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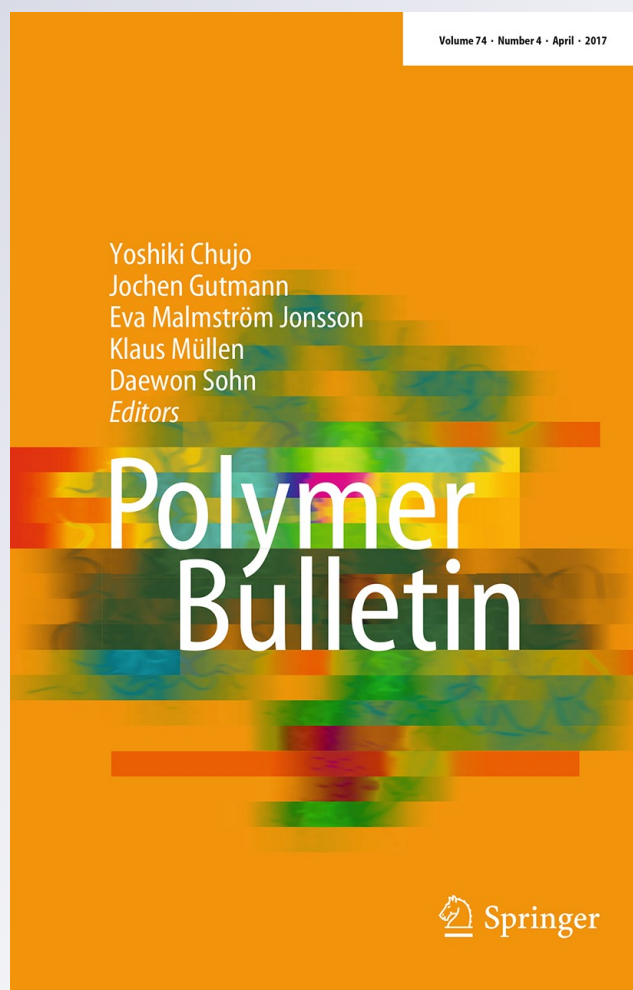
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Rheological properties of PVC stabilized with tannin based epoxy resin as non metallic thermal stabilizer

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Abstract In this study, an attempt is made to investigate the rheological behavior and thermo-rheological properties of PVC in the presence of new tannin based thermal stabilizer. Tannin based epoxy resin has been used as nonmetallic thermal stabilizer additive to study its effects on the rheological behavior of PVC. Frequency sweep tests were applied for monitoring and evaluating the rheological properties of PVC formulations with different levels from this derivative (0, 5, 10, and 20) parts per hundred ratio (phr) using a parallel plate rheometer at 165 °C. The general results indicate that the adding of tannin epoxy resin to PVC can provide enhanced dynamic thermal and process stability and improved the rheological properties. In these formulation systems, the rheological properties of PVC with tannin epoxy resin were more closed to that of PVC without plasticizer so that the plasticization effect of tannin epoxy resin was at very limited level. The rheological properties, such as storage modulus, complex viscosity and damping factor proved simultaneously that the PVC stabilized with tannin derivative exhibits excellent rheological behavior and melt thermal stability properties which were very comparable to that of PVC stabilized with 2 phr Reapak B-NT/7060; a commercial type thermal stabilizer.

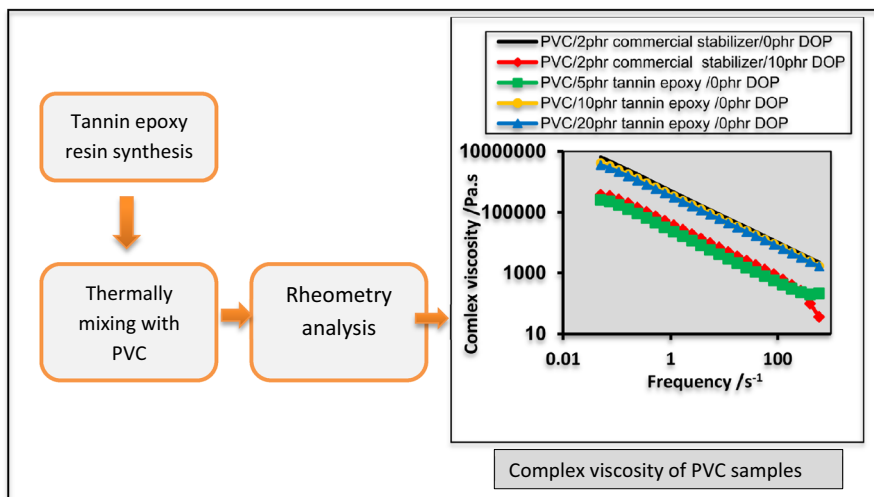
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Graphical abstract



Keywords PVC · Tannins · Tannin epoxy resin · Rheological properties · Melt stability · Thermal stabilizer

