Preparation and Properties of Some Filled Poly(vinyl chloride) Compositions

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ABSTRACT: Different samples of filled poly(vinyl chloride) (PVC) compositions were formulated from PVC, a polar plasticizer mixture consisting of dioctylphthalate (DOP) and a chlorinated paraffin, and variable proportions of a white filler such as barite, calcium carbonate, kaoline, quartz, or talc; a conductive filler such as High Abrasion Furnace (HAF) carbon black; or a hydrated mineral filler such as aluminium hydroxide, magnesium hydroxide, or calcium hydroxide. Epoxidized soybean oil as a heat stabilizer and sandorin red (BRN) pigment were added. Electrical and mechanical studies show that the incorporation of white fillers produces a plasticized PVC of good electrical insulation character whereas the addition of HAF carbon black produces a sample with some electrical conductivity; both of them have good mechanical properties. Of the hydrated fillers studied aluminium hydroxide has been found to impart the best fire retardancy and good electrical properties for electric wires and cables. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2657–2670, 1999

Key words: poly(vinyl chloride); inorganic fillers; electrical and mechanical properties; fire resistance

INTRODUCTION

Inorganic fillers are not only used as extenders but they also play an important role in improving the electrical and mechanical properties of plastics.^{1–3} However, the use of fillers at high loadings results in increased hardness and stiffness and leads to a decrease in yield stress, tensile strength, and ductility, compared with the base polymer. The interfacial adhesion between filler and polymer has a determining influence on the mechanical properties of composites.^{4,5} Different modifiers have been used to increase the low affinity of mineral filler to polymer matrix.^{6,7} Many polymers in their pure state are good electrical insulators. However, in some cases there is a demand for a conducting or semiconducting polymer. Electrical conductivity in plastics can be provided by incorporation of conductive materials.⁸ In practice, electrically conductive fillers such as carbon black, graphite, metallic powders, some metal oxides, and aluminium flakes are of current commercial interest.^{9,10} However, carbon black is the most commonly used filler, because it is much cheaper and lighter than metallic particles.^{11,12}

In recent years there has been widespread interest in the use of acid and halogen-free fire retardant additives for polymers. Fire retardant fillers in the form of metal hydroxides are being used increasingly in industrial formulations because they can achieve high levels of fire retardancy without producing the smoke and corrosive

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fumes often associated with other fire retardants. Their fire retardant properties are derived largely from an endothermic decomposition, which removes heat from the system and is accompanied by release of water or other nonflammable gases.^{13,14}

In this investigation, a wide variety of fillers have been used in the compounding of poly(vinyl chloride) (PVC) plasticized with dioctylphthalate (DOP) and chlorinated paraffin. These fillers include barite, calcium carbonate, kaoline, quartz, talc, HAF carbon black, aluminium hydroxide, magnesium hydroxide, and calcium hydroxide. The aim of this study was to investigate systematically the effect of adding increasing quantities of these fillers on the electrical and mechanical properties of the PVC–DOP-chlorinated paraffin system. This study also was concerned with the use of the hydrated mineral fillers as fire retarding smoke suppressing additives for the plasticized PVC.

EXPERIMENTAL

Formulations of Samples

In the present study, several formulations were obtained by mixing the components in the proportions shown in Tables I and II. The general procedure for the formulation is described as follows. Homogeneous samples were prepared by adding variable proportions of an inorganic filler, namely, barite, calcium carbonate, kaoline, quartz, talc, HAF carbon black, aluminium hydroxide, magnesium hydroxide, or calcium hydroxide portionwise at room temperature to a composition containing 100 parts PVC (K-value, 70; apparent bulk density, 0.3 g/mL; and viscosity number, 125 mL/g), 40 parts DOP, and 20 parts chlorinated paraffin [density at 25°C; 1.16–1.18 g/mL, average molecular weight (MW); 366, viscosity at 25°C; 150–350 candle power (cp); n_D^{25} , 1.4950; and Cl content, 42-45%] under stirring. The mixtures then were mixed with epoxidized soybean oil as a heat stabilizer, followed by the addition of sandorin red (BRN) pigment to give the required samples (gelation temperature at 175°C for 100 s). The obtained samples are denoted by $F_0, F_1, F_2, \ldots, F_{36}$. These formulations are shown in Tables I and II.

