

Modification of Poly(Vinyl Chloride) + Epoxy Systems for Improved Thermal and Aging Stability

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Summary: Functional oligomers were synthesized *via* a reaction of ED-24 epoxy resin or a peroxy derivative of that resin with free peroxy and epoxy groups with adipic acid and *via* interaction between derivative of pyromellitic dianhydride and peroxy derivative of the same resin in the presence of benzyl triethylammonium chloride. The effects of oligomer presence, oligomer nature and amount on the crosslinking of poly(vinyl chloride) (PVC) mixtures were investigated. The thermal stability of synthesized oligomers and PVC mixtures based on them were determined, as was resistance to aging. Schematics of cross-linking reactions of modified mixtures are proposed. Higher thermal stability and better resistance to aging have been achieved.

Keywords: aging stability; cross-linking; functional oligomers; poly(vinyl chloride); thermogravimetric analysis (TGA)

Introduction

Polyvinyl chloride (PVC) is one of the most widely produced polymers. Global production of PVC resins is estimated as about 50 million tons/year.^[1] Approximately 70 % of this amount are consumed by China, North America and Western European countries. PVC can be considered one of the most versatile plastics, with high flexibility or stiffness by incorporating additives to meet a wide range of properties, depending on the application.^[2] Among the various types of PVC compounds, plastisols and organosols are among the most versatile, as they offer several possibilities that yield new products. The technology used to obtain these materials includes a large variety of molding and coating processes.^[3] Karmalm and his colleagues^[4] reported that forming a

cross-linked structure contributes to the improvement of the thermal stability of PVC, what in turn greatly increases its range of applications. Crosslinking can be achieved by introduction of epoxy resins.

The stability can be conferred by opening of the epoxy rings and consequent stabilization of labile chlorine atoms, avoiding the generation of HCl created during the degradation of the chain.

We created PVC mixtures by incorporating chemical modifiers such as poly-functional epoxy resins in the presence or without an amino accelerator. We evaluated the effects of the functional epoxy resins and amino hardener content on the crosslinking process of PVC mixtures. Our objectives were improvement of thermal stability and mitigation of aging.

Experimental Section

Materials

The PVC grade is called SE1300N provided by Shintech Inc, Houston, TX, USA, and was used as the main polymer matrix. It contains vinyl chloride monomer up to 10 ppm by

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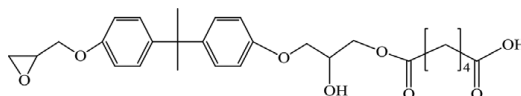
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weight and was used without further purification. Thermal stabilization of formulation was achieved by incorporating a Ca/Zn commercial salt. As plasticizer we have used dithridecyl phthalate (DTDP) and triisononyl trimellitate (TINTM) at the 2:3 ratio.



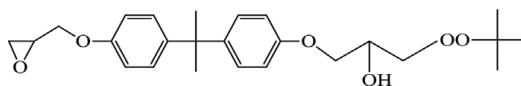
As modifiers of PVC mixtures, we applied an epoxy resin mixture of diglycidyl ether of bisphenol A (70–80 %) and alkylglycidyl ether (20–30 %) and also oligomers with carboxy and epoxy (CDER), peroxy and epoxy (PO), peroxy and carboxy (CPO) or carboxy, peroxy and secondary hydroxyl (PCOS) functional groups.

CDER is a carboxy derivative of ED-24 epoxy resin; it was synthesized in accordance to a method described in,^[5] leading to the formula:



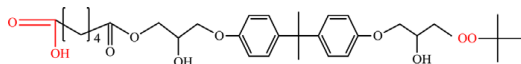
CDER has the molecular mass $M_n = 450$ g/mol, the carboxy groups content $X_{\text{COOH}} = 8.6$ % and the epoxy number $e.n. = 7.9$ %.

PO is a peroxy derivative of ED-24 epoxy resin; it was synthesized as described in,^[6] with the formula:



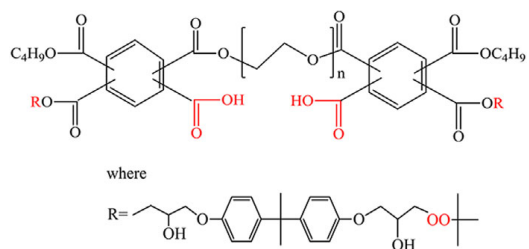
PO has $M_n = 420$ g/mol, $e.n. = 9.0$ %, and active oxygen content $O_{\text{act.}} = 2.9$ %.

CPO is the carboxy derivative of PO was synthesized in accordance to method^[7] with the formula:



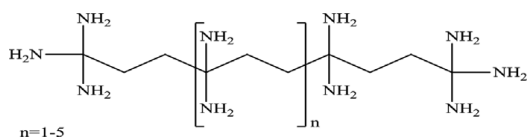
CPO has $M_n = 560$ g/mol, $X_{\text{COOH}} = 8.8$ %, $e.n. = 0$ %, and $O_{\text{act.}} = 2.0$ %.