Introduction

Poly(vinyl chloride) (PVC) thermal stabilizers are considered as an essential additives to protect this polymer during processing and uses ages. Commonly, the main used thermal stabilizers for PVC belong to one of these categories: lead salts, metal soaps, epoxy resins, many of organic tin compounds and some auxiliary stabilizing materials. Commercially, PVC is rarely used as a virgin resin since it is thermally unstable at the temperatures required for processing and even at environmental conditions when used for outdoor applications, and also, at sterilization temperatures when used into medical tool products. So it relies on the inclusion of stabilizers and other additives. As a result to the low thermal stability of PVC, it requires a range of additives, which are determined by the target applications. These additives are mainly plasticizers, stabilizers, antioxidants, antistatic agents, antifogging agents, impact modifiers, lubricants and flame retardants. Among them, the addition of thermal stabilizers as well as co-stabilizers, produce this polymer to become one of the most important commodity plastics and it has been produced for more than 60 years on an industrial scale [1–4].

More emphatically, natural or bio-based thermal stabilizers for PVC include metal soap of fatty acids from plant oils and their epoxides. More recently, many papers focused on using the epoxides of unsaturated natural products as secondary thermal stabilizer additives for PVC [5–7]. Epoxy compounds are well known as typical nonmetallic stabilizers. They are generally regarded as secondary stabilizers

used to enhance the effectiveness of metal soaps. So they can act as acceptors for liberated hydrogen chloride and as retardants for the appearance of discoloration. The effects of epoxidized sun flower oil (ESO) on the thermal degradation and stabilization of PVC in the presence of metal carboxylates (Ba/Cd and Ca/Zn stearates) have been investigated in the Benaniba et al. study [8]. According to the results of this study, ESO shows excellent properties as secondary thermal stabilizer for this PVC.

Furthermore, epoxidized soybean oil (ESBO), for examples, is a vegetable oil widely used as plasticizer and/or stabilizer for PVC in food contact materials. The aims of Bueno-Ferrer et al. study [9] were to evaluate the behavior of ESBO as a plasticizer and as a stabilizer for PVC at different concentration levels by means of structural and thermal investigations. Formulations based on PVC with different amounts of ESBO (30–50 %wt.) were fully characterized and show good compatibility and a clear increase in thermal stability. An evaluation of the use of ESBO for PVC stabilization in commercial lids was carried out using thermogravimetric analysis (TG). Most of analysis results of this study showed a significant increase in thermal degradation temperatures of PVC. It was reported that the ESBO stabilization mechanism involves a reaction between the epoxide ring and hydrogen chloride generated during PVC degradation. This reaction prevents PVC from further dehydrochlorination, preserving its color and limiting loss of PVC properties.

On the other hand, epoxidized sunflower oil (ESO) was used as an organic thermal co-stabilizer for rigid PVC in the presence and absence of mixture of tri calcium di citrate and mercury (II) acetate as thermal stabilizer by the work of Taghizadeh et al. [10]. It was found that the additives retard the thermo-oxidative degradation of PVC and reduce the extent of polymer chain scission associated with the thermal degradation of poly(vinyl chloride). In his conclusion, this researcher reported that the epoxidized sun flower oil shows excellent properties as a secondary stabilizer for PVC when used in combination with the synergetic metal soaps (Hg/Ca).

Sofia et al. [11] synthesized a bio-based epoxy resin by functionalization of green tea tannins with epichlorohydrin. The tannin based epoxy resin exhibits a high crosslinking density and high thermal stability upon curing with isophorone diamine. The authors in their conclusions show that these materials are interestingly promising for material (epoxy resins) applications. From the PVC rheological behavior point of view, the aims of Laranjeiro et al. [12] by their study were to determined the suitability of using very high molecular weight PVC resin as additive into a typical PVC industrial compound (with about 4 phr thermal stabilizer) for production of hoses. The final results obtained by this study were that the adding 10 % of very high molecular weight PVC will lead to an increasing in both elasticity and viscosity. And the final products were with a more pronounced viscoelastic character. Presently, in this paper, we try to study the effects of tannin epoxy resin and its content as thermal stabilizer additive on the rheological properties of PVC using a parallel plate rheometer. The rheological properties, such as the complex viscosity (η^*), storage modulus (G') and loss modulus (G'') were

measured by strain sweep mode. And also by this parameters the efficiency of tannin epoxy resin as plasticizer for PVC can be investigated.

Experimental part

Materials

The polymer which is used in this study was pure suspension grade PVC-S6558 powder (*K* value 65), supplied by Bandar Imam Petrochemical Co. (Iran). Tannins were isolated from eucalyptus bark by liquid–solid extraction which is used as sodium phenoxide salt. Sodium hydroxide, hydrochloric acid (HCl), epichlorohydrin and tetra hydro furan (THF) from Fluka. Dioctyl phthalate (DOP) as plasticizer for PVC was supplied by Farabi petrochemical industries Co. (Iran). Reapak B-NT/7060, a commercial thermal stabilizer type (Ca/Zn-based powder) was provided by Reagens Co. (Italy) which was selected as reference stabilizer and used for comparison.

