

Studies on Cenospheres as Fillers for PVC Compounds for Applications in Electrical Cables

B.R. Manjunath*, P. Sadasivamurthy[#], P.V. Reddy[#], Karickal R. Haridas*

*School of Chemical Sciences, Kannur University, Payyanur Campus, Edat P.O. 670 327, Kerala, India *Polymer Lab, Central Power Research Institute, Bangalore, India

(*E-mail: krharidas2001@yahoo.com)

Abstract: The presented work evaluated the behavior of Cenospheres as fillers for some compositions using PVC resin. Different compositions containing varying amounts of Cenospheres were made using Brabender Plasticorder. The compositions were cured using a Hot Press Tester and sheets prepared. Test specimens were cut from the sheets for the different tests as per requirements. The TGA curves at multiple heating rates were obtained. The glass transition temperatures (T_g) were measured for representative samples. It was observed that when Cenospheres are added to the PVC compositions, there was a decrease in Smoke Density Rating (SDR) values without much affecting Limiting Oxygen Index (LOI) and thermal stability. Also, the mechanical properties appeared to be sufficiently preserved. The results, on the whole, indicate that Cenospheres hold out promise as possible fillers for PVC compounds for use in electrical cable sheathing applications.

Key Words: Cenospheres, filler, PVC compound, thermogravimetry, glass transition temperature.

INTRODUCTION

For over two decades now, Cenospheres, which are lightweight, inert, hollow spheres, comprised largely of silica and alumina and filled with air and/or gases, have been used in a wide variety of products, including insulations, fire and heat protection devices, sports equipment, and automobile bodies. Due to their special characteristics, they are primarily used as high-quality, lightweight fillers. Their physical properties, particularly low density (due to hollow structure) and low thermal conductivity among others have made Cenospheres popular as fillers for polymer compositions for insulation products in the electrical industry [1].

Cenospheres are finding increasing use as substitutes for traditional fillers in sectors as diverse as ceramics, plastics, construction, recreation, automotive, energy and technology. Their use in preparing a fire-retardant coating for building materials has been reported [2]. Use of Cenospheres as reinforcing fillers in the preparation of HDPE lightweight composites has recently been reported [3]. Cenospheres have been in use for more than twenty years for improving the properties of a variety of finished consumer products. First introduced as an extender for plastic compounds (as they are compatible with plastisols, thermoplastics, latex, polyesters, epoxies, phenolic resins, and urethanes), their compatibility with specialty cements and other building materials, such as coatings and composites, was also quickly identified. Since then, Cenospheres have been used in many fields [2].

Cenospheres are formed as a by-product of coalburning power plants [4]. When pulverized coal is burned at power plants, fly ash is produced. Cenospheres are the lighter particles that are contained within the fly ash. Typically, they have a particle size range of 10 - 600 microns [5]. The composition of Cenospheres is: SiO₂ -53%, Al₂O₃ - 38%, CaO - 3.6%, K₂O - 1.5%, Fe₂O₃ - 1.3%, TiO₂ - 1.3%, MgO - 0.7%, P₂O₅ - 0.4%, Na₂O - 0.1%, Mn₂O₃ - 0.1% [5]. The main application of Cenospheres has been as inert fillers.

The objective of the present work is to study the influence of Cenospheres on the thermal behavior and flame-retardant low-smoke (FRLS) and mechanical properties of PVC-based compositions.

EXPERIMENTAL

The common chemicals used for the study are purchased locally (AR grade) and are used without further purification. Composite materials such as PVC and Martinal (high-grade) are also purchased and used as such. Cenospheres are obtained from the local plant of CPRI, Bangalore, India.

The PVC resin was first compounded (mixed) with Cenospheres as filler at filler concentrations of 0, 6, 12, 18 and 24 parts per hundred parts of resin (phr) (Table 1). The compounding was carried out in a Brabender Plasticorder (PLE 331) at 20 - 30 rpm for about 30 minutes. The torque developed was 4 - 7 N-m. The mixing temperature was 180 °C. After compounding, the compounded polymer-filler mixes were made into sheet specimens using Hot Press Tester (Labtech Co. Ltd., Seoul, Korea) maintained at a temperature of 175 °C and pressure of 90 kg/cm². The sheet specimens obtained were used for determining various properties.

