



Experimental study and comparative assessment on heat stabilized UPVC parts based on alternative standard test methods

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The quality of the manufactured poly(vinyl chloride) (PVC) products depends on the type and amount of modifier or additive used in the formulation. Determination of this quality was performed according to the standard tests. In this study swelling test and degree of gelation, were used along with the two comparative methods including Differential Scanning Calorimetry (DSC) and tensile tests. For this purpose, the PVC samples stabilized with the three type's commercial stabilizers, including commercial lead-based, Ca/Zn and Organic Based Stabilizers (OBS) conducted with melt mix method in the laboratory internal mixer. In terms of thermal properties by the relation between the measured enthalpy of fusion of two crystallites phases, with chemical swelling results proved the qualitative results of the dichloromethane resistance test (DCMT). Glass transition temperature of the modified PVC with all examined heat stabilizers were determined equal to 79°C for PVC stabilized with Ca/Zn compared with the value of about 77°C in lead stabilized PVC and 76°C in OBS stabilized PVC. The onset temperature corresponded to melting point of primary crystallites represented in highest value, around 195.1°C for PVC - Ca/Zn sample. Quantified degree of gelation measured with enthalpy ratio of two crystalline phases showed good agreement with the results of the chemical swelling test. From mechanical analysis, tensile strength at room temperature of PVC stabilized with Ca/Zn stabilizer showed the highest value among the other stabilizers. From all the results, it is evident that Ca/Zn showed high potential use as a safe and effective heat stabilizer for PVC to substitute traditional lead compounds. This is an open access article which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.22034/ASAS.2022.163112] All rights reserved.

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Introduction

Un-plasticized form of Poly(vinyl chloride) (UPVC) is widely used in many products such as, pipes, profile, insulator, adhesives, toys and other applications[1]. This is known, in high temperature, PVC to degrade by release the HCl, and this evidence could be accelerates the thermal degradation process and the PVC sample color changed to yellow, orange, red, brown, and black[2]. This thermal degradation of PVC samples could be affected mechanically, thermal as well as physical properties of this polymer[2, 3].

In the manufactures, PVC resin could be mixed with additives such as plasticizers in order to produce flexible PVC products. On the other hand PVC resin could be mixed with additives such as thermal stabilizers and processed in high temperature up to 200°C using extruder to form different products like pipes or window frames [4, 5].

Lead based stabilizers are used to improve the process thermal degradation in many manufacture, but this compound are limited as stabilizers used in PVC for

their toxicity[6]. Alternative heat stabilizer include calcium/zinc based products that are typical nontoxic heat stabilizers, another safe heat stabilizer that used in recent years, named organic based stabilizers (OBS) that provide safe and good stabilization for UPVC products, such as uracil derivatives, eugenol [7-9].

In all PVC applications, the quality of the PVC production process determines according to the degree of gel or its melting behavior, which directly affected on the final quality of the manufactured parts. In addition, during the forming process (such as injection, pipe extrusion, film extrusion, etc.), the temperature of the forming operation is the most effective parameter determining the degree of gelation of PVC[10]. For example, if the temperature of the forming process is low, the rate of gelatin of PVC will be low, and also if this temperature is high, it can lead to the destruction of the PVC structure and reduce its physical and mechanical properties[11, 12].

In hence, some properties such as mechanical behavior of PVC products are affected by the processing temperature and the degree of swelling or gelation. This factor is defined as the ratio of the amount of small

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new-formed second-ary crystallites by melting point below the processing temperature[13].

The above-mentioned solutions require the use of toxic solvents, but the safety regulation restricted the some uses of this substance (such as REACH), re-lated standards and test methods led to the proposed of alternative tests to meas-ure the degree of gelation of PVC pipes [14, 15].

Due to the high importance of the degree of gelation in determining the properties of PVC-based product, some alternative quantitative methods have been developed for the calculation of this parameter[16].

The Differential Scanning Calorimetry (DSC) device, is provided quantita-tive method for calculating the degree of PVC gelation. In fact, the DSC can de-tect the amount of crystals from the melting process, as well as the part of the structure that is not melted or gelled in the production process[17-19].

