

Highly Filled Blends of a Vinylic Copolymer with Plasticized Lignin: Thermal and Mechanical Properties

D. Feldman,¹ D. Banu,¹ R. St. J. Manley,² H. Zhu¹

¹Department of Building, Civil, and Environmental Engineering, Concordia University, Montreal, Quebec, Canada, H3G 1M8

²Pulp and Paper Research Center, McGill University, Montreal, Quebec, Canada, H3A 2A7

Received 29 May 2002; accepted 17 November 2002

ABSTRACT: The objective of this study was the development of new vinyl flooring formulations with increased resistance to attack by fungi and microorganisms, formulated with plasticizers having chemical compositions different from that of common dioctyl phthalate (DOP). Alkyl phthalate plasticizers are considered to be toxicological and ecotoxicological hazards, although this is still under debate. It is suspected that during the service life of poly(vinyl chloride) (PVC) flooring, the attack of fungi and microorganisms leads to the degradation of DOP and the release of some volatile organic compounds. For this reason, in the new flooring formulations, the vinyl chloride/vinyl acetate copolymer (VC-VAc) was partially replaced with lignin, a natural polymer and a major component of wood and vascular plants. Besides its other functions in wood, lignin imparts resistance to microorganisms. An organosolv lignin from Alcell Technologies, Inc. (AL), was used as a partial replacement of PVC. The influence of the new plasticizers, as

well as the influence of the partial replacement of VC-VAc with lignin, on the morphology and thermal and mechanical properties of the composites was investigated with scanning electron microscopy, differential scanning calorimetry, and tensile testing. Butyl benzyl phthalate and diethylene glycol dibenzoate were used as plasticizers; both were compatible with PVC and AL. The results indicated that diethylene glycol dibenzoate was the best plasticizer for these blend composites. In these formulations, AL could replace up to 20 parts of the copolymer. At this level of replacement, the key mechanical properties of the new composites compared very favorably with those of the DOP control formulations. The obtained formulation will be tested further for resistance to fungi and microorganisms. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2000–2010, 2003

Key words: blends; structure-property relations; thermal properties

INTRODUCTION

The varied usage of plasticized poly(vinyl chloride) (PVC) is largely due to the wide ranges of flexibility and softness that can be achieved by variations in the plasticizer contents. Plasticized PVC is used in a variety of items, such as flexible tubing, flexible sheets used as water barriers, thin sheets for domestic applications, cable insulation, footwear, wall coverings, and flooring.

Plasticized PVC is the basic component in various flooring products, including floor tiles, sheet flooring, carpet backing, walk-off mats, and wall bases. Each of these products has distinct requirements, both in processing and end use. Varieties of floor tiles, known as vinyl tiles, have different filler/binder ratios; the filler is usually calcium carbonate, and the binder is a plasticized PVC homopolymer or a vinyl chloride/vinyl acetate copolymer (VC-VAc). General-purpose plasti-

cizers, such as diisooheptyl phthalate, di-2-ethylhexyl phthalate (DOP), and diisononyl phthalate, are currently used at concentrations of 50–100% of the plasticizer systems in formulations for vinyl tiles.¹

As a major class of plasticizers, phthalates (particularly DOP) have been researched far more thoroughly for toxicological and ecotoxicological hazards than other types. They are now suspected of having adverse effects on humans, and the literature concerning this subject is very vast and somewhat puzzling.

According to the latest studies regarding the volatile organic compound emissions of plasticized PVC building materials (floor and wall coverings) performed in test chambers under normal living conditions, the concentrations of different phthalic esters in the air are very low, between 0.12 and 1.22 $\mu\text{g}/\text{kg}$ of body weight/day, and far below the tolerable intake of 37–66 $\mu\text{g}/\text{kg}$ of body weight/day, which is based on studies of oral toxicity.²

Studies were performed to establish the impact of temperature and humidity on chemical and sensory emissions from some building materials, including PVC flooring. These studies found little influence of temperature and humidity on the emissions from some such materials, including PVC flooring, whether expressed in chemical or sensory terms.³

Correspondence to: D. Feldman (feldman@vax2.concordia.ca).

Contract grant sponsor: EJLB Foundation.

Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada (NSERC).

In an update of phthalate plasticizers for PVC, Cadogan⁴ presented a current understanding of the health and environmental effects of phthalate plasticizers. It is concluded that the carcinogenic or reproductive effects produced by phthalates in rodents are species-specific and of little relevance to humans. The environmental impact of phthalates is considered to be low because of their ready biodegradability and low toxicity.

According to other authors,⁵ although phthalates and especially DOP are suggested to be of low acute toxicity, long-term exposure, especially in human beings at potentially higher risk, such as pregnant women and children, requires more in-depth studies.

Webb et al.⁵ showed that plasticization with DOP and dioctyl adipate increases the adhesion of the dermatogenic fungus *Aureobasidium pullulans* to plasticized PVC and stimulates its biodegradation. This fungus is omnipresent within the environment and is known to colonize many habitats.

Gumargalieva et al.⁷ showed that the loss of a dialkyl phthalate (not specified) plasticizer for PVC under the influence of surface biodegradation by the microscopic fungus *Aspergillus niger* is much faster than the loss without fungal overgrowth. In the absence of the fungus, the loss rate is limited by the volatility of the plasticizer, whereas in the presence of the fungus, it is limited by the diffusion of the plasticizer. Therefore, the fungus acts like a leaching solvent, presumably because it effectively removes the plasticizer from the surface of the material by biodegradation.

Fungi have been shown to produce esterase, an enzyme capable of breaking ester linkages. Both fungi and bacteria can metabolize the fragment molecules so produced. Studies have shown that there are significant differences in the stabilities of different plasticizers. The relative susceptibility to microbial attack is influenced, like their relative susceptibility to hydrolysis, by steric factors, which dictate the strength of the ester group. In general, linear structures are less resistant to fungal esterase than branched structures. Plasticizer biodegradation is especially prevalent in humid environments. Staining, commonly pink, is a result of bacterial activity. The familiar odor of mildew growth may also occur, as well as plasticizer decomposition products.⁸

The objective of this study is the development of new vinyl flooring tile formulations with other plasticizers that have chemical compositions different from that of common dialkyl phthalates. In addition, in the new formulations, the vinyl polymer has partially been replaced with lignin (L), a natural and inexpensive polymer, that is produced in large amounts by wood delignification in the pulp and paper industry. L is a major component of wood and vascular plants. It imparts rigidity to cell walls and acts as a binder between wood cells, creating a composite material that

is resistant to external forces and to microorganisms.^{9,10} White rot fungi are the only microorganisms that degrade L to any substantial degree.¹¹ They belong to a group of three fungi that decay wood, and in contrast to the other two (soft rot and brown rot fungi), they are capable of degrading not only cellulose and hemicelluloses but L also.

