

Study of Tin based CPVC compound with enhanced Dynamic Thermal Stability

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Abstract - We described the study of cost effective Tin based CPVC compound with acid scavenger, to enhance dynamic thermal stability, static stability and extrudate color stability which improves the performance of Chlorinated polyvinyl chloride (CPVC) pipes and fittings. Torque rheometers are used extensively as tools for characterizing the evolution of the feedstock component mixing process and for evaluating the mixture homogeneity and extrudate color stability.

I. INTRODUCTION

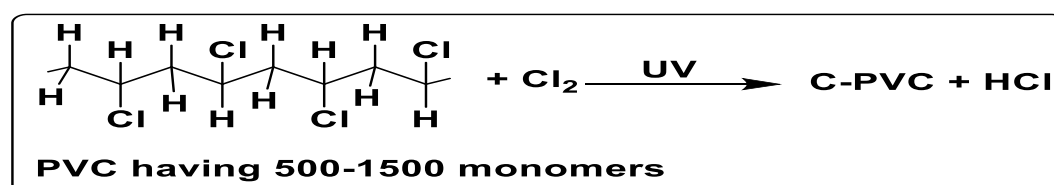
CPVC, or chlorinated polyvinyl chloride, boasts superior thermal stability compared to PVC (polyvinyl chloride) due to its increased chlorine content about 66%. However, exceeding its temperature limits can lead to degradation and difficult to process.

Considering CPVC is further product of PVC via chlorination, the reaction mechanism of CPVC can be speculated by that of PVC. Although CPVC is a derivative of PVC, it is a complex system. There are at least three different types of repeating units present in the polymer molecular structure: -CH₂-CHCl-, -CHCl-CHCl- and a small amount of -CCl₂- units (10)

CPVC is an important specialty polymer due to its high glass transition temperature, high heat deflection temperature, outstanding flame and smoke properties and chemical inertness. While the glass transition temperature of the CPVC generally increases as the amount of chlorine increases, increased chlorine content causes the CPVC to become more difficult to process and products made therefrom to become more brittle. (11)

Chemical structure of C-PVC& processing problems:

The PVC chlorination reaction as shown in scheme 1.



Scheme 1

To ensure good process ability, chlorination is restricted to 63-69% chlorine content. Thus, some vinyl chloride units remain unreacted in the chain. Since, Cl^{*} replaces H atom in the PVC backbone chain randomly, CPVC chain contains different chemical units like - Unreacted Vinyl chloride (VC), Di-chloro ethylene (DCE), and Vinylidene chloride (VDC). These groups are formed randomly, without any regularity, making CPVC more amorphous.

Due to the randomness of these three chemical units in C-PVC, it can be termed as a “Random Terpolymer”.

A typical CPVC chain have a configuration, as shown in Figure 1, where, X = 36, Y = 52 and Z = 12 approximate moles %.

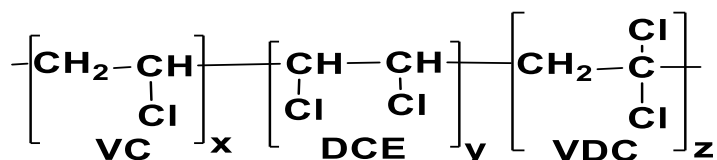


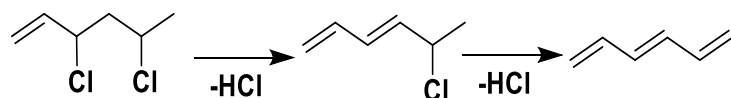
Figure 1

It implies that CPVC from different sources will have different rheology, even though its chlorine content is the same. Thus, CPVC made from different lots or different sources and different processes may have different thermal stability, processing problems and in turn have varying stress strain properties, needing fine tuning in the formulations. (1) When processing at elevated temperature, the CPVC tends to deteriorate. There is a possibility that the CPVC will deteriorate because the processing temperature and the degradation temperature are often fairly close to one another. During de-hydro chlorination, hydrogen chloride (HCl) gas is released as the chlorine atoms bonded to the carbon backbone of the CPVC chain break away. This leads to

