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Synergistic Effect of Sodium Aluminium Silicate and Fischer-Tropsch Waxes on the Thermal Stability of CPVC Compounds

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Abstract *- A Chlorinated Polyvinyl Chloride (CPVC) compound with enhanced static and dynamic thermal stability, improving the performance of pipes and fittings, is disclosed. The CPVC compound broadly comprises the following components: a Chlorinated Polyvinyl Chloride resin, an organotin stabilizer, pigments, lubricants, an impact modifier, a processing aid, and an acid scavenger.*

The disclosed CPVC compound provides the following synergistic advantages:

- *Requires a lower concentration of the tin stabilizer.*
- *Enables easy processing without scorching, ensuring a uniform surface appearance for pipes and fittings, thereby enhancing their aesthetic quality.*
- *Improves both static and dynamic thermal stability, contributing to superior performance and durability.*

I. INTRODUCTION:

Chlorinated Polyvinyl Chloride (CPVC) is well-known for its suitability in hot water applications, among other advantageous characteristics. CPVC typically contains over 66% bound chlorine. Due to its exceptional flame and smoke resistance, high glass transition temperature, elevated heat deflection temperature, and chemical inertness, CPVC is considered a significant specialty polymer.

Generally, an increase in chlorine content leads to a higher glass transition temperature in CPVC. However, CPVC is also known for its low impact resistance. As the chlorine concentration increases, the material becomes more difficult to process and more brittle. Most efforts in CPVC development have focused on rigid applications, where achieving an optimal balance of impact strength and dimensional stability under heat is crucial.

When processed at elevated temperatures, CPVC tends to deteriorate. This deterioration is attributed to the fact that the processing temperature is often very close to the degradation temperature. It is believed that the halide acid produced during CPVC processing causes or catalyzes degradation, which may attack and corrode the components of processing equipment. (1)

Due to its higher chlorine content compared to PVC, CPVC requires distinct formulations tailored to its unique properties. To protect CPVC during processing, stronger stabilizer formulations are necessary to withstand the higher temperatures required. Consequently, enhancing the static and dynamic thermal stability of the CPVC compound is essential for improved processing performance and durability.

The processing of conventional CPVC compounds with tin stabilizers is a challenging task due to the early degradation of CPVC resin at elevated temperatures. Enhancing the processing requires a high concentration of tin stabilizers, which is not only costly but also adversely impacts the product's performance.(1) and (2).

Therefore, there is a pressing need in the industry for a Chlorinated Polyvinyl Chloride (CPVC) compound that addresses these drawbacks and overcomes the associated limitations.

Potential Embrittlement: Extensive de-hydro-chlorination can make 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.

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.

Conventional CPVC compounds with tin stabilizers are sensitive to the concentration during processing, sometimes requiring high quantities, which results in increased costs and affects product performance. There is, therefore, a need in the art for a Chlorinated Polyvinyl Chloride compound that overcomes the aforementioned drawbacks and shortcomings.

The composition of a tin-based CPVC compound comprises 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 MBS impact modifier, and about 1–4% by weight acrylic processing aid.

In order to protect CPVC, stronger stabilizer 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. (3)

Acid Scavengers: 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.CPVC compounds with a mixture of acid scavengers like LDH and zeolites can stabilize by either neutralizing free hydrochloric acid through an ion exchange reaction or by complexing the tin in tin-containing stabilizers.

II. EXPRIMENTS

The cost effective Tin based CPVC compound comprising about 80–90 % by weight CPVC resin, 1-5% of butyltin marcaptide, 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%, Fischer tropsch wax about 0.5-1.5% and about 1 -3% 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 and cold water in plumbing applications, water in fire sprinkler 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 the 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.(4) and (15)

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 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 (Tg) increases significantly. Under normal operating conditions, CPVC becomes unstable at 70% mass of chlorine.

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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 (Mw: 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 an double bond or an aromatic monomer containing an 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 SiO_4 and AlO_4 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: $M_{2/n}O: [Al_2O_3]_x : [SiO_2]_y : [H_2O]_z$ 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 %. (6) (11) and (14)