L molecules are composed of phenyl propane units interconnected by about 10 different linkages in a complex matrix. This matrix consists of a variety of functional groups, including hydroxyl, methoxy, and carbonyl units, which impart polarity to the L macromolecules.¹¹

Because of the complex structure of native L, interest in the development of L blends containing synthetic polymers has been almost continuous in the past 20 years, but in most cases, the resulting materials have been brittle and weak, with poorly defined thermal transitions.

Recently published data show that generally the mechanical properties of L-synthetic polymer blends are strongly influenced by the degree of association of the L components.¹² Indeed, although the molecular weight of L ranges from 1000 to 12,000, its glass-transition temperature (T_g) is between 100 and 180°C, which is high compared with T_g 's of most synthetic materials. According to Yoshida et al.,¹³ the high T_g values of L are due, in large part, to the degree of association by hydrogen bonding caused by the presence of phenolic hydroxyl groups in the main chains.¹³

Studies done in our laboratory have demonstrated that it is possible to reduce T_g of L and, consequently, the degree of association between the individual molecular components through the use of specific plasticizers.

Blends of an organosolv lignin from Alcell Technologies, Inc. (AL; Miramachi, Canada) and 30 phr of three different plasticizers (diethylene glycol dibenzoate, butyl benzyl phthalate, and tricresyl phosphate) were homogeneous, with single sharp T_g 's of 35, 38, and 53°C, respectively, situated well below the T_g value of AL, which is 97°C. This study has indicated that the compatibility and efficiency of a plasticizer is strongly influenced by its solubility parameter, which was one of the criteria considered for choosing the plasticizers for the study.¹⁴

In this article, an analysis of several plasticized vinyl copolymer/AL blends used as matrices for a high level of calcium carbonate filler in a vinyl tile composite is investigated. This study focuses on the influence of different plasticizers (having chemical compositions different from those of common dialkyl phthalates), as well as the influence of the partial replacement of the vinyl copolymer with AL, on the thermal and mechanical properties of the composites. Because of the susceptibility of dialkyl phthalate plasticizers to microorganism attack, as well as the resistance of L to micro-

TABLE I
Characteristics of Plasticizers

Characteristic	DOP	160	2-45
Molecular weight	390	312	314
Specific gravity (20/20°C)	0.986	1.119	1.178
Viscosity (mPa s at 25°C)	82	46	65-66
Boiling point (°C at 4 mmHg)	230	240/10 mm	240/5 mm
Pour point (°C)	-47	<-45	16 and 28 ^a
T_g (°C)	-81	-65	-52

^a Freezing point°C; two crystal forms

organisms, the aim of this study is to obtain new formulations with comparable mechanical properties and increased resistance to fungi and bacteria. Although DOP is not compatible with AL,¹⁴ control and blend composites with this plasticizer have been prepared for comparison because it is the plasticizer of choice in vinyl tile formulations. Formulations with mechanical properties comparable to those of the control will be tested later for resistance to fungi and bacteria.

EXPERIMENTAL

Materials

AL was produced on a pilot scale by Alcell Technologies. The characteristics of AL, as determined by the manufacturer, were as follows: weight-average molecular weight (M_w) < 2000, number-average molecular weight (M_n) = 800-900, specific gravity = 1.27, and median particle size = 20-40 μm . T_g , as determined by differential scanning calorimetry (DSC) in our laboratory, was 97°C.

The plasticizers used in this study were diethyl hexyl phthalate (DOP; Fisher Scientific, Ottawa, Canada), butyl benzyl phthalate [Santicizer 160 (160), Solutia, St. Louis, MO], and diethylene glycol dibenzoate [Velsicol 2-45 (2-45), Velsicol, Rosemont, IL]. Their characteristics are listed in Table I.

The synthetic polymer was VC-VAc (Oxy 1810, Occidental Corp., Dallas, TX). It had the following characteristics: $K_{\text{value}} = 57$ ($M_w = 54,000$ and $M_n = 26,000$), specific gravity = 1.37, vinyl acetate (VAc) content = 9.7%, and T_g (determined in our laboratory by DSC) = 78°C. For convenience, this copolymer is called PVC in this article.

The filler was calcium carbonate (Snowwhite 12) supplied by Step Rock Resources (Perth, Canada). It had a specific gravity of 2.71 and a mean particle size of 12 μm , and it contained 96% CaCO_3 , 2% MgCO_3 and 2% insoluble acid.

All the composites were formulated with 100 phr polymer, 200 phr CaCO_3 , 35 phr plasticizer, 3 phr dibutyl tin dilaurate as a heat stabilizer (Sigma-Aldrich Canada, Ltd., Mississauga, Canada), and 1.5 phr

calcium stearate (grade L-155) as a lubricant (Blachford, Ltd., Mississauga, Canada).

For each plasticizer, a PVC control and PVC-AL blends were prepared. In these blends, AL replaced PVC in proportions of 20, 25, and 30 parts. Above 30 parts AL, the composites were very sticky, and it was difficult to remove them from the mixer parts. Consequently, only composites with 80/20, 75/25, and 70/30 PVC/AL ratios (parts/parts) were prepared and tested.

Procedures

Processing

PVC controls and blend composites were prepared by melt mixing for 8 min at 141°C at a rotor speed of 65 rpm in a Haake Rheomix 600 equipped with roller blades, a torque rheometer (Haake Rheocord M 300) for the continuous measurement of the mixing torque, and a thermocouple for the continuous measurement of the melt temperature. In all the mixes, the records show that a steady-state torque was reached about 2 min before the end of the mixing time.

Several batches were prepared for each formulation. After melt mixing, the product was ground to a 2-3-mm particle size. Subsequently, sheets 1.5 mm thick were molded by compression at 153°C and 4.37 MPa. The molded sheets were cooled in the mold at room temperature at a cooling rate of 10°C/min under pressure, and after cooling, 1.5-mm-thick sheets were cut with a cutting die into dog-bone specimens (ASTM D 638) for tensile testing.