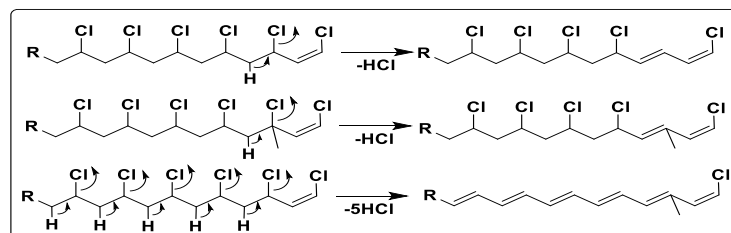
- Loss of chlorine content: Reduced chlorine content weakens the polymer chains, leading to loss of strength and rigidity.
- Formation of conjugated double bonds: The breakage of C-Cl bonds can create double bonds between carbon atoms, further reducing the material's stability.
- Potential embrittlement: Extensive de-hydro-chlorination can make the CPVC brittle and prone to cracking.

In the first degradation stage, the de-hydro chlorination of PVC macromolecules takes place and the evolved hydrogen chloride gas accelerates the progress of decomposition, leading to the formation of conjugated polyene sequences. (2)

During process CPVC compound passes between rollers (calendars) at about 200 °C, which causes elimination of some HCl at allylic defects in the polymer, as shown below (Scheme 2). Furthermore, the released HCl induces further elimination, giving a polyolefin structure with a yellow coloration (Scheme 3) , which turns red, and then black, after which the polymer becomes brittle (3)



Scheme 2



Scheme 3

Stabilizers have been developed to help deter such degradation. For example, heavy metal compounds such as tin are commonly used. However, heavy metal compounds are considered environmentally unfriendly, and there is a move to limit their use in many jurisdictions. In anticipation of increased regulation of heavy metal stabilizers in halogenated polymers, there is a desire in the industry to discover replacement stabilizers.

The practical limits for processing CPVC conventionally, are primarily determined by the chlorine content. Conventional CPVC having 63 to 68% chlorine can be formulated to perform under a hydrostatic design stress at about 80 °C, and is generally formulated with impact modifiers and flow enhancing 25 additives among other ingredients to arrive at a balance of processibility and the required physical properties. (12)

Conventional CPVC compound with tin stabilizer is sensitive to the concentration during processing, sometimes require high quantity which resulted as costly and also affect the product performance. There is, therefore, a need in the art, for a Chlorinated Poly Vinyl Chloride compound, which overcomes the aforementioned drawbacks and shortcomings.

The composition of tin based CPVC compound comprises about 80 – 90 % by weight CPVC resin, 1 -5% of butyltin marcaptide, about 2 -5 % by weight rutile titanium dioxide, about 2-4 % by oxidised high density polyethylene waxes, about 4-10 % by weight MBS impact modifier, about 1 – 4 % by weight acrylic processing aid.

In order to protect CPVC, stronger stabiliser formulations are needed, due to the requirement of higher processing temperatures for CPVC processing. Therefore, it is preferable to increase the static and dynamic thermal stability of the CPVC compound.

Acid scavengers are compounds that react with acid groups in the polymer reaction mixture to form compounds that are typically chemically inert. Such acid scavengers are often required as co-stabilizers in halogenated polymers to neutralize the acid generated during melt processing. (3)

CPVC compound with the mixture of acid scavengers like LDH and Zeolites liberated acids during processing or can stabilize by either neutralizing free hydrochloric acid by an ion exchange reaction along with tin stabilizers (6).

Table 1.