Methods

Preparation of tannin epoxy resin

In this method, 10 g of tannin (as sodium phenoxide salt) and 4 g NaOH mixture were dissolved in 100 ml water in a reactor vessel equipped with a mechanical stirrer, condenser and thermometer. The mixture was heated with continuous stirring for 30 min at 60 °C. Then the solution was heated to 98 °C and then 32 g epichlorohydrin was added slowly while stirring. The epoxidation process was carried out under continuous heating and stirring up to 4 h. At the end of reaction, the mixture is left to cool then dried at 60 °C by rotary evaporator. The epoxy product was dissolved in 100 ml THF and the salt by-product in the reaction vessel was filtered. The final product was dried at 60 °C for 24 h in vacuum oven under vacuum. The mass of tannins epoxy derivative after drying under reduced pressure for 24 h and was found to be about 30 g. The final physical state of this derivative was black thick liquid.

Samples preparation

The mixing process was carried out in a Brabender internal mixer, Lab. Station Plasti-Corder, W50-2002 (Germany) equipped with Cam blades using 60 g PVC and various amounts of tannins epoxy derivative, commercial thermal stabilizer and DOP according to the recipes in Table 1. The polymer and additives were physically mixed and homogenized by hand for 5 min prior to transferring to the internal mixture chamber. The samples were prepared after full addition of constituents to the mixing chamber and leveling off the torque curve for 4 min. The tannin epoxy derivative was used in the PVC formulations at (0, 5, 10 and 20) phr.

Table 1 Recipes of PVC samples

Samples designation	PVC Phr ^a	Tannin epoxy	DOP	Comm. stab. ^b
PVC/2phr com. stab.	100	0.0	0	2
PVC/2phr com. stab./10phr DOP	100	0.0	10	2
PVC/5phr tannin epoxy	100	5.0	0	0
PVC/10phr tannin epoxy	100	10.0	0	0
PVC/20phr tannin epoxy	100	20.0	0	0

^a phr part per hundred resin

^b comm. stab. commercial thermal stabilizer, only one formulation (PVC/2phr commercial thermal stabilizer/10phr DOP) contains plasticizer; the percentages of tannin epoxy selected in this study (5, 10, 20) phr were in the range of both PVC thermal stabilizer and plasticizer additives, to make a comparison between its effects and the effect of the commercial thermal stabilizer and of the effect of the DOP as well

Reference formulations with 2 phr commercial thermal stabilizer with and without 10 phr DOP were also prepared. All the mixing were carried out at 165 °C with 80 rpm.

Rheological characterization

The melt rheological investigations were accomplished using a Rheometrics MCR501, Anton Paar-Germany on the 25-mm diameter compression molded disc in a Toyseiki (Japan) mini press in oscillatory mode with 1 mm gap. The strain sweep test in the range of 0.01–100 % strain at a frequency of 10 rad/s at 200 °C is used to obtain the linear viscoelastic range of deformation. The frequency sweep tests were conducted from 0.05 to 600 Hz at a constant strain of 3 %. All rheological tests were carried out at 165 °C under inert atmosphere, N₂ gas with 50 L h⁻¹ flow rate to minimize the undesirable oxidative degradation reactions of the blends.

Results and discussion

According to the some other studies [6–10], PVC in the presence of epoxy resins shows high thermal stability that was fully comparable to the commercial thermal stabilizer. Epoxy derivative has been also proved an efficient stabilizing and plasticization efficiency for this polymer helping to prevent degradation even during processing. According to the results and conclusions obtained by these studies, the clear stabilizing efficiency is essentially based on HCl scavenger mechanism and then permitting their use for food grad PVC. According to the suggested mechanism which is shown by Fig. 1 and on the base of the well known antioxidant activities of tannins [13–15], it can be considered that the tannins after modification are active additives into PVC matrix. The presence of tannin epoxy resin into PVC leads to increased thermal stability temperatures and low degradation rate.

Generally, the ability of tannins to work as antioxidant is expected to increase the performance of tannin epoxy resin to act as excellent thermal stabilizer for PVC

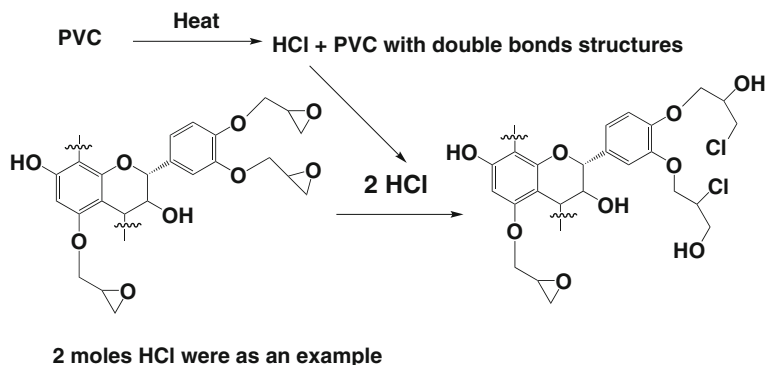


Fig. 1 Suggested inhibition mechanism for thermal degradation process of PVC by tannin epoxy derivative

resin. In other words, tannin derivative have ability to work as primary and secondary thermal stabilizer for PVC with self-synergistic effect and without heavy element ions chemical formulation.