Thermal characteristics

DSC measurements for specimens of about 20 mg, punched from 1.5-mm sheets, were carried out on a DuPont 912 differential scanning calorimeter at a heating rate of 20°C/min under a nitrogen atmosphere between -50 and 160°C. The reported T_g values were estimated from the second scan as the transition midpoint temperatures. At least two specimens were run for each formulation. T_g 's of AL/160 and AL/2-45 compatible binary mixtures (100/35), prepared by a

TABLE II
Mechanical Properties of PVC Controls and PVC-AL Blend Composites
as a Function of the Type of Plasticizer and AL Content

Sample identification	Modulus at 5% elongation (MPa)	Tensile strength (MPa)		Elongation at break (%)
		Yield	Break	
2-45 plasticizer				
PVC control	22.8	3.82	6.33	366
80/20 blend	26.2	3.44	4.30	350
75/25 blend	40.7	3.39	3.60	366
70/30 blend	47.9	3.52	3.31	348
160 plasticizer				
PVC control	29.0	4.07	6.06	312
80/20 blend	18.1	3.05	4.04	326
75/25 blend	28.2	3.00	3.20	315
70/30 blend	40.6	3.58	2.67	281
DOP plasticizer				
PVC control	22.7	3.51	6.01	336
80/20 blend	12.4	3.06	4.00	312
75/25 blend	12.8	2.92	3.56	304
70/30 blend	16.9	2.99	2.92	229

procedure described elsewhere,¹⁴ were determined by DSC in the same temperature range and with the same heating rate. T_g 's of the plasticizers were determined with specimens of about 5 mg at a heating rate of 20°C/min from -120 to 20°C.

Morphology

Scanning electron microscopy (SEM) was performed with a Geol 840 SEM instrument. Photomicrographs of DOP- and 2-45-related controls and 75/25 PVC-AL blends were made. Magnifications of 370× and 1900× and a 12-kV beam intensity were used to expose the sample in a backscattered electron imaging mode.

Mechanical characteristics

Mechanical properties such as the tensile strength at yield and break and the elongation at break were measured in accordance with ASTM D 638 with an Instron universal testing machine at a crosshead speed of 15 mm/min. The modulus at 5% elongation was determined at a crosshead speed of 2 mm/min. The testing temperature was $23 \pm 2^\circ\text{C}$. All the specimens for tensile properties were tested 1 week after preparation. They were conditioned at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for 48 h before the testing. The indicated values (Table II) are averages of at least five determinations. The coefficients of variance lower than 10% were taken into account for each set of specimens tested.

In addition, two other tests specific for flooring materials were performed. First, there was dimensional thermal stability after 6 h of heating at 65°C followed by 16 h of conditioning at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. The change in the distance between

two reference marks as a percentage of the original distance of the marks was measured. The specimen dimensions were 150 mm × 80 mm × 1.5 mm, and the distance between the marks was 100 mm. Second, Shore A hardness was tested according to ASTM D 2240. The hardness was measured 15 s after an indenter application. Eight separate readings were performed for each specimen.

RESULTS AND DISCUSSIONS

Processing

It has been demonstrated that the forces involved in mixing a highly viscous melt can be correlated with the melt viscosity.¹⁵ From the data shown in Table III, we see that the type of plasticizer, as well as the level of AL, has a distinct influence on the mixing torque of the controls and blends. PVC-AL blends in 2-45- and 160-related composites present a steady and slight decrease in the equilibrium torque in relation to their respective controls and the AL loading. In DOP-related blend composites, the decreases in the torque

TABLE III
Equilibrium Torque of PVC Controls and PVC-AL
Blend Composites as a Function of the
Type of Plasticizer and AL Content

Sample identification	Equilibrium torque (mg)		
	2-45 plasticizer	160 plasticizer	DOP plasticizer
Control	854	837	952
80/20 blend	833	779	769
75/25 blend	804	774	724
70/30 blend	776	757	686

TABLE IV
Experimental and Calculated T_g 's of PVC Controls and PVC-AL Blend Composites
as a Function of the Type of Plasticizer and AL Content

Sample identification	T_g (°C)					
	2-45 plasticizer		160 plasticizer		DOP plasticizer	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
Control	21.5	31.6	24.5	25.0	18.8	16.3
80/20 blend	21.3	26.0	20.2	20.0	12.0; 14.4	—
75/25 blend	19.1	24.6	17.3	18.7	6.2; 17.9	—
70/30 blend	18.9	23.2	15.9	17.5	14.8; 18.9	—

values are more accentuated as a result of AL loadings. This is due to the fact that in contrast to other plasticizers, DOP does not have much affinity to AL but probably has a large lubricating effect resulting in a lower torque.

Thermal analysis

AL-plasticizer mixtures

The DSC data for the binary mixtures of AL and 35 phr of the 160 or 2-45 plasticizer reveal single T_g 's of 36 and 33°C, respectively. The data for the AL/160 mixture agree well with the Fox relationship.¹⁶ For the AL/2-45 mixture, the experimental data are about 10°C lower than the calculated values. The binary mixture AL-DOP separates into two phases after cooling, and so its T_g cannot be determined.

PVC-AL blend composites

The DSC data for PVC controls and PVC-AL blends of composites with different plasticizers reveal a single reproducible T_g for the composites with 2-45 or 160 as a plasticizer. The single T_g is an indication of compatibility between PVC and AL in the composites obtained with these two plasticizers. Again, the data for 160-related composites agree well with the Fox relationship for PVC control and PVC-AL blend composites. For 2-45-related composites, the experimental data are 10°C lower than the calculated values for the PVC controls and about 5°C lower than the calculated values for the PVC-AL blends. The data are given in Table IV and Figures 1-3.

DSC data for PVC-AL blends in DOP-related composites apparently present a single T_g . Unlike the quite sharp and narrow glass-transition range for 160- and

