Synthesis, characterization and study thermal stabilization effect of calcium complex of anthocyanin on the poly (vinyl chloride)

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Abstract. In this study, calcium complex of anthocyanin was synthesized from anthocyanin, a flavonoid type natural phenolic product, which was extracted from eggplant peel. The structure of Ca-anthocyanin was characterized by FTIR spectroscopy. Its efficiency as bio-based thermal stabilizer to stabilize poly (vinyl chloride) was investigated and compared to that of Reapak B-NT/7060, a Ca/Zn-based commercial stabilizer. The influence of Ca-anthocyanin complex on the thermal degradation reaction of PVC was monitored by differential scanning calorimetry (DSC). The results indicated that the Ca-anthocyanin complex is an efficient thermal stabilizer and it reduces the rate of dehydrochlorination reaction of PVC already at a concentration as small as 2 phr, part per hundred of PVC resin. The thermal degradation reaction of PVC through the first degradation stage is clearly limited by the addition of Ca-anthocyanin complex as single (primary) stabilizer. Its efficiency is similar to that of Reapak B-NT/7060 used as reference stabilizer and it can enhance the performance of commercial stabilizer when used as co-stabilizer at mixing ratio (1:1). This study has allowed verifying and validating the usefulness of environmental friendly thermal stabilizer for PVC with very evident stabilization effect.

1. Introduction

It is well known that the thermal stabilizers are essential additives especially for PVC, one of the most important polymers intensively used as thermoplastics. Both flexible and rigid PVC products are highly dependent of thermal stabilizers and cannot be found at marking scale without these essential additives [1][2]. Thermal stabilizers in addition to plasticizers play crucial roles in the convertible of PVC formulations from raw material to commercial products in addition to their final quality and physical characters. They have been used for: (i) increase the resistance of this polymer against any thermal degradation which can easily initiated by heat or by another agent such as light (photo-degradation) and reduce its fragmentation, (ii) improve its processing and get various indoor, outdoor and food packaging with high quality applications and (iii) for long-term thermal, light and mechanical stabilities.

PVC is highly sensitive to whole the processing temperature ranges and undergoes thermal degradation when exposed to heat both during extruding, molding and recycle steps [3][4]. The thermal instability behavior of PVC which is a complex phenomenon leads to irreversible changes in most of its desirable physical and mechanical properties. Various thermal stabilizers types at average concentrations ranged from 2 phr to 5 phr, part per hundred of PVC resin, have been widely used in a large range of PVC commercial formulations to enhance its thermal stability especially through thermal process. The most common thermal stabilizer types include metal soaps which consist of long chain carboxylic acid salts, lead salts and organo-tin compounds [5][6] [7] and other types (auxiliary...
or co-thermal stabilizers). In particular, many PVC thermal stabilizers that based on heavy metals ions such as tin and lead, has been forbidden or at limited uses in many countries because of their deleterious impacts on human and environmental systems or because their high price. New thermal stabilizers or co-stabilizers with efficient stabilization and plasticization effects can be synthesized from various types of bio-based raw materials[8][9][10]. A large number of studies were carried out to synthesize and evaluation of new compounds with different chemical structures as PVC thermal stabilizes with or without another activity such as photostabilization, plasticization or even with any synergistic effects with all polymer formulations components. Mei Li and co-workers [11] synthesized thermal stabilizers from dipentene and gum rosin using two step; Diels–Alder addition used to prepare maleated dipentene and acrylopimaric acid in the first step; subsequently in the second one, the researchers converted these derivatives to the corresponding zinc salts and calcium salts. Johan Steenwijk et al. [12] reported a systematic investigation on the uses of natural polyols such as sorbitol and xylitol as PVC long-term thermal stabilizers. Other natural compounds, vegetable oils, have a potential to be modified and used as PVC thermal stabilizers or co-stabilizers with plasticization effects. In a recent studies, the stabilization effect of plant oils based epoxy compounds was investigated in detail [13][14][15].