The latest versions of national (INSO 13361-2-A1) and international stand-ards (ISO 1452-2) for PVC pipe systems, contain the dichloromethane resistance test (DCMT) recommended two alternative tests for determining the degree of gelation[20, 21]. These two tests can be adopted in compliance with the INSO 13361-2-A1, including the tensile test [22,23], and the other alternative method proposed by ISO standards related to PVC products, is based on the ISO 1452-2 [20], for determination of ‘onset temperature’ in PVC pipes according to ISO 18373-1 by DSC[21].

The main objective of this research the degree of gelation of PVC samples based on traditional lead stabilizer was investigated and compared by these al-ternative different standard methods and compared with safe commercial heat stabilizers i.e. Ca/Zn stabilizer and commercial organic based stabilizer in me-chanical and thermal analysis.

Materials and Methods

In this study, PVC resin was purchased from Persian Gulf Petrochemical in-dustris Co, Iran., the additives used in PVC compound are calcium carbonate as filler and calcium zinc (Ca/Zn) stabilizer as heat stabilizers supplied by polymer pajouhan danesh madar Co. All chemical solvent such as dichloromethane (DCM) and other used chemicals were purchased from Merck Chemical Co.

All PVC samples were prepared from PVC resin, calcium carbonate (10 mass%) and heat stabilizers (3 mass%) including commercial lead stabilizer (P-lead), Ca/Zn stabilizer (P-cazn) and OBS stabilizer (P-obs), were mixed to-gether up to 105°C using laboratory-scale equipment (internal mixer plastograph 70) with rotation speed of 50 rpm for 8 min[24]. The mixed samples obtained were moulded into sheets by laboratory hydraulic hot press machine (CEAST It-aly) at 150 °C and a pressure of 10 MPa for 6 min[24]. The PVC formulation used in this study was detailed in Table 1. Test specimens cutted from samples were kept for 16h at a temperature of (23 ± 2) °C and a relative humidity of (50 ± 5) %.

All prepared PVC samples were characterized by solvent resistance tests, DSC and tensile tests for comparison of this methods and effect of different type of commercial heat stabilizers in the formulation of these products[21, 22].

The DCMT is performed in compliance with the modified method of standard ISO 9852[25]. Test specimen with (20mm×6mm×100mm) dimension was cutted from molded samples for this test. To avoid dissolution problems affecting sample dimension and weighing compared to the standard size, the immersion time was reduced to 3 h. The specimens were previously immersed in a container equipped with an ice cooling system in the exhaust hood. The examined samples are evaluated for evidence of any chemically attacked and, subsequently, used for comparison with the results obtained from other alternative methods (tensile and DSC).

Thermal properties were determined by differential scanning calorimetry using a DSC (Cometech DSC-500B, Taiwan). Samples of about 14 mg were conditioned in aluminum pans and heated at 20 °C/min under an inert atmosphere of N2. An empty pan was used as reference during the determination. Then, sample were heated to 250°C at 20°C/min and held isothermally for 3 min at 200°C to eliminate previous thermal history accordance with EN ISO 1452-2 and ISO 18373-1 [20, 21]. Four specimens of each sample are tested accordance with ISO 18373-1.

Tensile data including tensile strength, modulus of elasticity and elongation at break for the PVC Samples were obtained at 23±2 °C using a gotech universal ten-

Table 1- The composition of the samples (given in mass%)

sample	PVC resin	CaCO ₃	Lead stabilizer	Ca/Zn stabilizer	OBS stabilizer
P-neat	100	0	0	0	0
P-lead	87	10	3	0	0
P-cazn	87	10	0	3	0
P-obs	87	10	0	0	3

sile testing machine. Experiments were conducted on at least three specimens in each formulation, at a cross-head rate of 50 mm min⁻¹.

Tensile testing were measured based on ISO 6259-1,2 standard test method[22,23]. The tensile force was applied to the samples were loaded in the grips of the testing machine, Young's modulus and its displacement were monitored and plotted on a stress-strain curve until failure.

Results and Discussion

Dichloromethane swelling test (DCMT)

During the production process of a piece of PVC, when the material is heated, the smallest grains are first melted. During the melting process, these molten grains become to form a semi-gel-gel state known as sintering or gelation[19]. The high rate of gelling or curing during the production process of PVC parts indicates the uniformity and cohesion of the composition and increases the physical, mechanical and chemical properties of the part [26].