The samples were subjected to thermal studies at various heating rates using Thermogravimetric Analyzer (Perkin Elmer TGA7 Model) and the data are as given in Table 2.

	Sample (Concentration in phr units)						
Substance —	C1	C2	C3	C4	Blank		
PVC	100	100	100	100	100		
TOTM	36	36	36	36	36		
CaCO3	16	16	16	16	16		
Martinal	28	28	28	28	28		
Mg(OH)2	04	04	04	04	04		
Sb2O3	03	03	03	03	03		
TBLS	08	08	08	08	08		
Calcium Stearate	0.6	0.6	0.6	0.6	0.6		
Paraffin wax	0.4	0.4	0.4	0.4	0.4		
Cenospheres	06	12	18	24			

Table 1. The composition of the samples used for study

Table 2. TGA data of the samples

	Sample									
β	Bla	ank	C	L	C	2	C	23	(24
(°C. IIIII -1)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
2	270	286	260	273	263	279	265	280	264	280
4	279	291	272	283	273	288	279	292	280	292
8	294	304	289	299	289	300	288	303	293	303
12	300	310	293	304	298	311	296	310	298	312

(a): t (°C) at 5% wt loss (b): t (°C) at 10% wt loss

RESULTS & DISCUSSION

Energetics of the reaction

Using different heating rates, a series of curves (shown in the Figure 1) are recorded, the 5% loss temperatures and 5% loss temperatures shifting to lower values with reduced scan rate.

The temperatures at 5% weight loss, as noted in Table 2, are used to calculate the E value using the following equation [6]-[8]:

- log β - 0.457(E/R) (1/T_p) = constant or - log β = constant + (- 0.457 E/R) (1 / 10³). (1/T_p*10³).

 β = heating rate,

E = energy of activation,

```
R = gas constant,
```

Tp = peak temperature (here, 5% loss temperature)

This equation is in the form of y = c + mx. Thus, slope (m) = (- 0.457 E/R) (1 / 10³) Knowing the slope, the activation energy, E, is calculated.



Figure 1. Representative TGA Curves

Evaluation of thermal rating

Reports on the application of thermal analysis for estimation of thermal life of wire enamels from the decomposition reactions are available in literature [7], [9]-[11]. The mathematical expression based on life theory and thermogravimetric theory is given by Toop [7]:

log t_f = $(E/2.303 \text{ R}\theta)$ + log $[E p(x_f) / \beta R]$ where log p(x_f) = -2.315 - $(0.457 E/R T_f)$ E = energy of activation,

- R = gas constant,
- T_f = temperature at which specific change is observed,
- β = heating rate,
- θ = thermal rating and
- t_f = time to condition at temperature θ

Because of the simplicity and reliability, this approach is generally preferred for determining thermal

rating where thermal degradation is the result of simple chemical reaction [12].

The E and the corresponding θ values are given in Table 3.

	and thermal ratings	•
Sample Name	E (KJ. K ⁻¹ . Mol ⁻¹) (cald at 5% wt loss)	θ (°C)
C1	129.93	148
C2	133.79	153
C3	147.26	162
C4	162.79	184
Blank	185.48	183

Table 3. Activation energies

Glass transition temperature studies

The glass transition temperature can be defined as the temperature at which the forces holding the distinct components of an amorphous solid together are overcome by thermally induced motions within the timescale of the experiment, so that these components become able to undergo large-scale molecular motions on this time-scale, limited mainly by the inherent resistance of each component to such flow [13]. The practical effects of the glass transition on the processing and performance characteristics of polymers are implicit in this definition [14]. The standard Tg value for PVC from literature is 75 - 82 °C [15].

For a few compositions, the Tg values were measured using the thermo mechanical analyzer (TA Instruments: TMA Q400 Model). See Table 4.

Table 4. Glass transition temperatures of the samples

of the sumples				
Sample	<i>T_g</i> (⁰ <i>C</i>)			
C1	66.55			
C3	77.63			
Blank	82.13			

Effect on properties

The Smoke Density Rating values were measured in accordance with ASTM D 2843 - 99. The lower the SDR value, the better. The Limiting Oxygen Index refers to the minimum amount of oxygen that is required to just support flaming combustion in a flowing mixture of oxygen and nitrogen and is expressed as volume percent.