Generally, the rheological investigations can be used as suitable tool to evaluate and monitor the behavior of thermal stabilizer as well as polymer matrix upon processing at relatively high temperatures and shear rate. Using oscillatory rheology, it is possible to evaluate the viscoelastic and processing properties of the PVC formulations with an additive. It is then an evaluable method to understand the structure and thermal stabilization properties upon and after processing treatments for these new formulations [16, 17].

Storage modulus of PVC formulations

Figure 2 showed the storage modulus variation versus frequency for all PVC with commercial thermal stabilizer and with tannin epoxy resin samples at 165 °C and under frequencies between 0.05 and 600 Hz. Due to the high elasticity of PVC with commercial thermal stabilizer and without DOP, the storage modulus values of this sample were significantly higher than that of all other samples. But the sample with DOP exhibits the lower values for storage modulus relative to this sample. These behaviors can be directly attributed to the action of the plasticizer which leads to increase the softening and flexibility of the polymer system.

On the other hand, the PVC formulations with 5 phr tannin derivative shows similar plateau lines along all applied frequencies with that of PVC with commercial stabilizer in the storage modulus curves. This finding clearly refers to more thermal resistance PVC as a result of tannin epoxy action which works equivalently to commercial thermal stabilizer. The storage modulus values of PVC with tannin derivative increased with increasing of the additive levels. This can be explained by the lower elasticity of the samples due to the absence of the plasticization effect of tannin epoxy resin. The results of storage modulus clearly show that the incorporation of tannin epoxy resin into PVC does not clearly affect the rheological

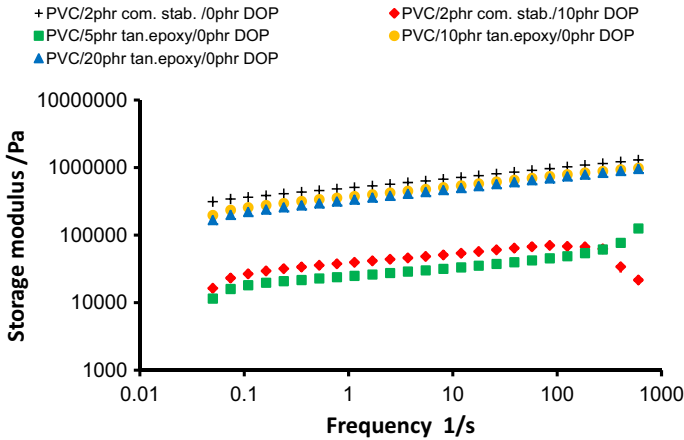


Fig. 2 Storage modulus of PVC stabilized with commercial thermal stabilizer and with tannin epoxy resin

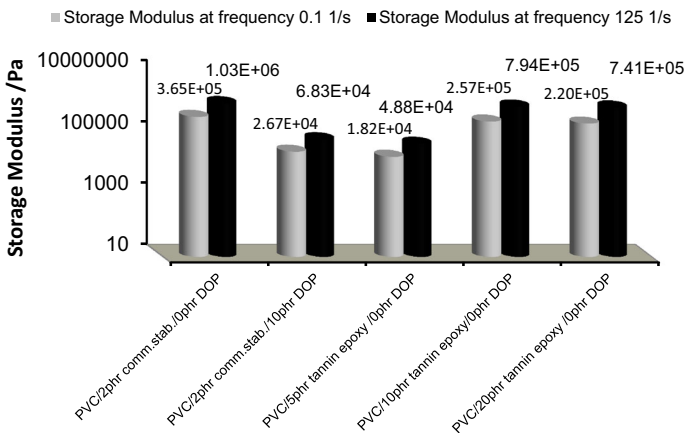


Fig. 3 Storage modulus of all PVC samples at frequencies 0.1 rad/s (low frequency) and 125 rad/s (high frequency)

behavior of PVC, whereas all the values of storage modulus stay in the medial region between that in the presence and absence of the DOP.

The storage modulus values at low frequency (0.1 rad/s) and at high frequency (125 rad/s) were shown in Fig. 3, and it can be clearly detect that the addition of tannin epoxy leads to an increase in the storage modulus values and the thermal stabilization effects of tannin epoxy resin at 10 and 20 phr are well shown by higher storage modulus relative to the polymer system with commercial thermal stabilizer and with DOP. The storage modulus values of PVC with commercial thermal stabilizer were 3.56×10^5 Pa at frequency 0.1 rad/s and 1.03×10^6 Pa at frequency 125 rad/s while these value decrease to become about 2.20×10^5 Pa

at low frequency and about 7.41×10^5 Pa at high frequency. Clearly, this behavior comes as results to the relatively high ability of polymer system to show more thermo elasticity and thermo stability properties for PVC.