Compound	Molecular Weight in [g/mol]	[%]		[%]		[%]		[%]	
Ca(OH) ₂	74.0	54.0	Ca						
Mg(OH) ₂	58.0	41.1	Mg						
Mg ₃ Al ₂ (OH) ₁₂ CO ₃ · 3H ₂ O	468.0	20.5	Mg	11.5	Al			9.4	CO ₂
Mg ₃ ZnAl ₂ (OH) ₁₂ CO ₃ · 3H ₂ O	509.4	14.1	Mg	10.6	Al	12.8	Zn	8.6	CO ₂
Ca ₃ Al ₂ (OH) ₁₂ CO ₃ · 5H ₂ O	568.0	28.2	Ca	9.5	Al			7.7	CO ₂
Ca ₃ Al ₂ (OH) ₁₂ HPO ₃ · 3H ₂ O	552.0	29.0	Ca	9.8	Al			5.6	P
NaAlSiO ₄ · 2.25H ₂ O	182.6	12.6	Na	14.8	Al	15.4	Si		

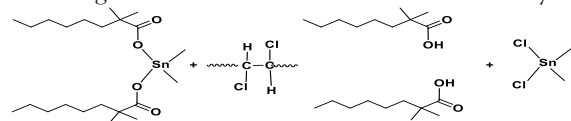
II. RESULTS AND DISCUSSION

Below the process explained the stabilizing process of CPVC with zeolites. Zeolites can stabilize by either neutralizing free hydrochloric acid or by “complexing” the Tin in Tin-containing stabilizers by an ion exchange reaction (Scheme 5 & Scheme 6). Organic tin heat stabilizers are one of the most widely used and effective heat stabilizers for CPVC, although they are gradually being replaced by more eco-friendly and non-toxic alternatives such as calcium–zinc heat stabilizers. (4) and (5).

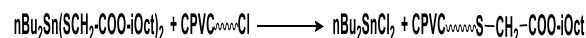
For example, Chemtura Vinyl Additives EP1044968B1 is taught using the uracil with formula I Derivative is used to stabilize chlorine-containing compound :

The patents of EP ' 968 teach zeolite can be used with Formulas I uracil derivative composition, and its dosage is about 0.1-20 To about 0.1-5 parts by weight, the chlorine-containing polymer meter based on 100 parts by weight. (7) and (8)

Exchange of liable chlorine atoms in CPVC by Organotin stabilizers (Scheme 4).

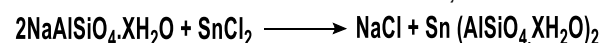


Scheme 4



Scheme 5

Stabilization mechanisms of zeolites by cation exchange as shown below.



Scheme 6

The cost effective Tin based CPVC compound comprising about 80–90 % by weight CPVC resin, 1-5% of butyltin mercaptide, about 2-5 % by weight rutile titanium dioxide, about 2–4 % by oxidized high density polyethylene waxes, about 4-10 % by weight impact modifier, about 1–4 % by weight acrylic processing aid, about 1-4 % by weight sodium aluminosilicate either alone or combination.

Chlorinated Polyvinyl chloride (CPVC) is a specially engineered thermoplastic polymer widely used for the transportation of potable Hot & Cold water in plumbing applications, water in fire sprinklers piping, and chemicals in industrial applications. As CPVC is a modified version of PVC, it has a higher level of chlorine than PVC. CPVC becomes an even higher polar polymer, and this polarity permits the use of a wide range of additives that can be incorporated into it. However, due to the higher chlorine content, the use of additives becomes very selective and hence needs more precision. Chlorinated polyvinyl chloride (CPVC) is PVC that has been chlorinated via a free radical chlorination reaction. This reaction is typically initiated by application of thermal or UV energy utilizing various approaches. In the process, chlorine gas is decomposed into free radical chlorine which is then reacted with PVC in a post-production step, essentially replacing a portion of the hydrogen in the PVC with chlorine.

Depending on the method, a varying amount of chlorine is introduced into the polymer allowing for a measured way to fine-tune the final properties. The chlorine content may vary from manufacturer to manufacturer; the base can be as low as PVC 56.7% to as high as 74% by mass, although most commercial resins have chlorine content from 63% to 69%. As the chlorine content in CPVC is increased, its glass transition temperature (T_g) increases significantly. Under normal operating conditions, CPVC becomes unstable at 70% mass of chlorine.

In an embodiment of the invention, the pigment is preferably titanium dioxide can be included and preferably from about 2 parts to 4 phr. The preferred pigment is titanium dioxide.