The general results of those studies revealed that the stabilization efficiency of epoxidized vegetable oils is based on ability of epoxy group to accept the evolved HCl and to formation of ester bonds with reactive chlorine atoms. Taghizadeh and co-workers [16] studied the synthesis of epoxy derivative from commercial sunflower oil. The new tannins based thermal stabilizers were synthesized by complexation with a base, Ca(OH)2 for example, through it phenolic hydroxyl groups using simple reaction conditions or by epoxidization reaction with epichlorohydrin [17][18]. Another naturally occurring phenolic compounds, anthocyanins, which might potentially be used for the stabilization of PVC. Anthocyanins are the main class of flavonoids which give different color (red and/or purple color) to fruits and many colored vegetables parts of plants. Anthocyanins are natural phenolic monomer which can be isolated from many plant parts such as eggplant peel, figs peel and other [19][20][21][22][23].

In present article, anthocyanins were extracted from eggplant peels obtained as waste of local food consumption. For that purpose, it had been converted to calcium complex and evaluated as a primary/single stabilizer as well as in combination with a Ca/Zn based commercial thermal stabilizer (co-stabilization effect). Differential scanning calorimetry (DSC) (dynamic mode) was used to characterize the stabilization efficiency of this complex.

2- Experimental

2.1. Materials

PVC (a suspension polymerization type with a k-value of 65 and dioctyl phthalate (DOP) used as plasticizer were kindly provided by state company of petrochemical industries, Basrah, Iraq. HCl was supplied by Biosolve BV, Netherlands. Calcium hydroxide was purchased from Hi-Media laboratories, India. Sodium hydroxide was purchased from Thomas Baker, India. Reapak B-NT/7060 (Ca/Zn-based powder), which used reference thermal stabilizer was supplied by Reagens Co. (Italy). All reagents and polymer involved in this work were used as received without further purification

2.2. Isolation of anthocyanins

Eggplant (Solanum melongena L.) was purchased from local market. Its peel was manually isolated by sharp knife and dried at 50°C for one week. The dried peel was crushed using coffee grinder. 30 g of this powder was extracted with 250 ml of 10% sodium hydroxide aqueous solution at reflux for 24hr. After that, the crude extract was filtered, acidified with 2% HCl solution to pH of 4-3, washed with distillation water and dried in oven at 60°C for 24 hr.

2.3. Calcium-anthocyanin complex synthesis

The Ca-anthocyanin complex used in this work was synthesized from anthocyanins as crude phenolic mixture and calcium hydroxide. The synthesis began with dissolved of 5g of anthocyanins in 250 ml of water using heat and continuous stirring to form homogenous solution. After complete dissolving of anthocyanins, filtered and saturated aqueous solution of calcium hydroxide was added slowly with contentious stirring. The addition of calcium hydroxide solution was contentious until the pH rise to about 10-12. The solution was allowed to stand for 24hr, then a brown thick precipitate was
obtained which was filtered and washed using distillation water for several times and dried at 60°C for 24 hr. The chemical structure of anthocyanin-calcium complex was confirmed using FTIR analysis.

2.4. Preparation of stabilized PVC samples

One series of PVC formulations was prepared from PVC, anthocyanin-calcium complex as thermal stabilizer and DOP as plasticizer. The DOP content was fixed at 10 phr (parts per hundred PVC resin) in all PVC blends. One PVC sample was fabricated by mixing 2 phr of commercial thermal stabilizer and used for comparison in this study. PVC was thoroughly mixed with varying proportions of this derivative and constant amount of DOP in a mortar. The composition of prepared PVC samples is reported in table 1.

Table 1. Samples designations and their corresponding compositions

| Ingredients     | PVC  | DOP | B-NT/7060 | Ca-Anthocyanin |
|-----------------|------|-----|-----------|----------------|
| Pure PVC        | 100  | 10  | 0         | 0              |
| PVC-BNT/2 phr   | 100  | 10  | 2         | 0              |
| PVC/Ca-anth/2 phr | 100 | 10  | 0         | 2              |
| PVC/Ca-anth: B-NT/1:1 | 100 | 10  | 1         | 1              |

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structures of anthocyanins and its derivative were confirmed by using FTIR spectroscopy (FTIR 4200, Jasco Corporation, Japan). The anthocyanins and its salt were mixed with dry KBr and pressed to form the pellet. Mixtures of these compounds with KBr were scanned in the range of 400-4000 cm⁻¹.