This phenomenon can be described as the action of thermal stabilizer (tannin epoxy resin in this state) which can help the polymer chain to be more resistance against the thermal degradation and then to any decomposition in its molecular weight. This continuity facilitates elastic energy recovery and increases the melt elasticity.

It is clearly seen from the Fig. 3 that the storage modulus of all PVC formulations with the commercial thermal stabilizer and with tannin epoxy resin was high and have increasing behavior with increasing of the tannin derivative levels, and have nearly parallel increasing behavior both in low and high frequencies. The storage modulus of PVC samples with 10 and 20 phr tannin epoxy have higher values at low and high frequencies per that of PVC with the DOP and lower that of PVC without the DOP. Based on all these values, the samples with tannin epoxy resin tend to be more melt elasticity (more fluid-like behavior) per that of PVC with the DOP and very similar in the thermal stability with that of PVC without the DOP.

Complex viscosity of PVC formulations

Figure 4 presents the effect of PVC additives on the complex viscosity (η^*) of all PVC formulations at 165 °C. As a matter of fact, the complex viscosity decreased when the bulk polymers are diluted with the plasticizers [17]. Therefore, the PVC sample with DOP shows the lower values for complex viscosity per that of PVC without the DOP or with tannin epoxy resin. For that reason, tannin epoxy resin cannot work as plasticizer to PVC or work at very limited level. It is well shown by Fig. 4 that the viscosity values of all PVC formulations decreased from the low to high frequencies at the same horizontal plateaus. This behavior can be attributed to a loss in the rigidity at test temperature and frequencies for PVC which was caused mainly by the mobility of the polymeric chains which can be associated with the

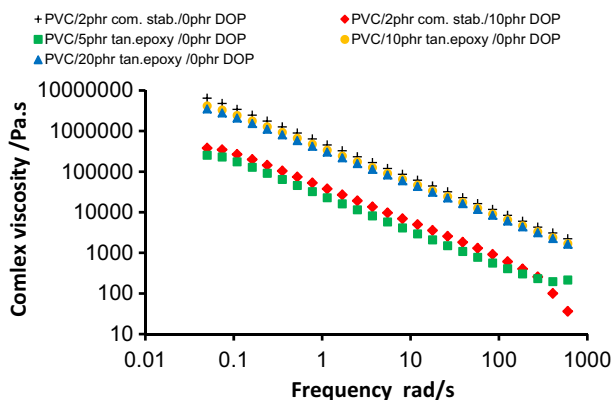


Fig. 4 Complex viscosity variation versus frequency for PVC samples

native chemical structure for the polymer matrix. There is very similarity between the viscosity behavior of PVC stabilized with commercial thermal stabilizer and that of PVC stabilized with tannin epoxy derivative.

The decreasing in the complex viscosity of all PVC formulations with increasing frequency and over all the frequency range investigated indicates that the PVC with tannin epoxy resin also have a non-Newtonian behavior [18]. Generally, all the PVC formulations with tannin based epoxy resin, especially at 10 and 20 phr levels show lower values for complex viscosity per that of PVC formulation with commercial thermal stabilizer and without using the plasticizer, means that the low viscosity at all frequency ranges is mirrored by the elasticity of PVC contains tannin derivative. According to the similarity between all PVC formulations in the complex viscosity, this was mainly caused by the stabilization effect of tannin epoxy resin. The viscosity–frequency curve of PVC formulation with commercial thermal stabilizer display a decrease at higher values of frequencies, this unusual behavior can be related to the action of the plasticizer which is not found in other formulations.

Figure 5 shows a comparison of the effects of various amounts of tannin epoxy resin and 2 phr commercial thermal stabilizer on the complex viscosity of PVC at two different frequencies; low frequency 0.1 rad/s and at high frequency 125 rad/s. The complex viscosity values of the PVC/2phr commercial stabilizer/0phr DOP sample shows maximum value and it was about 3.42×10^6 Pa s at low frequency. While as clearly seen, the presence of the DOP causes a plasticization effect which can induce a decrease in this property. It decreases to reach to about 2.67×10^5 Pa s, and at higher frequency of around 125 rad/s, the complex viscosity decreased from 8.39×10^3 Pa s in the presence of the DOP to reach to about 607×10^2 Pa s, (Fig. 5).