The CPVC compound may also include impact modifier, the impact modifier may be acrylic impact modifier is a composite interpolymer comprising a multi-phase acrylic base material. Acrylic impact modifiers are polyacrylates including (C4-C12) acrylate homo or copolymers, second stage graft copolymerized with methyl methacrylate and styrene, poly(ethylhexyl acrylate-co-butyl-acrylate) graft copolymerized with styrene, and/or acrylonitrile and/or methyl methacrylate; polybutyl acrylate graft polymerized with acrylonitrile and styrene. Methyl butadiene styrene (“MBS”) impact modifiers can also be added to the compounds of the present invention. MBS polymers are graft polymers. Generally, MBS impact modifiers are prepared by polymerizing methyl methacrylate or mixtures of methyl methacrylate with other monomers in the presence of polybutadiene or polybutadiene-styrene rubbers.

An inventive stabilizer composition may further comprise lubricants such as montan wax, fatty acid esters, purified or hydrogenated natural or synthetic triglycerides or partial esters, polyethylene waxes, amide waxes, chloro-paraffins, glyceryl esters or alkaline earth metal soaps. Preferred lubricants are oxidized polyethylene and levels generally ranging from about 4 % to 10 %..

Most of the commercially available processing aids are a high molecular weight polymer comprising as a main monomer only methacrylate having an excellent compatibility with a vinyl chloride resin, or a methyl methacrylate-based polymer composed of methyl methacrylate monomer as a main component; and a high molecular weight (M_w: 500,000 to 5,000,000g/mole) polymer, as an auxiliary component, obtained by emulsion-copolymerizing a small quantity of an acrylate, methacrylate, or nitrile-based unsaturated compound having a double bond or an aromatic monomer containing a double bond. . Processing aid employed at level generally ranging from about 1-4 %.

The CPVC compound is characterized by an effective amount of a stabilized sodium aluminosilicate, basically comprise a three-dimensional framework of SiO₄ and AlO₄ tetrahedra. The tetrahedra are cross-linked by

splitting oxygen atoms, so that the ratio of oxygen atoms to the total aluminum and silicon atoms is equal to 2. The spaces between the tetrahedra of the aluminosilicate zeolite are usually occupied by water. Zeolites can be either natural or synthetic. The basic formula for all aluminosilicate zeolites is represented as follows: $M^{2+}_n O : [Al_2 O_3]_x : [SiO_2]_y : [H_2 O]_z$ wherein M represents a metal, n represents the valency of the metal, and X and Y and Z vary for each particular aluminosilicate zeolite. The sodium aluminosilicate incorporated in the CPVC compound at level generally ranging from about 1 % to 4 %.

Table 2: Composition of control and example1 and 2 CPVC compound in PHR

S. No	Ingredient	Concentration in Parts Per Hundred Resin (PHR)		
		Control	Sample 1	Sample 2
1	CPVC Resin	100	100	100
2	Organotin stabilizer	2.5	2.5	2.5
3	Pigment	3.0	3.0	3.0
4	Impact Modifier	5.6	5.6	5.6
5	Processing Aid	2.0	2.0	2.0
6	Lubricants	2.6	2.6	2.6
7	Acid scavenger	0	1.0	2.0

Brabender graph comparison with regular / conventional CPVC compound and 1 & 2 PHR addition with zeolite observed significant change in thermal stability and the extrudate removed from the brabender rheometer after 15 min also found improved colour stability. Brabender graph (Fig.1) comparison with regular / conventional CPVC compound and 1 & 2 PHR addition with zeolite observed significant change in thermal stability the extrudate removed from the brabender rheometer after 21 min also found improved colour stability.

Vertical band of graph represents Torque and Temperature. Horizontal represents time. Observation duration 21 min. Red colour graph represents regular compound which is without Zeolite and found Torque and Time changed around 10min time (between 540 to 720 sec). The second graph green colour represents the recipe used with 1PHR of Zeolite. Where the stability increased and graph change observed around 15min (between 900 to 1080 sec). Blue color represents the recipe used with 2PHR of Zeolite and the stability increased and observed graph change at 20min. (Between 1080 to 1260 sec). Here observed stability increase by adding zeolites to conventional compounds) Figure s1, ESI).