Mechanical Measurements

Yield stress, tensile strength, and percent elongation were measured at room temperature on dumbbell specimens according to ASTM D 412-66T (1967) using a computerized (Zwick 1425) testing machine with a crosshead speed of 500 mm/min.

Shore hardness was determined using a Shore D durometer according to ASTM D 2240-75 $(1983)^{15}$ using a (Zwick 3102) hardness tester. The hardness value was taken as an average of five readings from different points.

Dielectric Measurements

Permittivity (ε') and dielectric loss (ε'') for the denoted samples were measured at different frequencies ranging from 100 Hz to 100 kHz. An LCR meter (type AG-4311B) Ando electric LTD with the test cell NFM/5T was used. The capacitance C and the loss tangent (tan δ) were obtained directly from the bridge from which ε' and ε'' were calculated. The samples were in the form of discs of 58 mm diameter and 3 mm thickness. Calibration of the apparatus was carried out using standard samples (Trolitul, glass and air) of 3 mm thickness; the accuracy for ε' was $\pm 1\%$ and for ε'' was $\pm 2\%$. The measurements were carried out at temperatures of 20, 40, and 60°C using an ultrathermostat.

Conductivity Measurements

The electrical conductivity (σ) of the investigated samples was measured by the application of Ohm's law using the NFM/5T test cell. A power supply unit (GM 45161/01) from Philips (the Netherlands) was used. The potential difference V between the plates holding the sample and the current I flowing through it was measured by a multimeter (type URI 1050) from Rohde and Schwarz (Garmany). The electrical conductivity is calculated using the equation

$$\sigma = \frac{dI}{AV}$$
 mho m⁻¹

where d is the thickness of the sample in meters and A is its surface area in square meters.

RESULTS AND DISCUSSION

Because of its high chlorine content, PVC burns with difficulty, but when plasticized with a plasticizer such as DOP, this property is depressed, because of the flammability of the plasticizer Table I Formulations and Mechanical Properties of Plasticized PVC Filled with Barite, Calcium Carbonate, Kaoline, Quartz, Talc, and Carbon Black

Carbon bis	ICK																							
Constituents,											S_{a}	mple l	Notatic	u										
Parts by Weight (g)	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F ₈	F ₉ 1	⁴ 10	F_{11}	F_{12}	F 13 .	F ₁₄ 1	7 ₁₅ F	$_{16}$ F_1	7 F 1	8 F ₁	${}^9 F_{20}$	F_{21}	F_{22}	F_{23}	F_{24}
PVC	100	100	100	100	100	100	100 1	00 10	0 1(00 1(00 1	00 1(1 00	00 1(00 10	0 10	0 100	100	100	100	100	100	100	100
DOP	40	40	40	40	40	40	40	40 4	10	FO	40	40	40	40	1 0 4	0 4	0 40	4(40	40	40	40	40	40
Chlorinated naraffin ^a	20	20	20	20	20	20	20	20 2	00	00	20	20	20	20	20 2	2	0 20	2(20	20	20	20	20	20
Epoxidized	က	က	က	က	က	က	ŝ	ŝ	co Co	co Co	ŝ	ŝ	co	ŝ	ŝ	ŝ	00 00	00	co 	က	က	က	က	က
soybean oil																								
Pigment	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1 1	-	. 1	1	1	1	1	1
Barite		10	20	30	40				I									I		I			I	
Calcium						10	20	30 4	10									I						
carbonate																								
Quartz										0	20	30	40	Ι		1		I	1				I	
Kaoline									ļ					10	20	0 4		I						
Talc	Ι		I					' 	Ι	Ι						' 	- 10	20	30	40				
Carbon black	Ι		Ι						Ι	Ι	Ι		Ι			1		I			10	20	30	40
Mechanical P	opertie	ş																						
Yield stress (N/mm^2)	9.2	9.8	9.1	6.9	5.5	8.0	5.9	4.0	4.2	17.6	11.7	7.6	3.8	7.1	5.9	5.1	4.4 7	6.	.4 4	1 3.4	7.8	7.0	5.3	3.9
Tensile strength (N/mm^2)	4.8	8.5	7.0	4.9	2.8	4.5	4.0	3.1	2.3	13.8	8.8	5.0	2.3	5.0	5.2	3.4	2.8 3	9.	8	3 2.4	6.1	3.9	2.7	1.4
Elongation (%)	141.6	184.3	149.8	108.7	86.5	111.3	94.8	83.4 8	30.5 3.	19.3 2	38.2 1	48.5	90.3 1	28.3	93.4 8	2.8 7	0.5 185	.0 140	.5 99	7 79.8	166.2	119.2	97.3	59.5
a Chlorina	ed pare	affin is	conside	red as	a seco	ndary	plastic	izer.																