The DOP plasticizer exactly shifted vertically the rheological behavior in all range of frequencies. There is a limited shifting in the complex viscosity of PVC samples containing tannin epoxy at low and high frequencies. Generally, all PVC

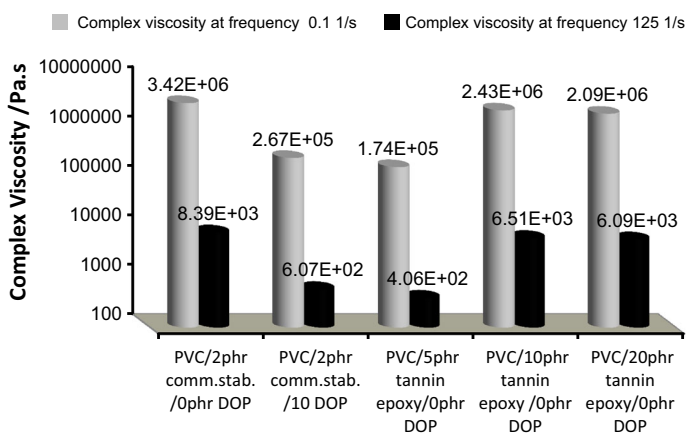


Fig. 5 Complex viscosity of all PVC samples at frequencies 0.1 s^{-1} (low frequency) and 125 s^{-1} (high frequency)

samples with tannin epoxy have relatively lower complex viscosity per that of PVC without the DOP both at low and high frequencies.

According to this comparison, tannin epoxy resin has small effect on plasticization process of PVC. The rheological behavior at low frequency arises from molecular weight and molecular architecture, and the processing behavior can be understood from high shear rate/frequency behavior. At higher amount of tannin epoxy when 20 phr is used, the complex viscosity and storage modulus shifted to lower values decreased in all range of frequency while the decrease is more significant at higher frequencies.

Damping factor ($\tan \delta$) of PVC formulations

In Fig. 6 the variation of damping factor with frequency are shown. As clearly seen, the PVC formulations with tannin epoxy resin occupy a position between the two PVC formulations with commercial thermal stabilizer. These values were above that of PVC sample without the plasticizer and this founding can be attributed to the polymer system with more flexibility and low crosslinking structures. The presence of tannin epoxy resin into PVC can lead to maintain the polymer properties during samples preparation process. At higher frequency, there are significant differences between the damping factor behavior of PVC stabilized with tannin epoxy and PVC stabilized with commercial stabilizer.

The damping factor drops of these formulations at higher frequency values in all PVC stabilized with tannin epoxy formulation but it appears more clearly in the PVC stabilized with 5 phr tannin epoxy and become less significant. This behavior can be attributed to that at 5 phr of tannin derivative; PVC has lower thermal stability relative to other samples. In this instance, the damping factor magnitudes of PVC samples in this study results from the presence and quantity of the DOP in the PVC with commercial thermal stabilizer or from the quantity and performance of tannin epoxy resin in this polymer.

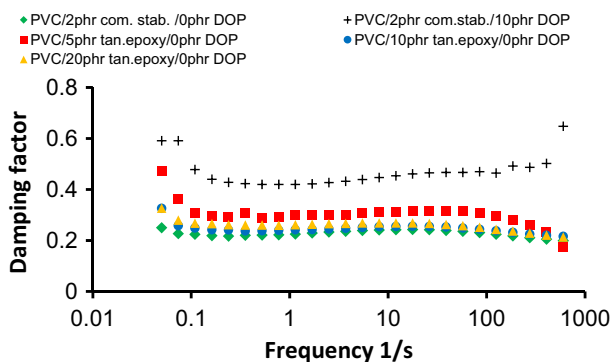


Fig. 6 Damping factor of PVC formulations versus frequency

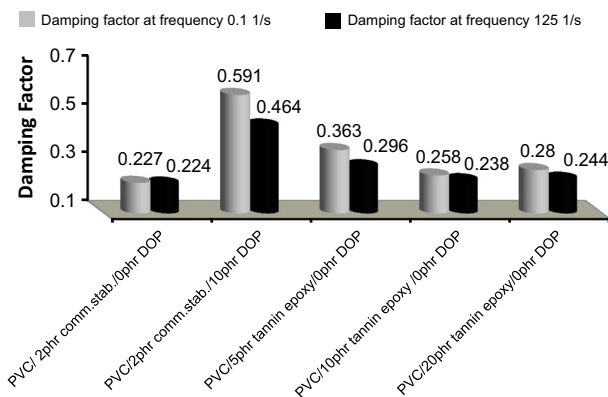


Fig. 7 Damping factor of PVC samples at frequencies 0.1 s^{-1} (low frequency) and 125 s^{-1} (high frequency)

Figure 7 shows the damping factor at low and high frequencies for PVC formulations with commercial stabilizer and with different levels of tannin epoxy resin. It was well established that the addition of this derivative into PVC matrix decreased the damping factor of the polymer melt both at low and high frequencies as comparison with that of the polymer in the presence of DOP. The damping factor was 0.363 for PVC with 5 phr tannin epoxy, 0.258 for PVC with 10 phr tannin epoxy and 0.280 for PVC with 20 phr from this derivative at 0.1 rad/s all these values were lower than that of PVC with the plasticizer and higher than that of PVC without it. Therefore, the PVC systems with tannin epoxy resin were more efficient to loss energy rearrangements and internal friction per that of PVC system without plasticizer.