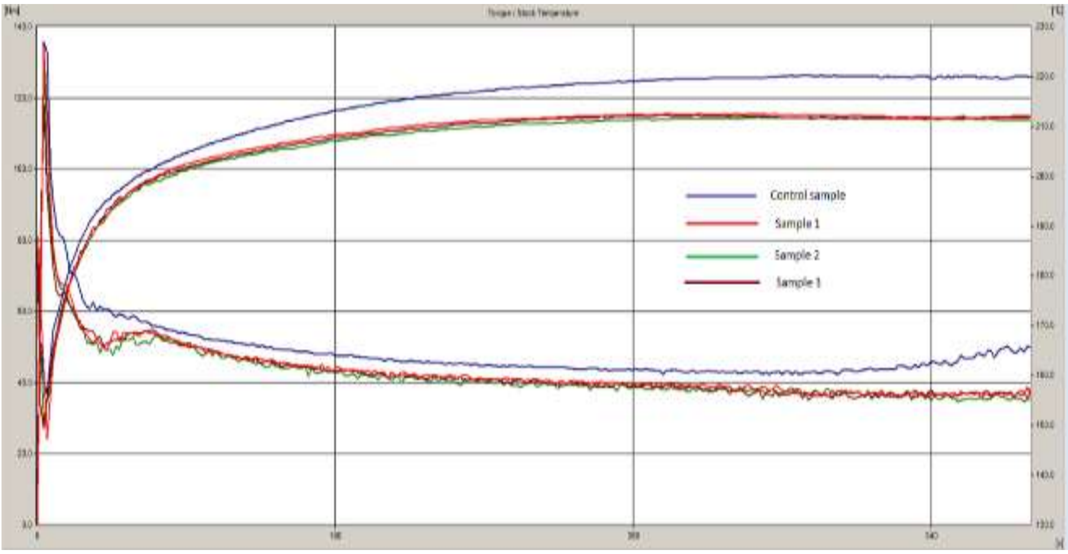
Fischer-Tropsch wax has obvious synergistic effect with stabilizers for CPVC processing, which can effectively extend the heat stabilization time and increase the adjustment range of process temperature. High melting point Fischer-Tropsch wax is especially obvious in the processing of CPVC resin, because the processing parameters of CPVC resin are narrowly adjusted to increase the processing difficulty of the product. The choice of high melting point Fischer-Tropsch wax can effectively improve the later lubrication of CPVC product processing, enhance the appearance of the product and mechanical properties. Fischer-Tropsch synthetic waxes have small molecular weight, low melt viscosity, high melting point, narrow melting range, and the same lubricating effect can be achieved with less dosage, reducing the negative impact of lubricants on the physical and mechanical properties of products. Fischer-Tropsch waxes employed at level generally in the range of 0.5 to 1.0 % (9) and (16).

Table 1: Composition of Sample 1, 2, 3 and 4 CPVC compounds in PHR.

S. No	**Ingredient**	**Concentration in Parts Per Hundred Resin (phr)**			
		Sample 1	**Sample 2**	**Sample 3**	**Sample 4**
1	CPVC Resin	100	100	100	100
2	Organotin stabilizer	2.5	2.5	2.5	2.5
3	Pigment	3.0	3.0	3.0	3.0
4	Impact Modifier	5.6	5.6	5.6	5.6
5	Processing Aid	2.0	2.0	2.0	2.0
6	Lubricants	2.6	2.6	2.6	2.6
7	FT wax	0	0.8	0.8	0.8
8	Acid scavenger	0	0.5	1.0	1.5

III. TESTING AND RESULTS

DYNAMIC THERMAL STABILITY:



Graph 1: Dynamic stability test by Brabender Plastograph EC.

The Dynamic thermal stability were tested by the torque rheometer (make-Brabender Plastograph EC). The test carried out at 190°C temperature at 35 rpm. From the graph 1 it is observed the dynamic thermal stability increased due to the synergistic effect of Fischer-Tropsch waxes and Acid scavenger.(10)

CONGO RED TEST FOR STATIC THERMAL STABILITY:

This test method is intended to determine the thermal stability of a CPVC compound when processed at a high temperature. The method is applicable to all CPVC compounds, copolymers and products based on them. A test specimen of the CPVC material is heated at a defined temperature, normally 180°C. The time taken for the material to degrade, indicated by evolution of hydrogen chloride is determined by a change of colour in a Congo Red test paper.