Constituents,						Sa	nple No	otation					
Parts by Weight (g)	F_0	F_{25}	F_{26}	F_{27}	F_{28}	F_{29}	F_{30}	F_{31}	F_{32}	F_{33}	F_{34}	F_{35}	F_{36}
PVC	100	100	100	100	100	100	100	100	100	100	100	100	100
DOP	40	40	40	40	40	40	40	40	40	40	40	40	40
Chlorinated paraffin	20	20	20	20	20	20	20	20	20	20	20	20	20
Epoxidized soybean oil	3	3	3	3	3	3	3	3	3	3	3	3	3
Pigment	1	1	1	1	1	1	1	1	1	1	1	1	1
Aluminium hvdroxide	—	10	20	30	40	—	—	_	_	_	_	_	—
Magnesium hydroxide	—		_	_	—	10	20	30	40	—	—	_	
Calcium hydroxide	_	_	_	—	—	—	—	—	—	10	20	30	40
Mechanical Prop	perties												
Hardness (Shore D)	32.2	34.0	35.4	38.0	39.0	36.6	38.0	41.0	43.8	34.6	36.2	39.0	40.5
Fire Retardancy	,32,33												
Weight loss (%) Flammability	18.97 B ^a	17.50 B	14.62 NB ^b	10.43 NB	7.0 NB	17.86 B	15.77 B	12.56 NB	9.02 NB	18.48 B	17.53 B	15.94 B	14.25 NB

Table IIFormulations, Shore Hardness, and Fire Retardancy of Plasticized PVC Filled withAluminium Hydroxide, Magnesium Hydroxide, and Calcium Hydroxide

^a B, burning.

^b NB, nonburning.

when used in high proportion. On the other hand, PVC is known to have kinetically rigid chains. On the addition of polar plasticizers such as DOP, they are present as clusters of molecules between clusters or bundles of polymer segments or molecules. As energy is applied to the system, the permittivity (ε') rises significantly, indicating that the PVC molecules are no longer held together rigidly but are free to move as if the polymer is rubbery rather than glassy. Thus, the plasticizer molecules have penetrated the clusters or bundles of PVC molecules and separated the polymeric chains. After heating this mixture, a toughening structure forms on cooling and may result from van der Waals forces, hydrogen bonding, or crystallization of polymer segments.

In this investigation, plasticized PVC has been filled with white fillers such as barite, calcium carbonate, kaoline, quartz, and talc; a conductive filler such as HAF carbon black; and hydrated mineral fillers such as aluminium hydroxide, magnesium hydroxide, and calcium hydroxide in different ratios up to 40 parts per hundred parts PVC (phr). The effects of filler loading on the properties of PVC–DOP-chlorinated paraffin system have been discussed.

Effect of White Filler Loading on Properties of Plasticized PVC

Electrical Properties

The permittivity (ε') and dielectric loss (ε'') for the prepared samples ($F_0, F_1, F_2, \ldots, F_{20}$) over the frequency range from 100 Hz to 100 kHz at room temperature ($\sim 27^{\circ}$ C) were studied. The results obtained for ε' and ε'' versus the frequency for these samples at room temperature are shown in Figure 1.