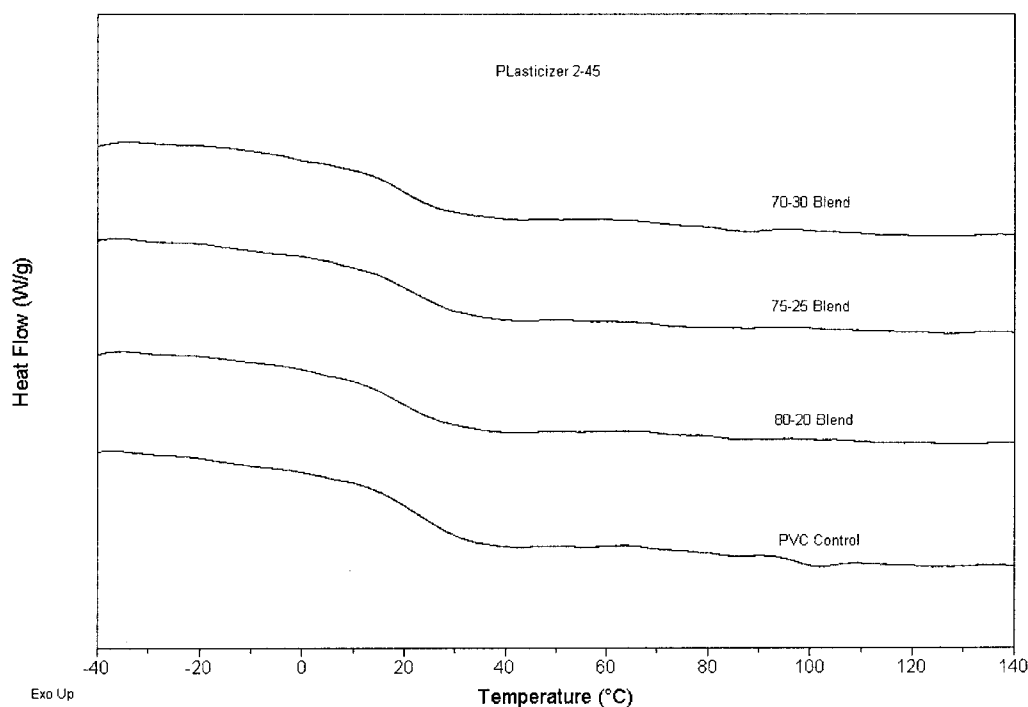


Figure 1 DSC curves for 2-45-related PVC control and PVC-AL blend composites.

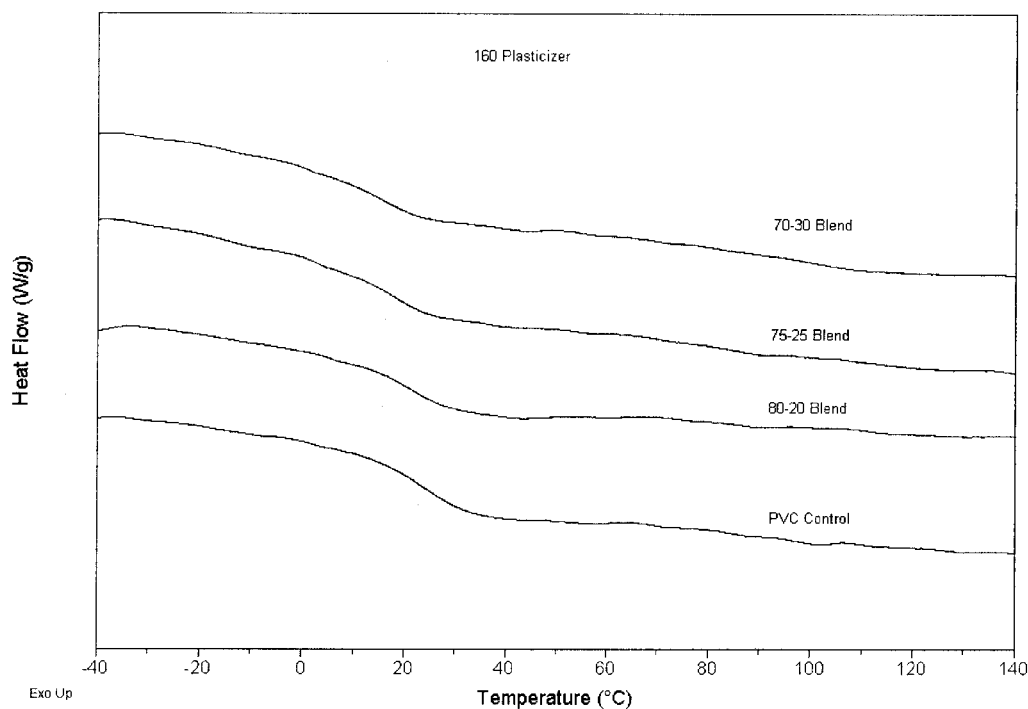


Figure 2 DSC curves for 160-related PVC control and PVC-AL blend composites.

2-45-related PVC-AL blend composites, the glass-transition regions of DOP-related PVC-AL blend composites are broad and less sharp. Although these composites apparently present one T_g , the data fluctuations are somehow erratic, with differences sometimes of more than 10°C within the same composite. These

differences suggest a degree of heterogeneity at the microscale, as the chain mobility is not always the same. The apparently single broad transition observed in DSC scans could be the result of two separate and overlapping T_g 's that occur in the same temperature range. For example, the T_g values of six specimens of

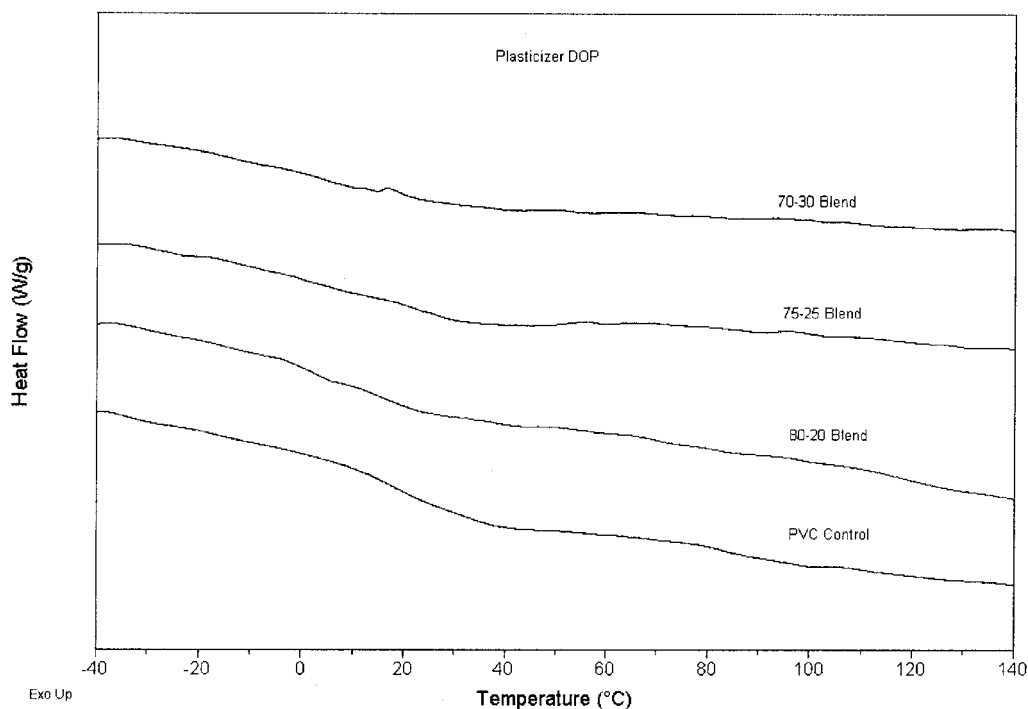


Figure 3 DSC curves for DOP-related PVC control and PVC-AL blend composites.