2.6. Evaluation the stabilizing efficiency

Thermal properties of PVC samples were analyzed with a DSC-60 (Shimadzu Cooperation, Kyoto, Japan) for evaluation of stabilizing efficiency on synthesized salt. A sample of 8-10 mg of each PVC samples was weighted and loaded into aluminum open pan, and the DSC scans were conducted from room temperature to 350°C. All DSC measurements were carried out at a heating rate 20°C/min in a N₂ atmosphere flow at 20 mL/min flowing rate.

3. Results and Discussion

Herein, the anthocyanins were isolated from the eggplant peel in alkaline aqueous medium then it used to prepare a new bio-based thermal stabilizer. Ca-Anthocyanin salt or complex was synthesized through precipitation process with calcium hydroxide. FTIR analysis were conducted to confirm the phenolic property of anthocyanins and to investigate its interaction with calcium ions. The FTIR spectrophotometry analysis results of anthocyanins before and after modification are shown in figure 1' and figure 2' respectively.

Figure 1. FTIR spectrum of anthocyanins obtained from eggplant peel by solid-liquid extraction.
As can be seen in figure 1, a wide and intense band appears at around 3350 cm$^{-1}$ related to the stretching vibration of phenolic –OH groups. Other characteristic peaks such as that for phenolic hydroxyl group in plane bending and C-O stretching at 1409 cm$^{-1}$ and 1050 cm$^{-1}$, respectively, also can be seen in this figure. The skeletal vibration which absorb at 1560 cm$^{-1}$ and 1600 cm$^{-1}$ related to C=C axial deformation are a characteristic peaks of aromatic carbon-carbon double bonds. The two bands obtained at 2920 and 2850 cm$^{-1}$ that corresponds to symmetric and asymmetric C-H vibration respectively. The absorption peaks at 1050 cm$^{-1}$ which was due to the symmetric stretching vibration of phenolic -OH almost disappeared in the spectrum of the calcium salt of anthocyanin indicated that the hydroxyl groups of anthocyanins are coordinated to metal ions.

![Figure 2. FTIR spectrum of anthocyanin-calcium salt.](image)

Around region of 720-770 cm$^{-1}$, it was observed a series of weak combination and less intense bands related to C-H asymmetric vibration of aromatic rings. The bonding between anthocyanins as ligand and calcium ion can be inferred by comparing absorption peaks of the anthocyanin-calcium complex with that of free anthocyanins. The FTIR spectrum of the calcium-anthocyanin salt is shown in Figure 2. This spectrum is very diverse to that of free anthocyanins, many characteristic peaks were disappeared or shifted and some new peaks appear. The combination of anthocyanins with calcium ion leads to weaken many bonds such as -O-H, -C=O- bonds so their position will appears at lower wave number value and intensity per that free or that combined with hydrogen because of bonding with low electron density ion. The strong absorption peaks of hydroxyl groups which appear at 3350 cm$^{-1}$ in the FTIR spectra of anthocyanins nearly transferred to 3470 cm$^{-1}$ with lower intensity after generating calcium salt, indicating to incorporation of most of hydroxyl groups of anthocyanins in the reaction with calcium hydroxide to produce anthocyanin-calcium complex. This spectrum also showed a new absorption peak at 1430 cm$^{-1}$ attributed to the symmetric stretching vibration of carbon-calcium bonds in anthocyanin-Ca complex. As can be seen in figure 2, this peak has relativly high intensity due to the high amount of –O-Ca-O- group in this complex. At wave number value 876 cm$^{-1}$, it was observed a sharp band related to O-Ca ionic bond [17]. These changes in the stretching vibration of OH group after complexation can be considered as an indicating to the involvement of this group in coordination with calcium ion and formation Ca-O bond.

The FTIR analysis suggests that the hydroxyl groups of anthocyanin were successfully converted to corresponding salt by direct reaction between calcium hydroxide and anthocyanins. However, there was still a small fraction of unreacted hydroxyl groups, which was not connected with calcium ion and still free.
3.1. DSC analysis

Alternatively to TGA, DSC technique has proven to be one of the most practical and powerful technique to study the thermal properties and degradation reaction of PVC and get enough information to evaluate the performance of an additive as thermal stabilizer to this polymer. In order to study the impact of Ca-anthocyanin on the thermal degradation behavior of PVC, DSC technique was used to analysis and monitored the degradation reactions of PVC mixed with appropriate amount from this product. Dynamic DSC scans of PVC samples from room temperature to 350°C are shown in Figures 3-6.