It is evident from Figure 1 that the value of ε' increases with the increase in the content of these fillers, especially at the very low frequency region, except in the case of talc in which ε' is decreased slightly. The increase of ε' may be attributed to the higher permittivity of these fillers compared with that of the filler-free sample. It also is apparent from Figure 1 that the value of ε'' in the lower-frequency region increases with increasing



Figure 1 The permittivity (ε') and dielectric loss (ε'') versus frequency (f) at room temperature for plasticized PVC filled with different white fillers $(\bullet, \text{unfilled}; +, 10 \text{ phr}; \bigcirc, 20 \text{ phr}; \times, 30 \text{ phr}; \text{ and } \triangle, 40 \text{ phr})$. Broken lines represent dielectric loss (ε'') versus frequency after removal of moisture.

the content of each filler. The low-frequency losses may be attributed to Maxwell–Wagner losses arising from the interfacial polarization caused by the presence of the ingredients added stepwise to the plasticized PVC sample. The increase of ε'' by the addition of these fillers is attributed to the moisture content of the filler. When the samples were heated at 70°C under vacuum for 24 h, the maximum of this low-frequency loss term lies around 500 Hz for all samples and the values of ε'' are found to be slightly higher than that of the filler-free sample whereas the values of ε' did not significantly changed. The results are shown in Figure 1. These measurements support the suggestion that the losses in the case of white fillers mainly are caused by moisture effects.

Mechanical Properties

The variation of yield stress, tensile strength, and percent elongation versus the concentration of barite, calcium carbonate, kaoline, quartz, or talc at $23 \pm 2^{\circ}$ C is given in Table I. The presented data show that increasing the content of barite and quartz to 10 phr increases the value of the tensile strength and then it decreases with a further increase in their content to 40 phr. From these data, it also is evident that the value of the tensile strength decreases with the increase of the concentration of calcium carbonate, kaoline, and talc. This decrease of tensile strength may be caused by the poor adhesion between the PVC and filler phases at a higher degree of loading leading to the retardation of crosslinks across the interfaces. For an example, Figure 2 represents the variation of tensile strength with the content of barite or calcium carbonate. On the other hand, data in Table I show that the percent elongation increases with increasing the content of barite, quartz, and talc to 10 phr and then decreases at higher concentrations. So, probably, intermolecular and interstructural processes may have been present. At low concentrations, the intermolecular process is predominant where the filler molecules interact with the active group of the PVC, leading to the breakage of molecular bundles (aggregates), and the chains are separated. At higher concentrations, the interstructural process is more prevalent, where the filler molecules are distributed in the interaggregate space. In the first process elongation increases with concentration whereas in the second process elongation decreases with the increase of filler concentration. Data in Table I also show a sharp decrease in percent elongation with the increasing concentrations of calcium carbonate and kaoline. Figure 2 also represents the variation of percent elongation with the content of barite or calcium carbonate.



Figure 2 The variation of tensile strength and percent elongation with the content of (a) Barite and (b) Calcium carbonate.

Effect of HAF Carbon Black Loading on Properties of Plasticized PVC

Electrical Properties

The ε' and ε'' for the samples $(F_0, F_{21}, F_{22}, F_{23},$ and $F_{24})$ were studied over the frequency region from 100 Hz to 100 kHz at different temperatures from 20 to 60°C. It is evident from Figure 3, which represents the variation of ε' with frequency at different temperatures, that the value of ε' increases with increasing temperature and decreases with increasing frequency. Similar behavior was noticed before in the literature.^{16–19} The increase of ε' with temperature can be explained by the increase in the mobility of polar groups, the decrease in density, and, hence, a decrease in the



Figure 3 The permittivity (ε') versus frequency (f) at different temperatures for plasticized PVC filled with HAF carbon black (same notation as in Fig. 1).

effect of the environment that facilitates the orientation of the mobile groups. The decrease of ε' with frequency may be caused by dielectric dispersion. Moreover, Figure 3 as well as Figure 4, which represents the relation between ε' and the content of HAF carbon black at frequencies 100 Hz and 100 kHz and different temperatures, show that the value of ε' increases with the increase in carbon content, especially at the very low frequency region.