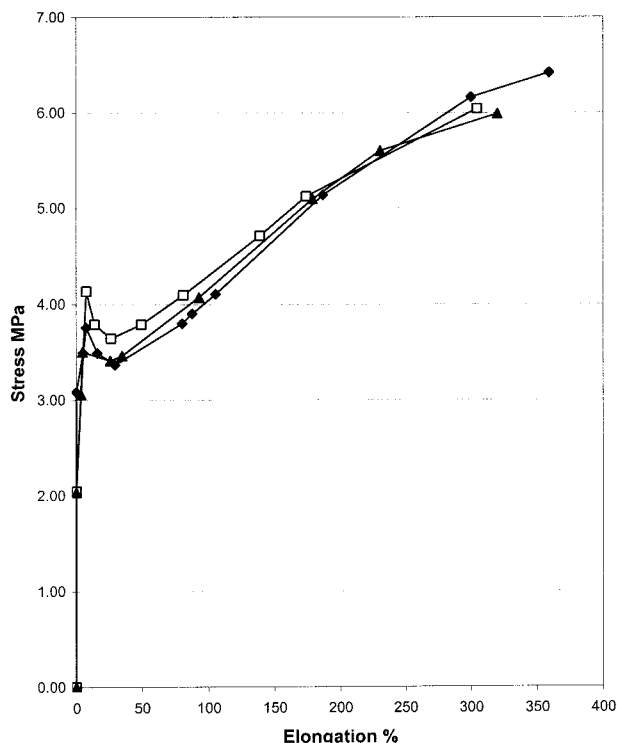


Figure 4 Stress-strain curves for PVC control composites: (◆) 2-45, (□) 160, and (▲) DOP.

the 75/25 PVC-AL blend are 11.1, 6.2, 17.1, 7.3, 17.9, and 8.9°C. In Table IV, the lowest and the highest T_g 's are indicated for each blend with DOP. Five specimens were analyzed by DSC for each DOP-related blend.

At an M_w value of less than 2000 and at an M_n value between 800 and 900, the polydispersity of AL macromolecules is quite high. Although DOP seems to be not compatible with AL, it is possible that DOP solvates some low molecular weight AL fractions and partially swells some high molecular weight AL fractions. Depending on the AL degree of solvation or swelling, the size and position of the transitions occurring in, or close to, the plasticized PVC temperature range will be different and will be reflected in the values of the overlapping transitions. As T_g has a cooperative effect, unfreezing some chains significantly helps the neighboring molecular segment to move.¹⁷

Mechanical properties

The mechanical properties of PVC-AL blend composites relative to the PVC controls and plasticizer type are shown in Table II. Figures 4-7 show the stress-strain diagrams for PVC controls and PVC-AL blend composites.

All these curves are representative of ductile compounds. They exhibit a more or less sharp yield point

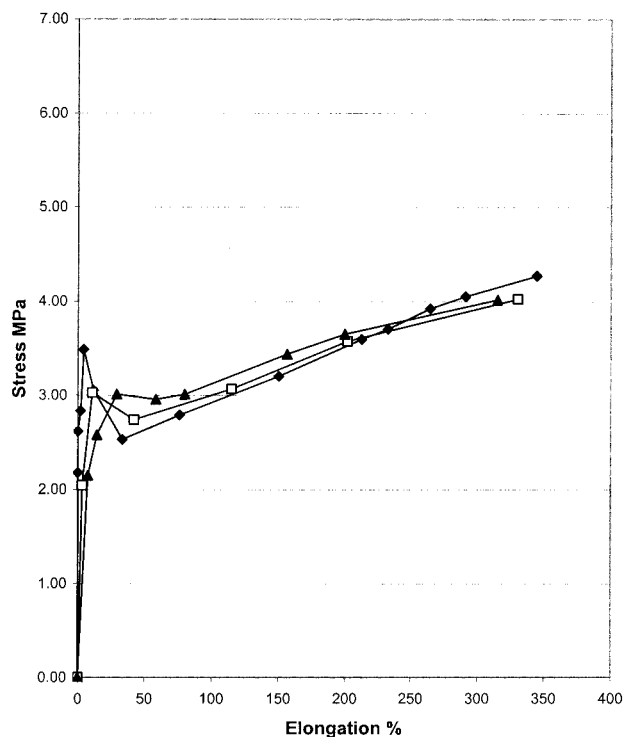


Figure 5 Stress-strain curves for 80/20 PVC-AL blend composites: (◆) 2-45, (□) 160, and (▲) DOP.

at which the tensile load reaches a maximum. Beyond this point, the load decreases because of necking and continues to decrease until the neck becomes stabi-

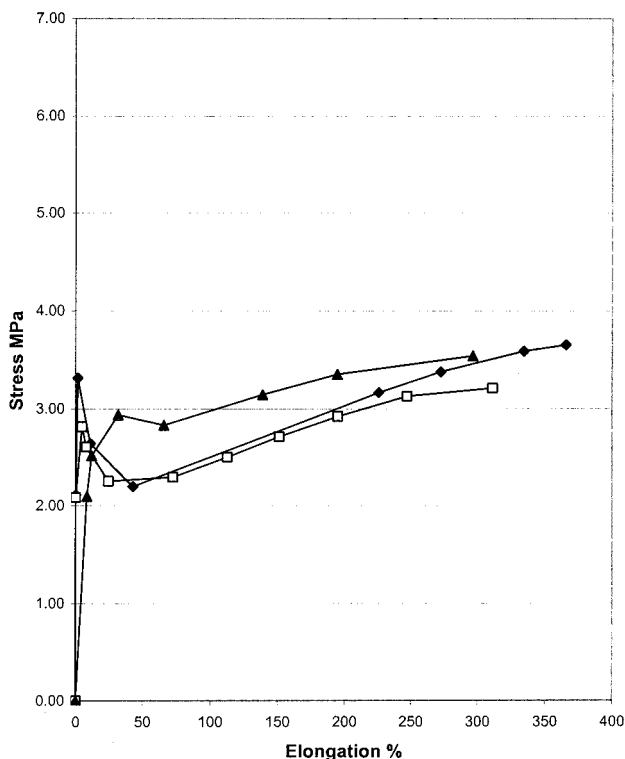


Figure 6 Stress-strain curves for 75/25 PVC-AL blend composites: (◆) 2-45, (□) 160, and (▲) DOP.