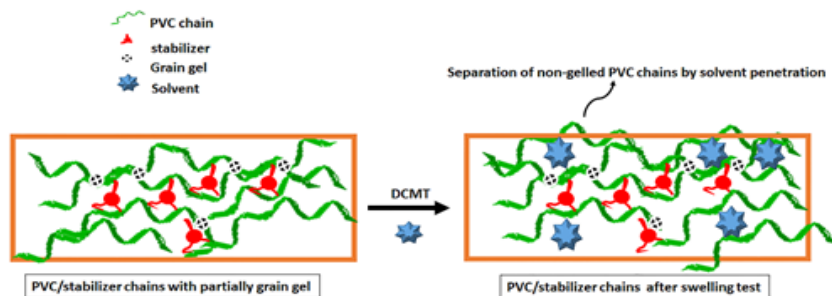
In fact, poor quality PVC part, has not been properly mixed or homogenized, the non-gelled section of PVC chains were separated from the surface part and evidence of these defect appears in the form of swelling and softening of the surface layer (scheme 1).

However, for a selected dimension, solvent absorption and edge deformation are observed in all test specimen, but the changing in weight of the sample compare with neat PVC and also evidence of any chemically swelling on the surface of test specimen were considered for fail/pass of result record and presented in Table 2.

The DCMT results showed that lead stabilizer in PVC matrix had no enough interaction with the PVC chains in the preparation method and process temperature

Table 2 -The result of DCMT

sample	Weight change (mass %)	DCMT result
P-cazn	8	pass
P-lead	15	failed
P-obs	10	pass



Scheme 1- DCMT analysis in PVC part

against two other stabilizers and maybe some of the intermolecular interaction collapse in moulding process. Although solvent immersion tests give us information about the proper curing and gelation of a PVC product, but this test do not give us accurate information about the PVC process history and only indicate whether the curing is acceptable or rejected.

As mentioned, the amount of gelling depends on the temperature of the process, and the higher the temperature, the higher the amount of gelling. The information about this event is estimated by the DSC device.

With the help of DSC analysis, a quantitative method was provided for calculation of degree of gelation in PVC. In fact, the DSC can detect the amount of crystals from the melting process, as well as the section of the structure that is not melted or gelled in the production process[27].

3.2 DSC characterization

DSC test was performed in order to determine the glass transition temperature (Tg), the melting of primary crystallites in high temperature (TonsetB), first peak corresponding to the melting of secondary crystallites in lower temperature (TonsetA) and the enthalpies of these two peaks as a quantitative PVC gelation level measurement (see Eq. 1): are summarized in Table3.

$$\text{degree of gelation} = \frac{\Delta H_A}{\Delta H_B + \Delta H_A} \times 1 \quad (1)$$

According to the standards, the degree of gelation of samples can be evaluated by the relevancy among the enthalpy of fusion of primary and secondary crystallites, which are determined from DSC curves[17, 21]. Two types of crystallites have been described for PVC: primary crystallites resulting from the polymerization and secondary crystallites formed upon processing [2, 26] and decrease of crystallinity was observed by the enhancement of the gelation level (when primary crystallites are replaced by secondary ones) [26]

Considering the DSC patterns the integration limits of the two endotherms are well defined, enthalpy values can be determined (see Figure 1) and a gelation level can be calculated.

Table 3- thermal and degree of gelation result of sample

sample	Tg	TonsetA	TonsetB	ΔH_A (J/g)	ΔH_B (J/g)	Degree of gelation
P-lead	77	110.8	188.0	9.83	2.16	82
P-cazn	79	109.3	195.1	11.70	1.97	86
P-obs	76	105.9	191.6	12.35	2.05	86

The glass transition of samples showed a value of about 76°C, 79°C, and 77°C corresponding to P-obs, P-cazn and P-lead, respectively. This temperature followed immediately by a small relaxation phenomenon.

The incorporation of the lead stabilizer into the PVC chain resulted lower (Tg) of 77°C as compared with other stabilizers. A slight increase of Tg for P-cazn was observed, indicating an enhanced immobilization of chains due to the stronger interaction of this additive to the PVC chains. The Tg is principally controlled by the structure and interaction of the stabilizer in the polymer matrix. An enhancement in the Tg of the P-cazn sample can be attributed to the good dispersion of Ca/Zn particles in PVC. The decreased value of Tg in P-lead (Table 3) could be explained by a destruction in the number of intermolecular interaction between the lead stabilizer and PVC chains.