It is apparent from Figure 5, which represents the variation of ε'' with frequency at different temperatures, that the value of ε'' is increased greatly at higher temperatures, especially in the lower-frequency region. Moreover, Figure 5 reveals that, at each temperature, ε'' in the lowerfrequency region increases with increasing the content of HAF carbon black. Figure 4 also shows the relation between ε'' and carbon content at frequencies 100 Hz and 100 kHz and temperatures from 20 to 60°C. The increase in ε'' in the very low frequency region with increasing carbon concentration may be caused by either the Maxwell–Wagner effect²⁰ as a result of an alternating current (ac) in phase with the applied potential or the direct current (dc) conductivity^{21,22} resulting from the increase of ion mobility or both. To confirm this, the dc conductivities of the investigated samples were measured by application of Ohm's law to the dc flowing through the samples at 200 V and at temperatures from 20 to 60°C. All investigated samples showed appreciable dc conductivity. The dielectric losses caused by the dc conductivity (σ) at the different frequencies (ω) are calculated using the equation²³

$$\varepsilon_{\rm dc}'' = {9 \times 10^{11} 4 \pi \sigma \over \omega}$$

and subtracted from the values of ε'' in the lowfrequency region. The data of ε'' after subtracting ε''_{dc} are plotted versus log f and are represented in Figure 5. From this figure, it is clear that for all samples there is an absorption region at the different temperatures. The increase in the maximum loss peak is noticed with the increase of carbon content. As the temperature increases, the maximum loss peak also increases and becomes clear and is shifted to higher frequency.



Figure 4 The variation of permittivity (ε') and dielectric loss (ε'') with the content of HAF carbon black at different temperatures and two different frequencies.

It may be concluded that the low-frequency losses are not totally dc losses and that they may comprise Maxwell–Wagner losses, because the differences between the permittivities and conductivities of the different ingredients in the investigated samples are relatively large.

The analyses of the absorption curves are done in terms of the superposition of two absorption regions represented by two Fröhlich equations²⁴

$$arepsilon''(\omega) = \sum_{i=1}^n rac{arepsilon_s - arepsilon_\infty}{P_i} \arctan rac{\sinh P_i/2}{\cosh \ln(\omega ar au_i)}$$

where $P_i = \ln(\tau_1 | \tau_2)$ is a parameter describing the width of distribution of the relaxation times, $\bar{\tau}_i$

= $\sqrt{\tau_1 \tau_2}$ is the mean relaxation time, ε'' is the dielectric loss, and ε_s and ε_{∞} are the static permittivity and the permittivity at infinite frequency, respectively.

The obtained data are analyzed and the results of the analyses are given in Table III. The relaxation time τ_1 of the first absorption region in the lower-frequency range is the same for all carbon contents and decreases with increasing temperature. This absorption region could be attributed to Maxwell–Wagner losses. The second absorption region in the higher-frequency range may be attributed to the large aggregates caused by the polarity of the ingredients added to PVC. The increase in the relaxation time τ_2 with increasing



Figure 5 The dielectric loss (ε'') and $\varepsilon'' - \varepsilon''_{dc}$ versus frequency (f) at different temperatures for plasticized PVC filled with HAF carbon black (same notation as in Fig. 1).

carbon content may be caused by the interaction between HAF carbon black and PVC sample. Figure 6 shows an example of the analysis of the experimental measurements for PVC sample containing 40 phr carbon black at different temperatures ranging from 20 to 60° C. It is clear from this figure that the two absorption regions previously described are defined accurately as the measured points that lie on both sides of the absorption maximum. It also is clear that there is a third absorption region at higher frequencies. This region could not be defined accurately because there