CPVC compound and 1 & 2 PHR addition with zeolite observed significant change in thermal stability and the extrudate (Fig:2) removed from the brabender rheometer after 21 min also found improved colour stability. Also check stability using Congo red apparatus and found significant improvement in static Thermal stability (Figure s3, ESI).

Figure 4 shows the TGA and DTG curves for the synthesized samples. The data obtained from this curve are the onset of degradation (T5%), half decomposing temperature (T50%), and maximum decomposition temperature (TMax). These data clearly show that the three temperatures introduced above in composites containing Zeolite are higher than pure regular. In three tested samples, zeolite at 2phr dosage, has higher TMax than the other two samples. From these data, it can be concluded that the presence of zeolite can improve CPVC resistance to thermal degradation. This thermal stability can be described by the good dispersion of zeolite particles, especially at optimized dosage in the CPVC matrix.

The static stability of CPVC (Chlorinated Polyvinyl Chloride) compound was tested at 180°C in a hot air oven. The results, as shown in Fig. 5, indicated a significant improvement in stability when the compound was treated with zeolite, particularly at concentrations of 1 and 2 PHR (Parts per Hundred Resin), when compared to the sample that did not contain any zeolite. (14)

III. CONCLUSION

The Brabender torque rheometer graphs (Figure 2), the color of the extrudate compound (Figure 3), the Congo red test (Figure 3), the TGA curve (Figure 4), and the hot air oven exposure test (Figure 5) all indicated that the control sample and the samples containing Zeolite (sodium aluminosilicate) at 1.0 PHR and 2.0 PHR exhibited higher thermal stability and improved color stability.

CONFLICTS OF THE INTREST

“There are no conflicts to declare”.

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Figure 1: Dynamic thermal stability of CPVC compound in brabender torque rheometer.

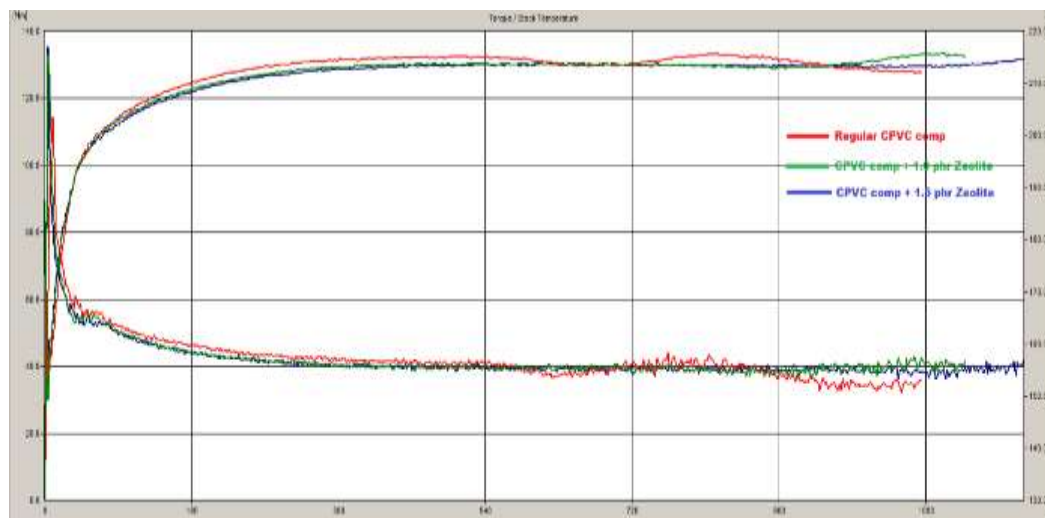


Figure 2: Colour stability of extrudate compound of CPVC compound in Brabender torque rheometer.