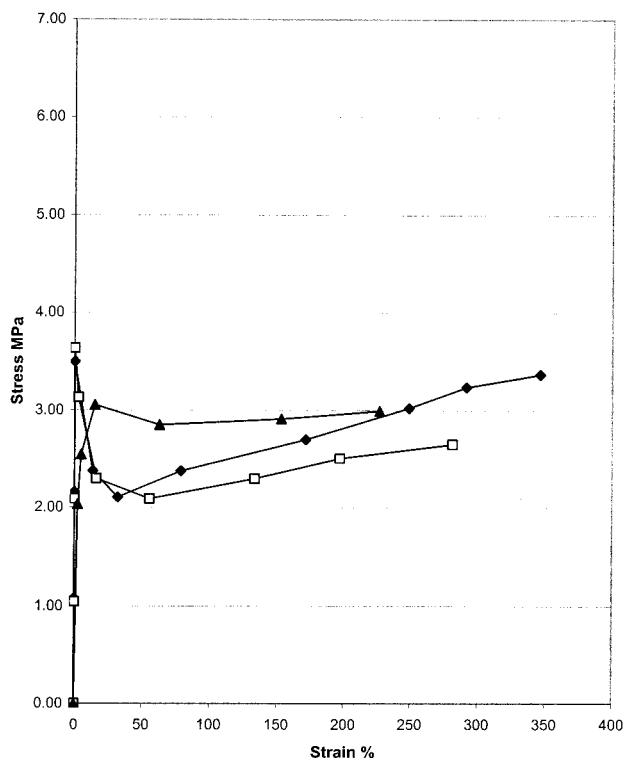


Figure 7 Stress-strain curves for 70/30 PVC-AL blend composites: (◆) 2-45, (□) 160, and (▲) DOP.

lized by strain hardening. The load then increases again as the sample is permanently deformed by cold drawing until failure occurs.

All the specimens were tested at room temperature, and as can be seen from Table II, the testing temperature was in all cases very close to or above T_g of the sample. It can also be seen from Table II that an increase in the AL loading effects T_g reductions, which are particular for each type of plasticizer. Actually, the T_g value of the blends represents the T_g value of the polymer matrix, which bonds together the inert filler particles.

The tensile properties or load-bearing properties are highly dependent on interchain (PVC-PVC and AL-AL) or intermolecular (PVC-AL, PVC-plasticizer, and AL-plasticizer) attractions. Above T_g , increasing molecular mobility leads to diminished bond strength by interchain or intermolecular separation.¹⁸ Consequently, one may expect a decrease in the modulus and tensile strength at yield and break and an increase in the elongation in correlation with the decrease in T_g .

By inspecting the data presented in Table II, we see that in relation to PVC controls, the decreasing values of the tensile strength at break of the PVC-AL blends with increasing AL loadings are almost the same for all the plasticizer formulations; this points to the smaller contribution of the relatively small AL macromolecules ($M_w = 800-900$) to the breaking stress of the composites.

In relation to PVC controls, the elongation at break is almost unchanged for 2-45- and 160-related blends with 20 and 25 parts AL, and decreases of 5 and 10% are observed for 30 parts AL in these related plasticizer composites, respectively. For DOP-related blends, a decrease of about 10% is observed for 20 and 25 parts AL, and a 30% decrease is seen for 30 parts AL.

Previous studies have shown that the morphology of PVC-AL blends (70/30 PVC/AL) with equivalent proportions of the same plasticizers used in this study is strongly influenced by the type of plasticizer. A photomicrograph (100 \times magnification) indicated a large AL domain size in the PVC continuous matrix in the 160-related blends and especially in the DOP-related blends, whereas in 2-45-related blends, the AL dispersion was excellent.¹⁴ The almost consistent lowering of the elongation at break with AL loading for DOP-related blends suggests that the material has increasing difficulty undergoing cold drawing because it is hampered by the larger AL particles.

As can be seen in Figure 4 the, yield stress of PVC controls correlates well with their T_g 's. The 160-related composite with the highest T_g is stiff and has the sharpest yield point. In contrast, the DOP-related composition with the lowest T_g is more ductile and has a rather broad yield domain. For the blend composites, as can be seen in Figure 5, the 80/20 blend in 2-45-related composites gives a stiffer material with the sharpest yield point, whereas the 160-related and especially DOP-related composites are characterized by a lower and broader yield domain. This also applies to 75/25 blend composites (Fig. 6), with the observation that the stiffness of 160-related blend composites increases more than that of DOP-related blend composites.

At 30 parts AL in the blends, the effect of plasticizers on the respective stress-strain curves is very clear. The 160-related composite now has the highest yield stress value and some successive cold drawing, followed by the 2-45-related composite with almost the same yield stress value but with the highest cold drawing. The DOP-related composite is still characterized by a discrete yield point but also experiences increased difficulty undergoing cold drawing.

Earlier results have indicated that DOP is not a good plasticizer for AL.¹⁴ However, in DOP-related composites, as thermal and morphology analyses have indicated, AL is only partially plasticized, and so more plasticizer is available for the PVC matrix, which will become softer, as can be seen from the profiles of the respective stress-strain curves.

Although the DOP-related blend composites are softer, they are less ductile because the DOP plasticizer is not able to break most of the hydrogen bonds present in AL and so the coarse and irregularly dispersed AL particles prevent the PVC matrix from