Carbon Content (phr)	$\varepsilon''_{ m max/1}$	$\tau_1 \times 10^4 \\ (\text{seconds})$	$arepsilon_{ ext{max/2}}^{\prime\prime}$	$\begin{array}{c} \tau_2 \times 10^6 \\ \text{(s)} \end{array}$
A+ 20°C				
0	0.32	5 31	0.20	5 14
10	0.52	5.21	0.20	6 37
20	0.40	5.31	0.22	7 96
20	0.05	5.91	0.20	0.37
30 40	0.74	5.31	0.30	9.97 11.40
40°C	0.50	0.01	0.00	11.40
0	0.45	3 18	0.25	4 19
10	0.40	3 18	0.20 0.27	4.83
20	0.80	3 18	0.21 0.42	5.69
30	0.00	3 18	0.12	6.92
40	1.05	3 18	0.40	7 96
At 60°C	1.00	0.10	0.01	1.00
0	0.68	2.65	0.27	3 32
10	1.05	2.00 2.65	0.21	3.61
20	1.65	2.65	0.49	4 42
30	2.10	2.65	0.55	4.68
40	2.40	2.65	0.90	5.90

Table IIIRelaxation Data of Plasticized PVCFilled with Different Concentrations of HAFCarbon Black at Different Temperatures

are no experimental measurements beyond 100 kHz. It could only be approximated by the dotted lines. This absorption region may be caused by rotations that can occur by segmental rotations or local twisting motion of the main chain.

By plotting log τ_2 as a function of carbon content at different temperatures, a linear relationship is obtained, as shown in Figure 7. This relation can be used to find out the relaxation time for any other concentration of HAF carbon black.

On the other hand, the change of the electrical conductivity (σ) of samples F_0 , F_{21} , F_{22} , F_{23} , and F_{24} with temperature is shown in Figure 8. It is evident from this figure that at lower temperatures the σ of these samples is low and increases as the temperature is increased. This may have been caused by the increase of the mobility of the ionic bodies that take place as a result of the excitation by heat, leading to an increase in the conductivity of the investigated samples. Figure 8 also shows that the value of σ increases with the increase in the concentration of HAF carbon black, which is considered to be a polar material. Figure 8 shows the relation between conductivity (σ) and carbon content at temperatures from 20 to 60°C.



Figure 6 The absorption curves of plasticized PVC filled with 40 phr carbon black (×) at different temperatures. Fitting $\varepsilon'' - \varepsilon''_{dc}$ values (0) using Fröhlich terms (solid line).



Figure 7 The variation of $\log \tau_2$ with carbon black content at different temperatures.

Mechanical Properties

The variation of yield stress, tensile strength, and elongation percent versus the concentration of HAF carbon black at $23 \pm 2^{\circ}$ C is given in Table I. The presented data show that the yield stress decreases from 9.2 to $3.9N/\text{mm}^2$, the tensile strength decreases from 4.8 to $1.4N/\text{mm}^2$, and the percent elongation decreases from 141.6 to 59.5 as the content of HAF carbon black is increased to 40 phr.

Effect of Hydrated Mineral Filler Loading on Properties of Plasticized PVC

Electrical Properties

The ε' and ε'' for the samples $(F_0, F_{25}, F_{26}, \ldots, F_{36})$ were studied over the frequency region from 100 Hz to 100 kHz at room temperature (~ 27°C). It is evident from Figure 9, which represents the variation of ε' and ε'' with frequency at room temperature, that ε' increases whereas ε'' slightly decreases with the increase in the content of either of these fillers, especially at the very low frequency region. This means that the PVC sample filled with a high concentration of the hydrated filler possesses good electrical insulation character. The decrease of ε'' may be attributed to the decrease in the mobility of polymeric chains caused by both adsorption into filler surface and retardation effect of crosslinking.²⁵

Mechanical Properties

Shore hardness was measured for plasticized PVC filled with aluminium hydroxide, magnesium hydroxide, or calcium hydroxide and the obtained data are given in Table II. From these data, it is clear that hardness is increased gradually with increasing filler content up to 40 phr. Figure 10 gives a straight-line relationship in a plot of the permittivity (ε') versus shore hardness for all the investigated samples at two different frequencies of 1 and 100 kHz, indicating that the permittivity is proportional directly to the hardness.