According to the literature data, the thermal degradation reaction of PVC consist of two main distinct reactions, the first reaction is evolving of hydrogen chloride from PVC chains which named dehydrochlorination (DHC) reaction and forming a conjugated double bonds structure named polyenes sequence and fracture or cyclization of the double bonds structures to form other cyclic or cross-linked structures. The second one is polymer fragmentation and chains scission to low molecular weight or gaseous products. The second stage of PVC thermal degradation or decomposition usually takes place at a temperature degree higher than 400°C [24] which is higher than of the DSC scales used in this study. Figure 3 show the dynamic calorimetric curve of PVC sample without any additive (non-stabilized PVC). It can be seen that the DSC curve shows two endothermic degradation peaks of PVC degradation, the first peak located about 250°C and the second peak located at 305°C. Both two peaks associated with the first degradation stage (DHC reaction and some other reactions). Because a huge amount of literature resources about PVC thermal degradation process and mechanisms showed that the second degradation stage which consist of loss of low molecular weight fragments usually take place at temperature region higher than 400°C, the two endothermic peaks attributed to the first degradation stage.

The first peak is corresponding to the main degradation reaction which is evolving of HCl with auto catalytic effect by HCl while the second one is corresponding to secondary reactions such as crosslinking or cyclization reactions. The reason for splitting of this stage into two peaks or two steps is unclear and may be due to the formation of polyenes sequences in the first step and formation of crosslinking and cyclic structures in the second step. In order to monitor the thermal degradation reaction of stabilized PVC, a PVC samples with and without additives were typically heated to a certain temperature and then the temperature regions and absorbing or releasing heat related to thermal degradation reactions were recorded by DSC apparatus. All the DSC thermal data for the thermal degradation of PVC samples were summarized in Table 2. As mentioned above, the first stage of PVC thermal degradation occurs by complex process or chain-stripping process through two reactions. DSC curves of all PVC samples containing thermal stabilizer, in the first degradation stage, can be divided into two peaks. One can be seen that the first reaction appears as endothermic process and started in the range of 200-220°C and the second one started at about 275-320°C. Before this temperature region, PVC sample do not exhibit any thermal transition except the glass transition relaxation that seen at about 88-89°C. This temperature was specific for pure PVC without any thermal treatment and depends on its native physical and chemical properties and on the amount of the plasticizer. The Tg relaxation of PVC sample followed by relatively strain line or thermal stability phenomenon up to 200°C. After that, a broad endothermic peak appears at 250°C in the DSC curve with peak area or enthalpy equal to (-35.55 J/g) which is associated with the first type of degradation reaction (DHC reaction) for non-stabilized PVC.
Figure 3. The DSC curve of non-stabilized PVC

During the course of PVC degradation, PVC eliminates HCl with the formation of alternating double bonds with different longs across the polymer chains. The HCl elimination reaction is endothermic process because the released energy from this reaction has been used to production of less stable double bonds [25]. The result unsaturated polymeric chains containing double bonds split up into lower molecules such as benzene and toluene or enter in additional reaction with itself or other molecules in the polymer system, crosslinking and chain scission for examples [26][27].

Attention should be paid to the fact that the main action of a primary thermal stabilizer should be in the first stage (both in the first and second steps) of PVC degradation in which all HCl molecules release from the polymer backbone and other secondary reactions. Therefore, much attention must be directed toward the two peaks in the DSC scans. In the second step of PVC thermal degradation which appears as endothermic peak at 305°C with reaction enthalpy -74 J/g followed directly by high exothermic transition. Complex series of reactions occur simultaneously during the second stage. However, this cannot be taken as an indication of HCl scavenging ability by thermal stabilizers because it takes place at a temperature at which the additive is thermally degraded and do not consist of HCl releasing. But this process would account for the ability of stabilizer or its fragments to work with unstable groups and its retardation effects to the crosslinking and cyclization reactions as results to its action in the first stage.