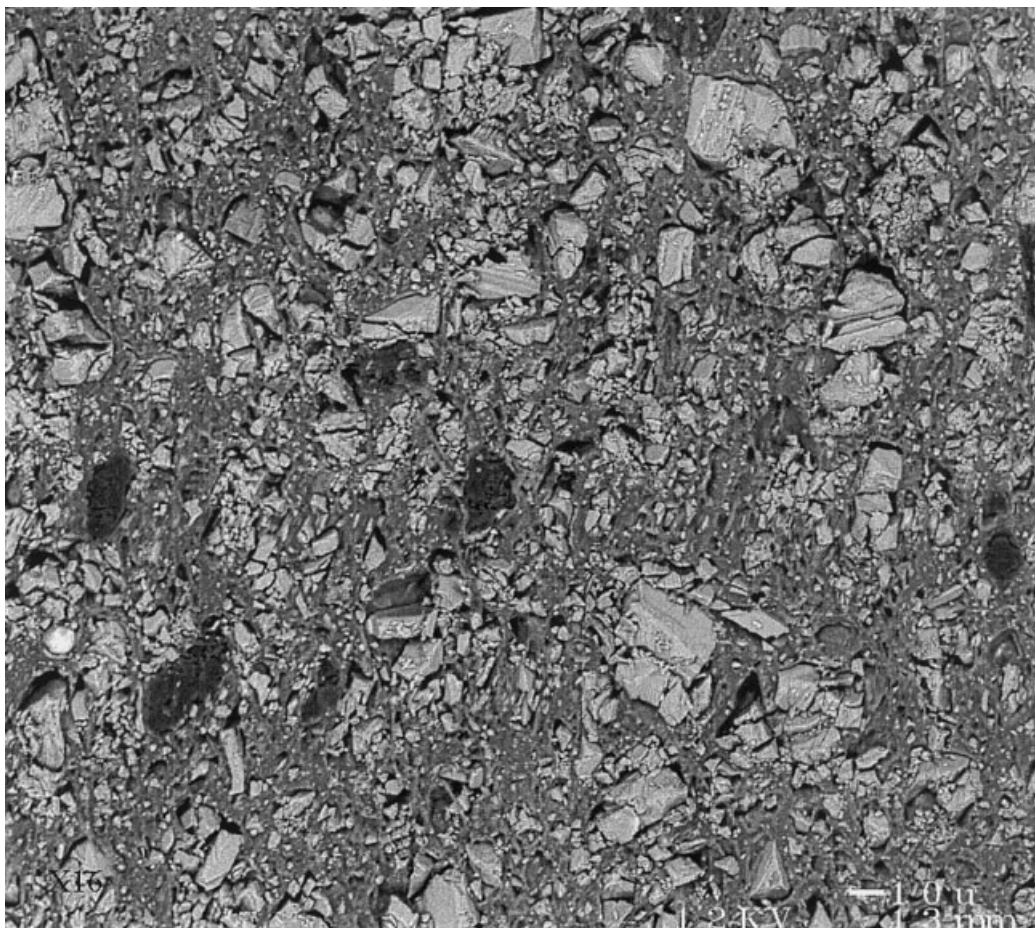


Figure 8 SEM photomicrograph (340 \times) of a DOP-related 75/25 PVC-AL blend composite.

undergoing cold drawing. Therefore, the material will elongate less.

The toughness of the composites can be estimated from the area of the stress-strain curves, which are indicated in Figures 5-7. These curves reveal that 2-45-related blend composites give tougher materials than 160-related and especially DOP-related composites. These results are not surprising given the dimensions and dispersion of AL particles in 2-45-related composites, as discussed previously.

SEM also supports these results. SEM micrographs of 2-45-related and DOP-related 75/25 PVC-AL blend composites, which are illustrated in Figure 8 and 9, clearly indicate differences in the size and dispersion of AL within the continuous PVC matrix in these composites.

The plasticizers are, therefore, seen to play complex roles in determining the morphology and mechanical properties of the PVC-AL blend composites.

Former and present results have indicated that of all studied formulations, those with 2-45 (2-45/AL blends and 2-45/PVC-AL blend composites) have the smallest and best dispersed AL particles. As the size decreases, the surfaces of the particles increase. This causes increased particle interaction and adherence.¹⁹

Therefore, the polar AL particles could better interact with polar PVC particles, and this results in hydrogen bonds between OH of AL and α -hydrogen of PVC, or the carbonyl group of VAc, making the polymer matrix stronger. The good dispersion and good interaction of AL particles within the PVC matrix and with PVC matrix particles allow the good adherence of the polymer matrix to the calcium carbonate filler, and this results in a stronger and tougher composite. The modulus values and stress-strain curves of these particular blends confirm this fact.

Hardness

The values of the Shore A indentation hardness for PVC controls and PVC-AL blend composites are given in Table V. These data show that the gradual replacement of PVC with AL has little effect on the hardness; this is understandable because the high load of the calcium carbonate filler is the component most responsible for the composite hardness.

Dimensional thermal stability

The results of the dimensional thermal stability are given in Table VI. In comparison with PVC controls,