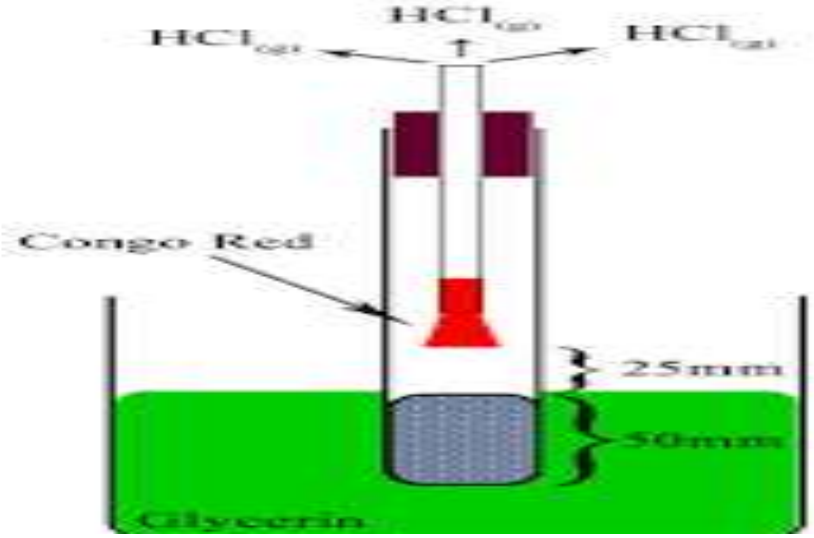
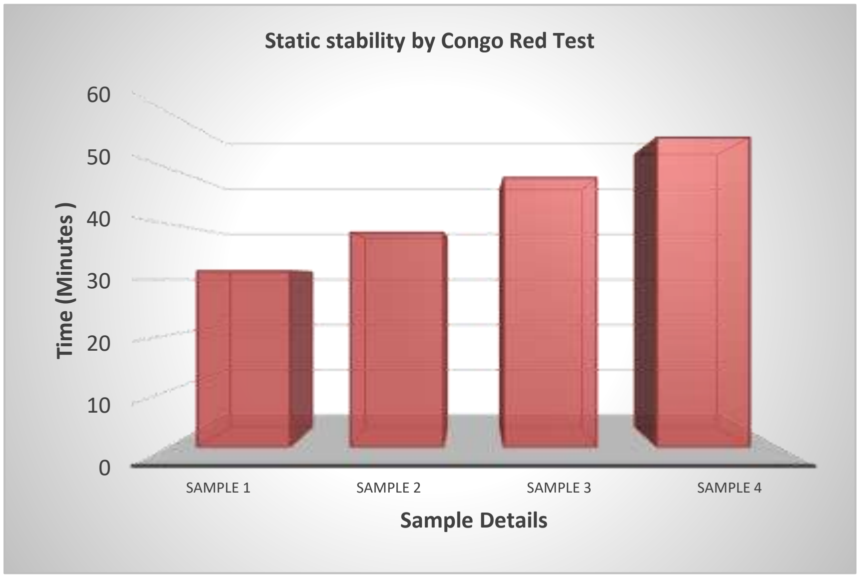
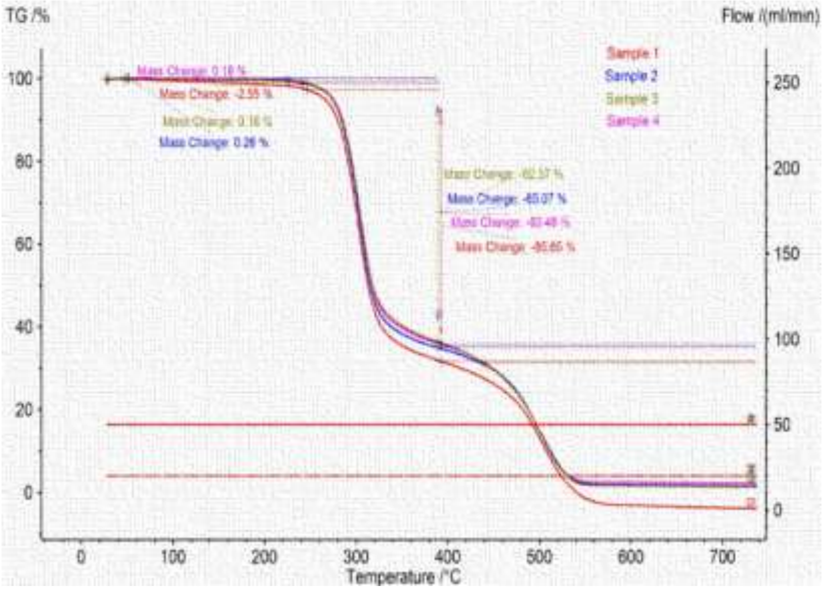