In P-lead sample a broad endotherm peak zone “A” related to the melting of partly gelled PVC and also corresponded to the melting of secondary crystallites. This peak starts at approximately in 110.8°C (TonsetA). An onset temperature at about 188.0 °C which is proposed to be the processing temperature (TonsetB), indicates the PVC melting temperature. A broad endotherm (zone B) which is proposed to be the melting of the previously non-gelled part of the PVC related to the primary crystallites resulting from the polymerization. According to the calculated degree of gelation in Table 3, this percentage value for P-lead sample showed a decreased equal to 82% against the 86% for P-cazn and P-obs, which matched to the DCMT results and showed that the purchased dimension of these samples may have a negative influence on the swelling effect, probably due to the introduction of defects by cutting stage, which is not visible to the naked eye, and also some interaction of this stabilizer was collapsed in the preparation process.

From the data shown in Figure 1, it can be seen that the results of the onset temperature obtained in the DSC method as well as the DCMT results for comparison purposes.

Mechanical properties.

Stabilizers are often added to a PVC formulation to improve the thermal properties during the manufacturing, improve the physical and mechanical properties of the final product.

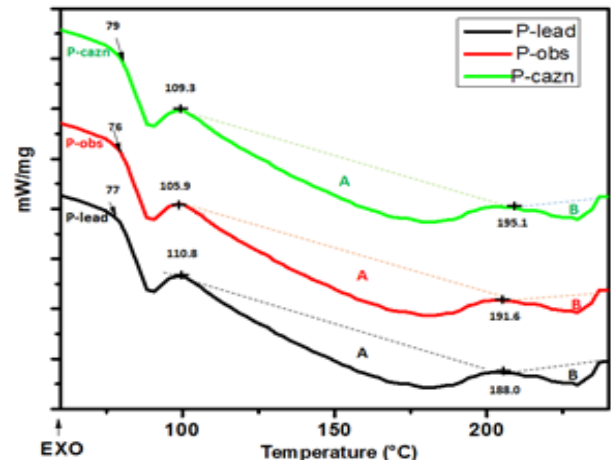


Figure 1 - DSC curves of samples

Then, the tensile test is the other commonly used method to characterize the efficiency of the processability and preparation method of different formulation samples by using different stabilizer types.

Tensile tests to be conducted to identify the mechanical properties for compared with thermal and swelling properties for all samples.

Tensile tests of P-obs, P-cazn, and P-lead including the tensile strength (Ts), Young’s modulus (YM) and elongation at break (EB), were measured (Figure2) for the study of the influence of different additive on the mechanical properties and the data are listed in Table 4. As it can be seen from Figure.2 and Table 4, the tensile properties of stabilized PVC were influenced by the type of stabilizer used. The tensile strength of P-cazn, P-lead, and P-obs, were about 20.71, 17.58, and 15.86 MPa, respectively, which means that by addition of Ca/Zn stabilizer samples shown increased value about 15 % against the sample strength with OBS stabilizer and about 23% against the sample strength contained lead stabilizer.

According to the additive definitions, the elongation should increase with the incorporation of, additive corresponding to the flexibility degree of compound structure which is observed with all the modified samples, that represented in Figure.2 and Table 4 Among the sample tested, P-obs shows the maximum changed where the percent elongation (83%).

The Young’s modulus showed the elastic deformation of the sample. Highest values of Young’s modulus corresponded to the stiffer sample. As shown in Fig-ure.2

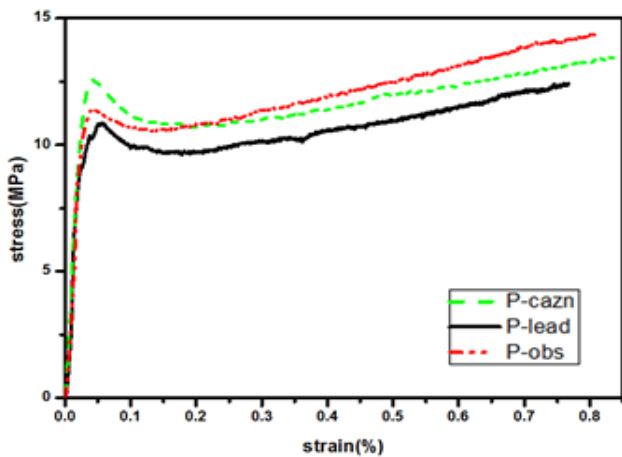


Figure 2- Tensile strain-stress curves for P-lead, P-obs and P-cazn samples

and Table 4, Young’s modulus decreased with the addition of the two type agents, from 439, 299 and 212 MPa for P-cazn, P-lead, and P-obs, respectively. Among the additives tested ca/zn is the most effective stabilizer for PVC matrix.