By knowing the total enthalpy of totally non-stabilized PVC sample, the performance of any thermal stabilizer can be calculated by DSC. Differently to most of thermoplastics, PVC thermal degradation reaction especially the DHC reaction is endothermic process therefore it can be detected by DSC. Clearly, the total degradation enthalpy of PVC was lower in the presence of commercial thermal stabilizer compared to the pure sample. B-NT was efficient stabilizer for PVC since it can retard the degradation reaction of PVC due to its action as an effective HCl scavenger and possibly by other activities, due to the presence of metal carboxylates groups. The DSC curve obtained for PVC stabilized with 2 phr B-NT scanned in the temperature range 25-350°C is shown in Figure 4. From this curve, it is evident that the PVC sample has more thermal stability in comparison with pure sample which was shown in Fig 3. And the thermal degradation peaks and enthalpies become smaller per that of previous sample.

Both the thermal data of the two samples as presented in Table 2 and DSC curves show that the degradation reaction of stabilized PVC start relatively at nearby temperature of pure sample but it contentious for higher temperature. This observation may explained by the effect of thermal stabilizer which leads to decrease the rate of thermal degradation reaction in this stage. As the first step of PVC thermal degradation reaction appears as endothermic peak, the second step shows several small
peaks expand to 350°C. This may be a result of accompany between the thermal degradation process of PVC and that of thermal stabilizer. It can be observed from the DSC curve in Fig 4. that the initial degradation of PVC sample occurred at 200°C, while PVC mixed with commercial thermal stabilizer displayed initial degradation at 216°C.

**Figure 4.** The DSC curve of PVC stabilized with 2 phr B-NT

It is observed that the DSC curve of PVC stabilized with 2 phr of ca-anthocyanin complex shows an evident endothermic peak at around 320°C corresponding to the second step of PVC thermal degradation, whose decomposition peak similar in its shape to that of un-stabilized PVC. In the second step of PVC thermal degradation, the absorbed energy (reaction enthalpy) equal to -2.56 J/g which is very lower than that obtained for pure PVC. By analysis these results, it was observed that the Ca-anthocyanin complex showed thermal stabilization activity closed to that of commercial one only in the first degradation step. The addition of Ca-anthocyanin complex to PVC leads to stabilize this polymer in the first stage of thermal degradation process whereas most of PVC thermal process and molding are carried out at below or around this temperature range (below 200°C). For all PVC samples with pure Ca-anthocyanin complex, or with commercial thermal stabilizer, or with mixture of the two additives, Fig. 5, this stage appears as small and broad endothermic peak in the range of 225-280°C with reaction enthalpy -2.56 J/g. Table 2.

**Table 2.** The DSC results of pure PVC and PVC stabilized with various thermal stabilizers.

| Samples                  | $T_{\text{start}}$/°C | $T_{\text{max}}$/°C | $T_{\text{end}}$/°C | Deg. rate$^b$/ mW min$^{-1}$ | Deg. heat$^c$/J g$^{-1}$ |
|--------------------------|------------------------|----------------------|----------------------|-----------------------------|--------------------------|
| PVC neat                 | 222                    | 251                  | 270                  | 8.71                        | -32.55                   |
| PVC-2phr B-NT            | 216                    | 254                  | 280                  | 3.28                        | -15.44                   |
| PVC-2phr Ca-Antha        | 226.6                  | 246                  | 276                  | 1.14                        | -2.56                    |
| PVC-1phr BN-T7060:1phr Ca-Antha | 212                  | 245                  | 255                  | 1.23                        | -2.02                    |

$^a$ start, maximum and end temperatures of first stage of PVC degradation. $^b$ Curing rate of PVC degradation was calculated from the first derivative of degradation peak at first stage. $^c$ Degradation heat was calculated for the first degradation stage.

The thermal degradation reaction of PVC became slower in the presence of this derivative per that of pure PVC. These results confirm that the complex of anthocyanin with calcium increase the thermal stability of PVC which exerted more thermal stabilization behavior at less by HCl scavenging
mechanism. Compared the DSC results of the DSC scan of PVC mixed with Ca-eggplant anthocyanin complex with the DSC of non-stabilized PVC sample, the temperature of initiation (Ti) and temperature of maximum rate (Tmax) of degradation reaction increased from 200 to 225 °C and from 305 to 320°C, respectively, which is due to stabilization effects of this additive. The performance of this derivative derived from its ability to scavenge HCl from the polymer system and retard its thermal degradation reaction at this temperature range was shown by scheme 1. During thermal scanning of PVC/Ca-anthocyanin complex sample, not only changes in the total enthalpies and rate of degradation reaction were noticeable, but also the peak temperature of the secondary degradation reaction which consists of polyenes reactions appears at higher temperature region. Based on the changes in the positions and peaks enthalpies of the two degradation reactions of PVC thermal degradation process, it can be present the Ca-anthocyanin complex act as efficient primary thermal stabilizer for PVC. This derivative can stabilize PVC polymer through at least by one mechanism which is including direct absorption of HCl from the polymer system during thermal process or at DSC test. In other words, in spite of that the primary products of thermal degradation process such as isolated double bonds, HCl and free radical groups have the a dominant influence on the thermal ageing degradation reaction of PVC.