Application of Hydrated Mineral Fillers as Fire Retardant and Smoke-Suppressing Additives for PVC Compositions

Aluminium hydroxide $[Al(OH)_3]$, magnesium hydroxide $[Mg(OH)_2]$, and calcium hydroxide $[Ca(OH)_2]$ have been identified as having properties potentially suitable for use as fire retardant additives.^{13,14,26,27} In this investigation, the treatment of PVC with a polar plasticizer (DOP) increases its flammability, but when it is filled with $Al(OH)_3$, $Mg(OH)_2$, or $Ca(OH)_2$ in different proportions, this flammability is depressed. The presented data given in Table II show that, of the hydrated mineral fillers, aluminium hydroxide of higher concentration has been found to possess the highest fire retardancy as indicated by the lowest weight loss percent whereas calcium hydroxide possesses poor fire retardancy.²⁸



Figure 8 The relation between conductivity (σ) and temperature (t) or carbon content for plasticized PVC filled with HAF carbon black.



Figure 9 The permittivity (ε') and dielectric loss (ε'') versus frequency (f) at room temperature for plasticized PVC filled with hydrated mineral fillers (same notation as in Fig. 1).

Mode of Action of Fillers on Fire Retardancy

Additionally, interaction between the filler and the polymer may influence its decomposition and also its melt viscosity, which can be especially relevant where dripping occurs during combustion. What distinguishes hydrated fire retardant fillers from so-called "inert" fillers is their ability to undergo endothermic decomposition at welldefined temperatures with concomitant release of water vapor, which reduces the heat release rate of the combustion reaction.^{29,30} It has been found³¹ that enthalpies of decomposition for Al(OH)₃ and Mg(OH)₂ are broadly similar (around 1300 kJ g⁻¹) releasing 34.5 and 31.4% by



Figure 10 The relation between permittivity (ε') and shore hardness for plasticized PVC filled with hydrated mineral fillers.

weight of water, respectively, on complete breakdown. Further differences are found between the temperatures of decomposition of these hydrated mineral fillers. Aluminium hydroxide dehydrates at temperatures between 180 and 200°C and magnesium hydroxide undergoes dehydration at temperatures in excess of 330°C, whereas calcium hydroxide is significantly more stable, decomposing at temperatures around 580°C. This may explain the differences between the three hydroxides with respect to their ability to act as fire retardant additives for polymers.

It is well-established that in addition to functioning as fire retardant additives, hydrated mineral fillers can be highly effective smoke suppressants. It is thought that the highly active oxide surface, produced when $Al(OH)_3$ or $Mg(OH)_2$ decomposes, adsorbs carbonaceous soot species, catalyzing their oxidation and lowering smoke emission.³¹

CONCLUSIONS

The study leads to the following conclusions:

White Fillers

- Of white fillers, the samples of plasticized PVC filled with calcium carbonate have the best dielectric properties (highest permittivity and lowest dielectric loss), that is, possess good electrical insulation character.
- A high degree of loading brings about deterioration of the mechanical properties. For example, the PVC sample containing 10 phr quartz has high-yield stress, tensile strength, and percent elongation whereas the sample containing 40 phr quartz has much lower values. Therefore, very low content of either of these fillers may be preferable.

HAF Carbon Black

- The samples of plasticized PVC filled with HAF carbon black have high dielectric loss, that is, possess some electrical conductivity.
- The relaxation time τ_2 of the second absorption region in the higher-frequency range increases with increasing carbon content be-

cause of the interaction between carbon black and PVC sample.

• Higher loadings of carbon black greatly decrease the yield stress, tensile strength, and percent elongation; therefore the carbon black content must be reduced as much as possible.

Hydrated Mineral Fillers

- The treatment of PVC sample with high concentrations of hydrated mineral fillers especially aluminium hydroxide produces a fire retardant electric insulating composition for electric wires and cables.
- Shore hardness for samples filled with hydrated fillers is increased gradually with increasing filler content up to 40 phr.
- The permittivity (ε') is proportional directly to shore hardness at frequencies of 1 and 100 kHz.

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