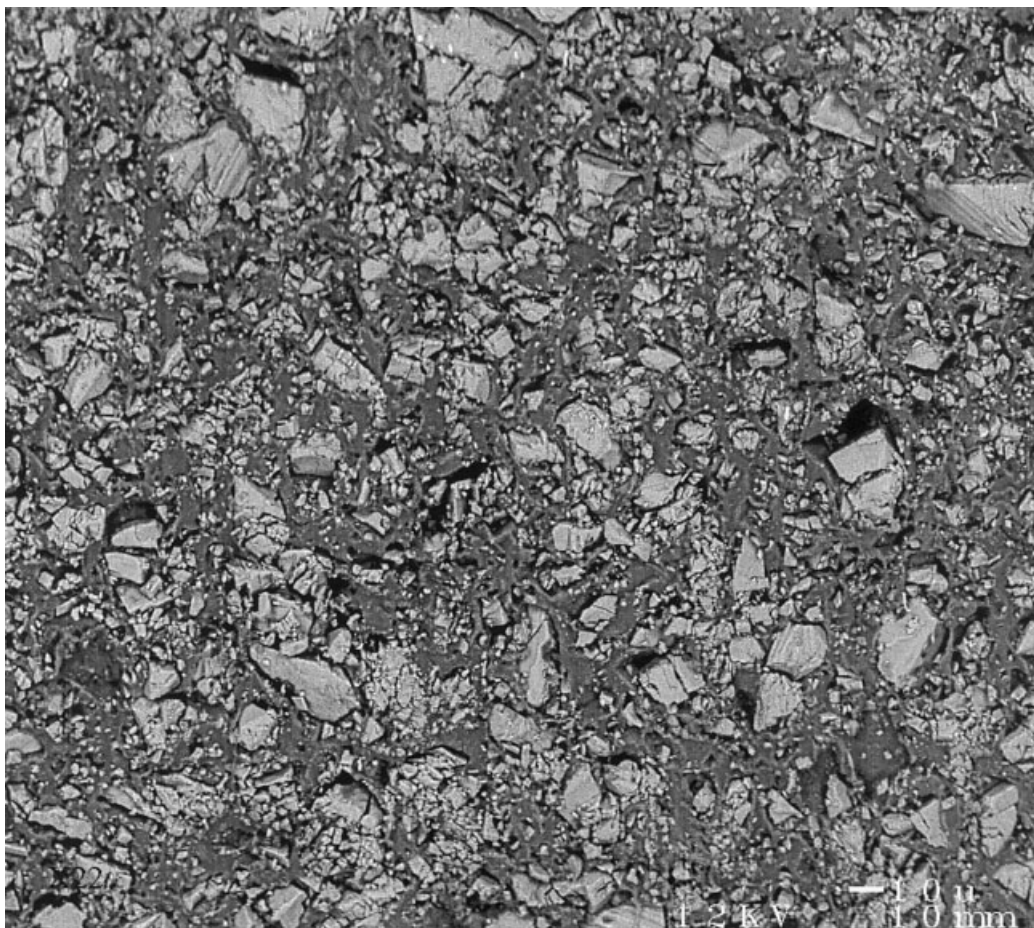


Figure 9 SEM photomicrograph (340×) of a 2-45-related 75/25 PVC-AL blend composite.

the PVC-AL blends contract slightly less; this means that they possess better thermal stability.

CONCLUSIONS

This research was carried out to obtain and evaluate highly filled vinyl tile composites. The influence of two plasticizers, with chemical compositions different from that of the common DOP plasticizer, as well as the influence of the partial replacement of the VC-VAc copolymer (called PVC for convenience) with AL, on the morphology, thermal, and mechanical properties

of the composites was investigated. The aim of the research was to obtain new PVC formulations with characteristics comparable to those of the existing formulation but with increased resistance to fungi and bacteria.

In these formulations, the matrix (polymer) level was always the same, that is, 100 phr to 200 phr calcium carbonate filler, but its composition varied (80/20, 75/25, and 70/30 PVC/AL). DOP, 160 (butyl benzyl phthalate), and 2-45 (diethyleneglycol dibenzoate) were used as plasticizers at a level of 35 phr. All the plasticizers were compatible with PVC, but only 2-45 and 160 were compatible with AL. DOP was

TABLE V
Hardness of PVC Controls and PVC-AL Blend Composites as a Function of the Type of Plasticizer and AL Content

Sample identification	Shore A hardness		
	2-45 plasticizer	160 plasticizer	DOP plasticizer
PVC control	96.9	97.1	96.3
80/20 blend	97.5	95.9	94.0
75/25 blend	95.5	96.4	93.7
70/30 blend	97.1	94.0	93.4

TABLE VI
Thermal Dimensional Stability of PVC Controls and PVC-AL Blend Composites as a Function of the Type of Plasticizer and AL Content

Sample identification	Dimensional stability (%)		
	2-45 plasticizer	160 plasticizer	DOP plasticizer
PVC control	0.17	0.16	0.17
80/20 blend	0.16	0.16	0.16
75/25 blend	0.16	0.11	0.14

chosen for comparison. On the basis of the mechanical and thermal properties, it appears that 2-45 was the best plasticizer for the PVC-AL blend composites. In these composites, AL could replace up to 20 parts PVC. At this level of PVC replacement, the key mechanical properties of the new 2-45 formulation compared very favorably with those of the DOP control formulation.

The modulus was about 15% higher, and the elongation at break was about 4% higher; the tensile strengths at yield and break were about 10 and 28% lower, respectively. The hardness was practically unchanged, and the dimensional thermal stability was slightly better. In addition, its processing did not present difficulties.

This new formulation will be tested further for resistance to fungi and bacteria.

In addition, this study has demonstrated that specific plasticizers could break some of the secondary hydrogen bonds present in L, creating possibilities of interactions on a molecular scale with other polar polymers by intermolecular hydrogen bonds.

References

1. Krauskopf, L. G. In *Handbook of Polyvinyl Chloride Formulations*; Wickson, E. J., Ed.; Wiley: New York, 1993; p 203.
2. Uhede, E.; Bednarek, M.; Fuhmann, F.; Salthammer, T. *Indoor Air* 2001, 11, 150.
3. Fang, L.; Clausen, G.; Fanger, P. O. *Indoor Air* 1999, 9, 193.
4. Cadogan, D. F. *Plast Rubber Compos* 1999, 28, 476.
5. Latini, G. *Biol Neonate* 2000, 78, 269.
6. Webb, J. S.; Vander Mei, H. C.; Nixon, M.; Eastwood, I. M.; Greenhalgh, M.; Read, S. J.; Robson, D.; Handley, P. S. *Appl Environ Microbiol* 1999, 65, 3575.
7. Gumargalieva, K. Z.; Zaikov, G. E.; Semenov, S. A.; Zhdanova, O. A. *Polym Degrad Stab* 1999, 63, 111.
8. Wilson, A. S. *Plasticizers: Principle and Practice*; Institute of Materials: London, 1995; pp 105 and 136.
9. Gandini, A. In *Comprehensive Polymer Science*; Allen, G.; Agrawal, S. L.; Russe, S., Eds.; Pergamon: London, 1992; Suppl. 1, p 543.
10. Monties, B.; Fukushima, K. In *Biopolymers: Biology, Chemistry, Applications*; Hofriecher, M.; Steinbuchel, A., Eds.; Wiley-VCH: Weinheim, 2001; p 2.
11. Sterjiades, R.; Erkiesson, E. L. In *Polyphenolic Phenomena*; Scalbert, A., Ed.; INRA Editions: Paris, 1993; p 115.
12. Li, Y.; Mlinar, J.; Sarkanen, S. *J Polym Sci Part B: Polym Phys* 1997, 35, 1899.
13. Yoshida, H.; Morck, R.; Kringstad, K. P. *Holzforschung* 1987, 41, 171.
14. Feldman, D.; Banu, D.; Campanelli, J.; Zhu, H. *J Appl Polym Sci* 2001, 81, 861.
15. Mckinney, P. V. *J Appl Polym Sci* 1965, 9, 3359.
16. Shalaby, W. S.; Bair, E. B. In *Thermal Characterization of Polymeric Materials*; Turi, E. A., Ed.; Academic: New York, 1981; p 412.
17. Cheng, S. Z. D. *J Appl Polym Sci Appl Polym Symp* 1989, 43, 315.
18. Powel, P.; Housz, J. I. *Engineering with Plastics*, 2nd ed.; Stanley Thornes: Cheltenham, England, 1998; p 137.
19. Ferigno, T. H. In *Handbook of Fillers and Reinforcements for Plastics*; Katz, H. S.; Milewski, J. V., Eds.; Van Nostrand Reinhold: New York, 1978; p 29.