The higher the LOI value, the better. The LOI test was performed as per the standard test method ASTM D 2863 - 00. The T.S. values and % elongation-at-break were determined under standard laboratory conditions in accordance with ASTM D 412. See Table 5.

Table 5. FKLS and mechanical propertie	Table 5	5. FRLS	and	mechanical	propertie
--	---------	---------	-----	------------	-----------

Sample	SDR (%)	LOI (%)	Tensile Strength (T.S.) (N/mm²)	(%) elongation- at- break
C1	68.8	34.4	16.8	139.6
C2	70.6	33.9	16.9	71.0
C3	56.3	33.5	15.0	58.5
C4	56.8	32.9	12.8	53.3
Blank	55.6	32.6	19.0	127.7

CONCLUSION

The possibility of Cenospheres as fillers for PVCbased compositions is explored. In the filler concentration range studied, the 5% and 10% loss temperatures somewhat increase with the filler concentration. The activation energy for decomposition of the compound decreases in presence of Cenospheres, the magnitude of this decrease being maximum at 6 phr of filler and becoming progressively less pronounced at higher filler concentrations. A similar trend is noted for thermal rating values as well.

The Tg value decreases in presence of Cenospheres, again the decrease being maximum at the lowest concentration studied. Lower Tg would mean increased polymer flexibility. The SDR data indicate that the optimal filler concentration may lie in the 18 - 24 phr interval. The LOI values above 30% are acceptable. Decrease in SDR without much affecting LOI values and thermal stability is noteworthy. The mechanical properties seem to be sufficiently preserved, though percentage elongation-at-break needs to be improved.

It appears that there is a critical concentration of the filler content where desired improvements in thermal and FRLS properties become optimal, the advantage being lost if concentration is increased or decreased. More detailed studies are necessary to determine the most appropriate value for Cenospheres concentration for obtaining required levels of change in thermal behavior and other properties of the compositions.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support from Central Power Research Institute (CPRI), Bangalore.

REFERENCES

- Nelson GL, Kinson PL, Quinn CB. Annual Review of Materials Science, 1974, 4, 391.
- 2. Bourbigot S, Duquesne S. J. Mater. Chem., 2007, 17, 2283.
- 3. Deepthi M.V, Sharma M, Sailaja RRN, Anantha P, Sampathkumaran P, Seetharamu *S. Mater. and Design*, 2010, 31, 2051.
- Korshak VV, Rusanov AL. Russ. Chem. Rev., 1989, 58, 588.
- Cardoso RJ, Shukla A, Bose A. J. of Mater. Sci., 2002, 37, 603.
- 6. Ozawa T. J. Thermal Anal., 1970, 2, 301.
- 7. Toop DJ. IEEE Trans. Electr. Insul., EI-6, 1971, 2, 11.
- 8. Ozawa T. Bull. Chem. Soc. Japan., 1965, 38, 1881.
- 9. David DJ. Insulation, 1967, 38.
- 10. Brown GP, Haao DT, Metlay M. *Thermochim. Acta*, 1970, 1, 441.
- 11. Krizanovsky L, Mentlik V. J. Thermal Anal., 1978, 13, 571.
- 12. Thiagarajan R, Reddy PV, Sridhar S, Ratra M. J. *Thermal Anal.*, 1990, 36, 277.
- 13. Bicerano J in Prediction of Polymer Properties, 3rd ed., Marcel Dekker, Inc., New York, 2002.
- 14. McKinney PV. J. of Appl. Polym. Sci., 1965, 9, 3359
- 15. Wilkes CE, Summers JW, Daniels CA, Berard MT in PVC Handbook. Hanser Verlag. 2005, **414**.

Notes:

- 1. TOTM Plasticizer (Tris (2-Ethylhexyl) Trimellitate) is a PVC plasticizer for use in applications where low volatility is important. The applications include wire and cable insulation.
- 2. Martinal, a white powder, is a special grade aluminium hydroxide used as a filler and flame-retardant in polymers, processed at temperatures below 200 °C.
- 3. TBLS, Tri-Basic Lead Sulfate, is a heat stabilizer for PVC resin. It is popularly used in insulation/sheathing compound for wires and cables.