Loss modulus of PVC formulations

The rheological properties obtained for PVC with tannin epoxy describe fundamental behavior of these formulations during processing conditions. The loss modulus is related to the amount of dispersive energy by the polymeric chains during the deformations. Loss modulus curve for a melt also mirrors changes due to thermal processing effects on the polymer native properties such as molecular weight and molecular weight distribution. The loss modulus variation with frequency of PVC samples are shown in Fig. 8. For all PVC with tannin epoxy formulations, a very plateau behavior are observed in the loss modulus curves, even high frequency where at this frequencies the samples have more elastic property and with efficient thermal stabilization effects there are low crosslinking point and then the flexibility will be more enhanced.

The polymer material with high loss modulus provides too thick, for this the samples without the DOP show higher values for loss modulus. In spite of PVC with tannin epoxy at 10 and 20 phr samples are free from the DOP, the loss modulus curve of this samples appears lower than that of PVC stabilized with commercial

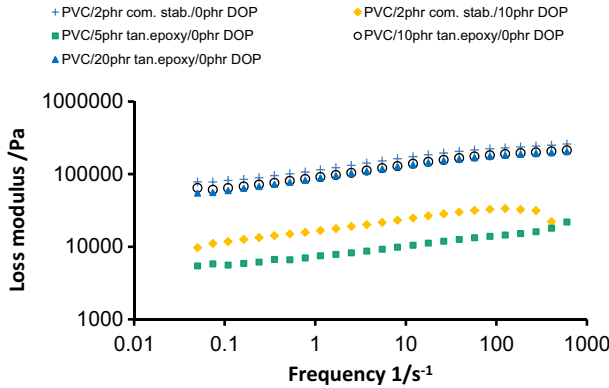


Fig. 8 Loss modulus variation versus frequency of PVC samples

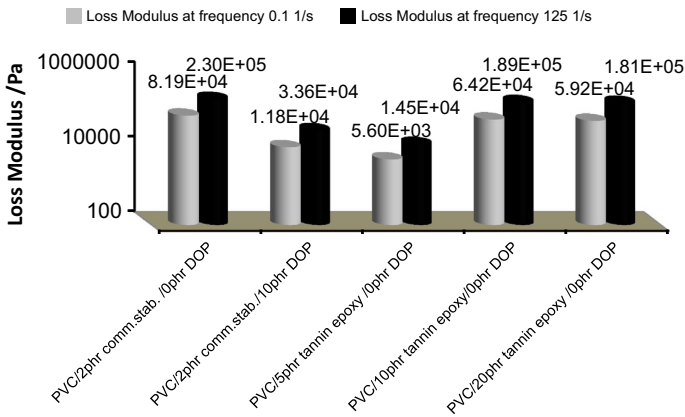


Fig. 9 Loss modulus of all PVC samples at frequencies 0.1 rad/s (low frequency) and 125 rad/s (high frequency)

thermal stabilizer. Figure 9 showed point values of loss modulus at low and high frequencies for PVC stabilized with tannin epoxy resin and for PVC stabilized with commercial thermal stabilizer.

By contrast, the loss modulus at high frequency was higher than that at low frequency in all samples. The loss modulus increase with increase in frequency and with the presence of tannin epoxy resin at 10 and 20 phr levels into PVC which was about 6.42×10^4 Pa and 5.92×10^4 Pa at 0.1 rad/s, respectively. Additionally, the loss modulus behavior at low and high frequencies (Fig. 9) indicated that the ability of impact absorption was improved for all PVC samples with tannin epoxy resin which work mainly as thermal stabilizer.

It was observed that the using of tannin based epoxy resin as additive and stabilizer for PVC leads to get rheological properties comparable to that obtained from non-plasticized PVC and stabilized with commercial thermal stabilizer.

However, since tannin epoxy resin can play a role in improving the thermal stability of PVC, it could be a good alternative as a primary new and bio-based thermal stabilizer for PVC plastisols. Generally, all the rheological results of PVC with tannin based epoxy resin which investigated in this work dependent of the stabilization effect of this derivative and were in agreement with the general results of some investigated that deal with uses and evaluation of epoxy resins derivatives as thermal stabilizer for PVC [5–10].

Conclusions

Rheological measurements were carried out at 165 °C and increased frequency to describe the fundamental behavior of PVC stabilized with tannin epoxy derivative and compared with that stabilized with commercial thermal stabilizer. In light of these results which were correlated with melt viscosity and other rheological properties of PVC confirm that the tannin based epoxy resin have high efficiency as thermal stabilizer associated with interesting complex viscosity, modulus and damping factors for PVC formulations with this derivative. According to the results of this study, the tannin based epoxy resin shows significant effects on the rheological properties of PVC. The rheological properties such as melt viscosity and storage modulus of PVC in the presence of tannin derivative were founded to be very similar to that of PVC with commercial thermal stabilize. And it occupies a position between that of PVC with plasticizer and without it. Although the PVC contains tannin epoxy derivative as thermal stabilizer additive follows the same rheological behavior in term of storage modulus, complex viscosity, damping factor and loss modulus as non-plasticized PVC. In addition, this derivative was interestingly promising for PVC thermal stabilizers and processing additives applications.