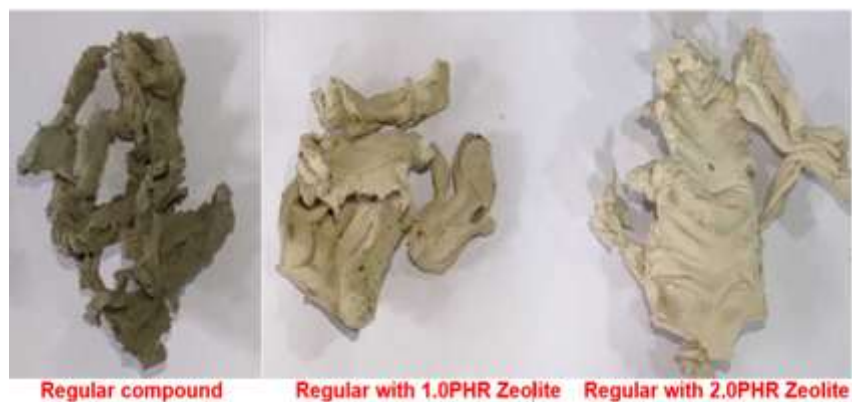


Figure 3: Static stability test results

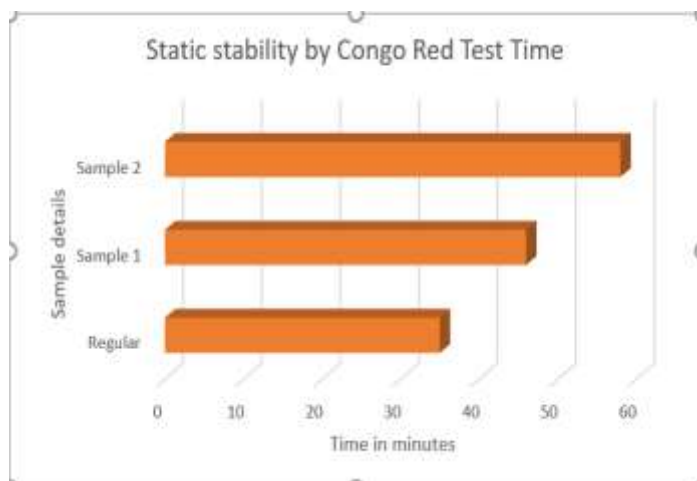


Figure 4: Thermogravimetric (TGA) curves and DTG thermograms of the PVC samples.

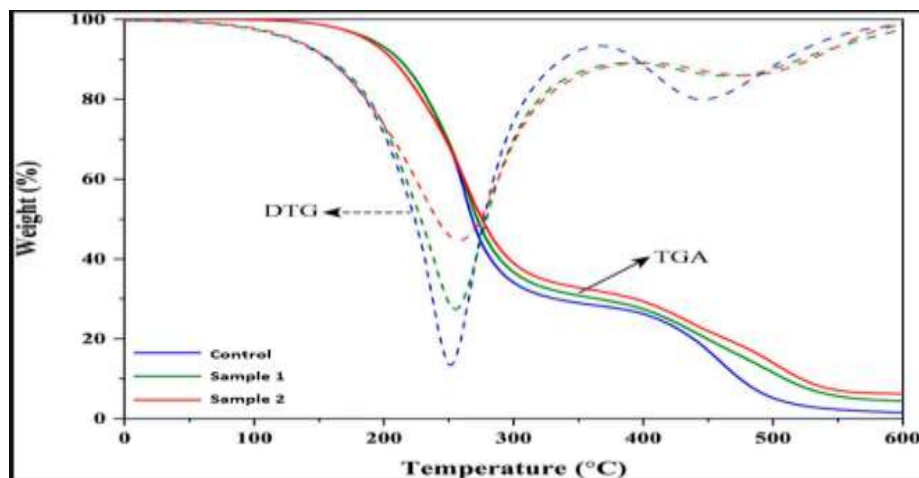


Figure 5: Static stability test at 180°C in air oven

Static stability at 180°C exposure results					
Time	10	20	30	40	50
Regular					
Sample 1					
Sample 2					