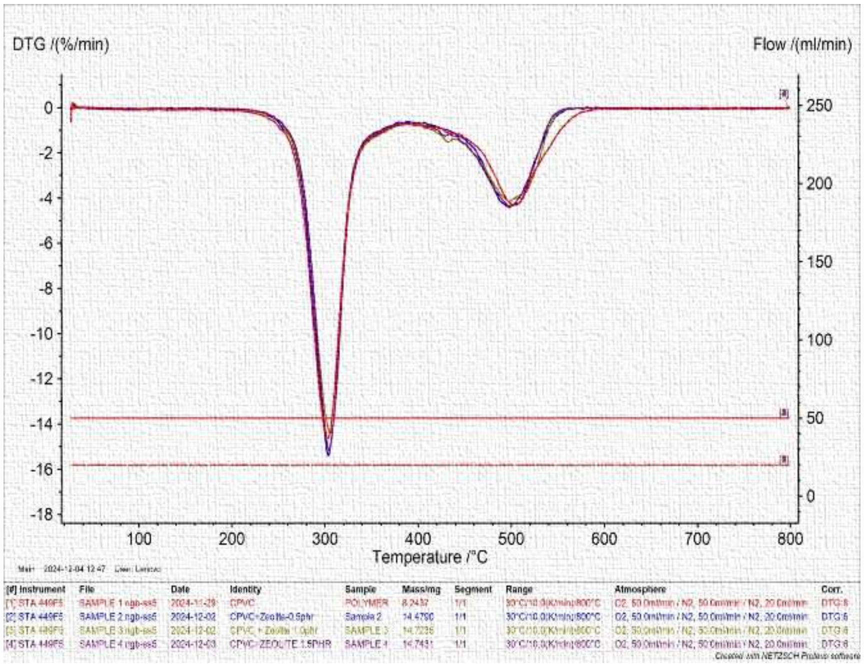
Figure: Schematic of the device for the Congo red test.



The graph 1 shows the results of static stability of the different CPVC compound by congo red test. From the graph 1 it was observed that the static stability improves by the synergism of the Fischer-Tropsch wax and the sodium aluminum silicate.(5)



Graph 2: TGA curves of CPVC compounds.



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 449F5	SAMPLE 1.ngb-ss5	2024-11-29	CPVC	POLYMER	8.2437	1/1	30°C/10.0(K/min)/800°C	O2, 50.0ml/min / N2, 50.0ml/min / N2, 20.0ml/min	DTG:8
[2] STA 449F5	SAMPLE 2.ngb-ss5	2024-12-02	CPVC+Zeolite-0.5phr	Sample 2	14.4790	1/1	30°C/10.0(K/min)/800°C	O2, 50.0ml/min / N2, 50.0ml/min / N2, 20.0ml/min	DTG:8
[3] STA 449F5	SAMPLE 3.ngb-ss5	2024-12-02	CPVC + Zeolite 1.0phr	SAMPLE 3	14.7235	1/1	30°C/10.0(K/min)/800°C	O2, 50.0ml/min / N2, 50.0ml/min / N2, 20.0ml/min	DTG:8
[4] STA 449F5	SAMPLE 4.ngb-ss5	2024-12-03	CPVC+ZEOLITE 1.5PHR	SAMPLE 4	14.7431	1/1	30°C/10.0(K/min)/800°C	O2, 50.0ml/min / N2, 50.0ml/min / N2, 20.0ml/min	DTG:8

Graph 3: DTA curves of the CPVC compounds.

The result of the thermogravimetric analysis of CPVC compounds is presented in Graph1 and 2. Examination of the thermal degradation characteristics of CPVC reveals no mass loss observed up to 260℃. Beyond this temperature, the CPVC's thermal degradation process is divided into two distinct stages: the first extends from 260 to 370℃, followed by the second from 370 to 600℃. From the TGA graph it was observed that in the all stages the mass loss decreases from sample 1 to sample 4 which shows that the synergism of the Fischer-Tropsch wax with the Zeolite as a results improves the thermal stability of the CPVC compound.(9) and (12)

Table 2: Accelerated weathering test results for the control and batch samples:

Exposure time (Hrs)	Change in colour dE value			
	Regular	Sample 1	Sample 2	Sample 3
24	0.826	1.2	0.991	1.485
48	5.68	3.649	3.546	2.964
72	10.856	7.461	6.611	4.566
96	14.199	10.393	10.121	7.073
120	17.019	14.481	12.496	8.798
144	17.627	15.202	13.283	10.025
168	17.824	15.459	13.422	11.987
192	18.447	15.635	13.691	12.056

III. CONCLUSION

Graph 2:Graph for the UV Accelerated Weathering test.

The accelerated weathering test carried out as per the ASTM standard ASTM G154 cycle 1 by using UVA-340 lamps with the irradiance 0.77 W/m^2/nm, exposure cycle 8 hours UV at 60(±3) °C black panel temperature and 4 hours condensation at 50(±3) °C black panel temperature. The test duration was 192 hours and It was found the accelerated weathering properties improves in the batch sample compare with the control sample. It shows the by synergistic effect of Fischer-Tropsch wax and acid scavenger which is arrest the early degradation and improves the outdoor service life of the product.

IV CONCLUSION

From the Congo red test graph 1 and thermogravimetric analysis (TGA) graphs 1and 2, it was observed that the CPVC compound samples 2, 3 and 4 improves the thermal stability than the sample 1 because of the synergistic properties of the Fischer-Tropsch wax and the acid scavenger zeolite.

CONFLICTS OF THE INTREST

"There are no conflicts to declare".

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