). In *Proceedings of the 58th Congresso Anual da Associação Brasileira de Materias Metalurgica*. Rio de Janeiro, pp. 21–24.
- [4] Homma, A. O aproveitamento industrial de resíduos; www.mdic.gov.br/tecnologia/revistas/artigos/200112pa/alfredohomma.pdf; accessed August 2003.
- [5] Rosa, M. F., Santos, F. J. S., Montenegro, A. A. T., de Abreu, F. A. P., Correia, D., de Araújo, F. B. S., and Norões, E. R. V., *Technical Communication, Embrapa Agroindústria Tropical* **54**, 1 (2001).
- [6] Dias, C. G. B. T. (2004). Adesão interfacial de polipropileno reciclado carregado com fibras naturais. In *Anais do XVI Congresso Brasileiro de Engenharia e Ciência dos Materiais*. Porto Alegre.
- [7] Aziz S. and Ansell, M. P., *Composites Sci. and Technol.* **64**, 1219 (2004).
- [8] Rout, J., Misra, M., Tripathy, S. S., Nayak, S. K., and Mohanty, A. K., *Composites Sci. and Technol.* **61**, 1303 (2001).
- [9] Van de Weyenberg, I., Ivens, J., De Coster, A., Kino, B., Baetens, E., and Verpoest, I., *Composites Sci. and Technol.* **63**, 1241 (2003).
- [10] Jayaraman, K., *Composites Sci. and Technol.* **63**, 367 (2003).
- [11] Pothan, L. A. and Thomas, S., *Composites Sci. and Technol.* **63**, 1231 (2003).
- [12] Sato, A. and Hage, E., *Plástico Industrial*, June, 70 (2003).
- [13] Keener, T. J., Stuart, R. K., and Brown, T. K., *Composites Part A* **35**, 357 (2004).
- [14] Cantero, G., *Composites Sci. and Technol.* **63**, 1247 (2003).
- [15] Cross, M. M. (1968). *Polymer Systems: Deformation and Flow*, Wetton and Whorlow-Macmillan, London.