The results of experimental studies show that mechanical properties such as tensile strength and strain percentage of PVC depend on the amount of degree of gelation. Determining the amount of gel and its relationship to the final mechanical properties can be a powerful tool to evaluate the quality of PVC and analyze its failure, and the lower the amount of gel, the more damage and cracking of the sample.

Comparative assessment.

In order to evaluate the effectiveness of this research in comparing this alternative method including a chemical swelling method based on weight change mass%, DSC test results based on TonsetB and degree of gelation result and finally with mechanical results based on tensile strength, represented in Figure 3.

As can be seen from Figure 3 and determined in the Table 2-4, a one-to-one agreement is between three methods. Then these methods could be create results with comparable accuracy instead of each other.

As Figure 3 shows, the degree of gelation results obtained by the enthalpies of both the lower and upper endothermic area in DSC curve, ΔH_A and ΔH_B , in agreement with the chemical swelling results.

And also DSC is the method indicated the good potential to estimate the percent gelation of the PVC samples, hence showed good agreement with the DCMT test.

Conclusions

In this study, three common commercial heat stabilizer was introduced in the PVC matrix via the melt mixing method and then conducted to three alternative standard method for assessment of sampling procedures, homogeneity corresponded to mixing of stabilizers and PVC and also effect of all these factor on the properties of the PVC products. The type of stabilizer in the PVC system and interaction quality that formed in the melt mixing method was analyzed by DCMT, DSC, and tensile studies. The DCMT results showed that lead stabilizer in PVC matrix had not enough interaction with the PVC chains in the preparation process temperature against two other stabilizers and maybe some of the intermolecular interaction collapse in moulding process. The Tg and Tonset and also comparative degree of gelation value for pvc modified with ca/zn stabilizer, that obtained from DSC analysis were improved as compared with the P-lead and P-obs samples, that showed a good agreement with the DCMT analysis. In tis regard the increase in distance between the PVC chains due to reduce intermolecular intractions between lead stabilizer and PVC chains, maybe cause a relative decrease in Tg temperature in the crystalline growth in P-lead sample in DSC test, like solvent test method. In mechanical properties studies, tensile strength, Young’s modulus, and elongation at break of the P-lead, P-cazn and P-obs have been increased due to the additive interaction with the PVC matrix corresponded to processing temper-ature and preparation method in agree with DSC and DCMT analysis. From all the results, it is evident that Ca/Zn showed high potential use

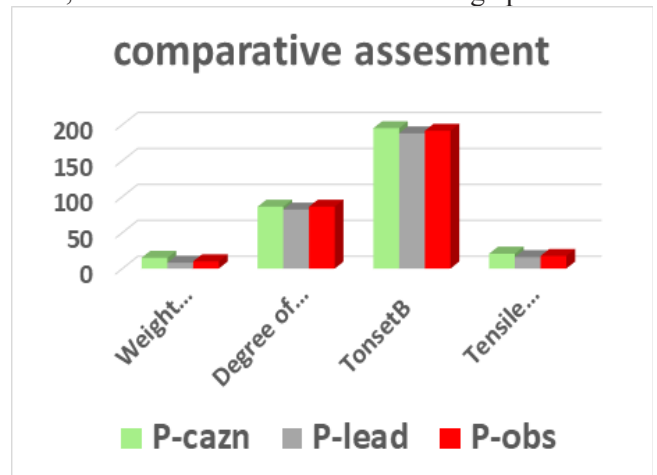


Figure 3- Comparative plot of three standard method

Table 4- The tensile properties of the samples

sample	Tensile strength(MPa)	Elongation at break (%)	Young's modulus(MPa)
P-lead	20.71	69	439
P-cazn	15.86	75	299
P-obs	17.58	83	212

as a safe and effective heat stabilizer for PVC to substitute traditional lead compounds.

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