Figure 5. The DSC curve of PVC stabilized with 2 phr Ca-anthocyanin Complex.

Therefore, the thermal stabilization of PVC samples could take place as a result to one of chemical interaction between one these products and thermal stabilizer. The chemical properties of this derivative such as its coordination bonds with calcium ion and its anti-oxidation feature of phenolic groups give it its stabilization ability. The free anthocyanin reproduced by stabilization mechanism has the advantage of being an active antioxidant and therefore its phenolic hydroxyl groups could act as free radical quencher. But the salt segment or basic group of this derivative clearly had the predominant thermal stabilization effect by replacement of metal ions by relatively more chemically stable sites Scheme 1
Scheme1. Possible thermal stabilization of PVC through direct removal of HCl by Ca-anthocyanin complex.

Figure 6. The DSC curve of PVC stabilized with 1 phr Ca-anthocyanin complex and 1 ph B-NT at weight ratio 1:1.

From the DSC whole results, it can be observed that the calcium complex with anthocyanin has a significant property in term of thermal stabilization of PVC and its ability is comparable to that of commercial thermal stabilizer. In order to study the synergistic of the synthesized stabilizer with commercial one, B-NT/7060, the calcium complex with anthocyanin was examined as co-stabilizer with that used as reference in this study. The mixing ratio was done used equal amount from both additives (1:1), Table 1. The total amount of the mixture stabilizers in PVC was kept constant at 2phr based on the polymer amount. The result of DSC test for PVC mixed with Ca-anthocyanin/B-NT stabilizer is shown if Figure 6. It can be observed from the DSC curve that the first stage of PVC thermal degradation take place at the same temperature range but became very small reaction enthalpy (-2.02 J/g) in comparison with that for PVC stabilized with single of these additives. As shown by Table 2, the rate of dehydrochlorination (DHC) reaction of PVC stabilized with mixture of the two stabilizers is dramatically reduced by the cooperative effect of these additives. Interestingly, the significant reducing of PVC degradation enthalpy by about 16.1 times means that the thermal stability of PVC was efficaciously improved by this mixture of stabilizers. The combination of commercial stabilizer with Ca-anthocyanin complex reveals a true synergism effect. By comparing the thermal data in table 2, it can be confirmed that the mixture of anthocyanin based thermal stabilizer and Ca/Zn based commercial stabilizer displays a better stabilization behavior for PVC than that obtained from each one. The observed enhanced in the thermal resistance of PVC sample is considered to results
from the varied in stabilization mechanisms and increase the active functional groups in each stabilizer type.

4. Conclusion
Calcium-anthocyanin complex was employed in this work to improve the thermal stability of PVC. It has been investigated to act as thermal stabilizer and co-stabilizer. The results obtained through thermal analysis clearly reveal that the Ca-anthocyanin complex. The addition of this derivative alone or with another stabilizer lowered the rate and enthalpy of degradation reaction of PVC. A critical analysis of DSC revealed an increase in thermal stability of the PVC through HCl removal process mainly due to the presence of -O-Ca coordination bonds. One possible mechanism was suggested to explain the stabilization effect of this derivative in which it act as thermal stabilizer. Mixing of anthocyanin based derivative with equal proportion of reference stabilizer, Reapak B-NT/7060 (1:1) greatly improves the thermal stability of PVC by synergism effect between the two additives.

Good stabilization performance can be obtained by using this derivative at a ratio similar to that of commercial stabilizer used as reference. The potential stabilization effect, renewable and environmentally friendly characters of Ca-anthocyanin, gives this derivative an important added value to submit it as PVC stabilizer in many applications.

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