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References

1. Starnes WH (2002) Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride). *Prog Polym Sci* 27:2133–2170. doi:[10.1016/S0079-6700\(02\)00063-1](https://doi.org/10.1016/S0079-6700(02)00063-1)
2. Xu Xiaopeng, Chen Si, Wu Bozhen, Ma Meng, Shi Yanqin, Wang Xu (2015) Effect of allantoin on the stabilization efficiency of Ca–Zn thermal stabilizers for poly(vinyl chloride). *J Therm Anal Calorim* 119(1):597–603
3. Navarro Rodrigo, Perrino Mónica Pérez, García Carolina, Elvira Carlos, Gallardo Alberto, Reinecke Helmut (2016) Opening new gates for the modification of PVC or other PVC derivatives: synthetic strategies for the covalent binding of molecules to PVC. *Polymers* 8:152–164
4. McKeen LW (2014) Plastics used in medical devices, chap. 3. In: Ebnesajjad S, Modjarrad K (eds) *Handbook of polymer applications in medicine and medical devices*. Elsevier Inc, Oxford, pp 21–53. doi:[10.1016/B978-0-323-22805-3.00003-7](https://doi.org/10.1016/B978-0-323-22805-3.00003-7)

5. Karmalm P, Hjertberg T, Jansson A, Dahl R (2009) Thermal stability of poly(vinyl chloride) with epoxidized soybean oil as primary plasticizer. *Polym Degrad Stab* 94:2275–2281
6. Karmalm P, Hjertberg T, Jansson A, Dahl R, Ankner K (2009) Network formation by epoxidised soybean oil in plastisol poly(vinyl chloride). *Polym Degrad Stab* 94:1986–1990
7. Benaniba MT, Belhaneche-Bensemra N, Gelbard G (2001) Stabilizing effect of epoxidized sunflower oil on the thermal degradation of poly(vinyl chloride). *Polym Degrad Stab* 74:501–505
8. Benaniba MT, Belhaneche-Bensemra N, Gelbard G (2003) Stabilization of PVC by epoxidized sunflower oil in the presence of zinc and calcium stearates. *Polym Degrad Stab* 82:245–249
9. Bueno-Ferrer C, Garrigós MC, Jiménez A (2010) Characterization and thermal stability of poly(vinyl chloride) plasticized with epoxidized soybean oil for food packaging. *Polym Degrad Stab* 30:1–6
10. Taghizadeh MT, Nalbandi N, Bahadori A (2008) Stabilizing effect of epoxidized sunflower oil as a secondary stabilizer for Ca/Hg stabilized PVC. *Express Polym Lett* 2:65–76
11. Benyahya Sofia, Aouf Chahinez, Caillolb Sylvain, Boutevin Bernard, Pascault Jean Pierre, Fulcrand Hélène (2014) Functionalized green tea tannins as phenolic prepolymers for bio-based epoxy resins. *Ind Crops Prod* 53:296–307
12. Laranjeiro R, Marques RP, Maia JM (2002) Rheological behavior of high molecular weight pPVC compounds. *e-rheo pt* 2:42–48 at: <http://www.dep.uminho.pt/e-rheo.pt1/papers/V002P005.pdf>
13. Formagio ASN, Volobuff CRF, Santiago M, Cardoso CAL, Vieira MDC, Pereira ZV (2014) Evaluation of antioxidant activity, total flavonoids, tannins and phenolic compounds in psychotria leaf extracts. *Antioxidants* 3:745–757. doi:10.3390/antiox3040745
14. Rosales-Castro M, González-Laredo RF, Bae YS, Kim JK, Morre J, Karchesy JJ (2014) Characterization and antioxidant properties of the condensed tannins from Alaska Cedar inner bark. *Rec Nat Prod* 8:217–227
15. Wei SD, Zhou HC, Lin YM, Liao MM, Chai WM (2010) MALDITOF MS analysis of condensed tannins with potent antioxidant activity from the leaf, stem bark and root bark of acacia confusa. *Molecules* 15:4369–4381. doi:10.3390/molecules15064369
16. Sadiku-Agboola Oluranti, Sadiku Emmanuel Rotimi, Adegbola Adesola Taoreed, Biotidara Olusesan Frank (2011) Rheological properties of polymers: structure and morphology of molten polymer blends. *Mater Sci Appl* 2:30–41
17. Eisenberg A, Kim JS (1998) Plasticization. Introduction to ionomers. Wiley, Canada, pp 244–256
18. Abu-Abdeen M (2012) Investigation of the rheological, dynamic mechanical, and tensile properties of single-walled carbon nanotubes reinforced poly(vinyl chloride). *J Appl Polym Sci* 124:3192–3199