PCOS was synthesized in accordance to the method described in,^[8] with the formula:

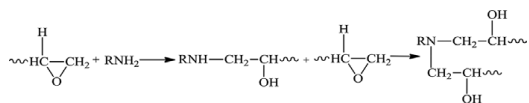


PCOS has $M_n = 1890$ g/mol, $X_{\text{COOH}} = 6.5$ %, $e.n. = 0$ %, and $O_{\text{act.}} = 1.4$ %.

As the crosslinking agent, we have used polyethylene polyamine (typically used in the chemical industry) (PEPA), with the formula:



The mechanism usually accepted for the crosslinking process of epoxy resins involves a reaction with amines:



Preparation of PVC Samples

At first PVC powder was mixed with 1.0 % Ca/Zn powder. Then a functional oligomer and PEPA were dissolved in the plasticizer. After that, the organic solution was added to the mixture of PVC with Ca/Zn. All components were mixed at room temperature; then the homogeneous composition was filled into a steel mold for 20 samples with dimensions of 20*20*2 mm. Compression molding process was carried out at 150 °C and consisted of heating for 10 min before applying 3 cycles of 10 metric tons of pressure for 2.5 min. Afterwards the pressure was released and the samples were cooled to the room temperature in 15 min.

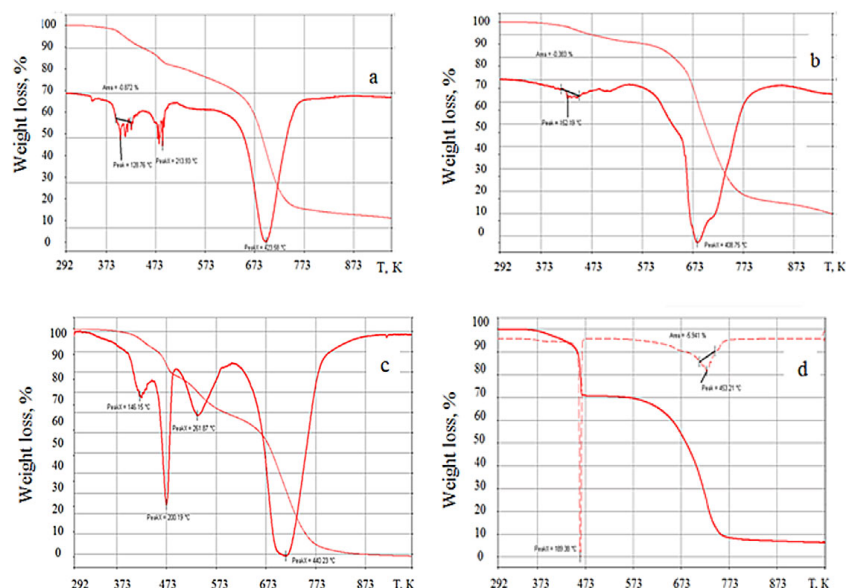


Figure 1. Thermogravimetric diagrams of several oligomers: PCOS (a), CDER (b), CPO (c) and PO (d).

Thermogravimetric Analysis (TGA)

Thermal stability of all compositions was determined by TGA 7 machine from Perkin Elmer, USA. The TGA technique is well described by Menard,^[9] Lucas and her colleagues^[10] or Gedde.^[11] The measurements were performed under nitrogen gas (commercial grade). The heating rates varied between 5 and 20 °C/min. The maximum temperature was 900 K. We have also considered DTG curves (first derivatives of TGA curves), which describe the weight loss rate (dm/dT) where m is the mass.

Aging Stability Investigation

Aging stability of all compositions was determined by samples' weight loss. The samples obtained after compression molding process were kept in a thermal chamber at 422 K for 7 days. Every day all the samples were weighed and the percentage of weight loss calculated.

TGA Results

Modifying Agents

Given our objectives, it was necessary to assure thermal stability of our additives. The technique used has been described above.

The results are presented in Figure 1 and the respective numerical values reported in Table 1. The beginning of a weight loss period is defined by the loss of 0.5 % of the original or previous weight. The end of a weight loss period is defined similarly, that is changes in weight not exceeding 0.5 %. The second number pertaining to the end of a weight loss period provides the total weight loss for that period. Thus, for instance 743/85 means that at the temperature of 743 K the total weight loss since the beginning of the run amounts to 85 %.

We find that the most thermostable oligomer is CDER, with the highest beginning temperature of the first region of weight loss equal to 433 K; it is well stable until 620 K or so; it can be used in polymeric

Table 1. Thermal stability of functional epoxides.

Oligomer	Weight loss temperature/K and amount/%			
	The first period of weight loss		The second period of weight loss	
	Beginning	End	Beginning	End
PCOS	393	743/85	743	949/90
CDER	433	773/78	773	949/88
CPO	403	763/85	763	873/89
PO	373	430/63	463	873/85

mixtures for creation of thermostable materials. Oligomers PCOS and CPO which contain in their structures labile –O–O– bonds can be used in polymeric mixtures as sources of free radicals. The formation of the radicals takes place by decomposition of –O–O– bonds. Our results confirm the presence of –O–O– bonds in the molecules of synthesized PCOS and CPO oligomers. Further, CDER contains oxirane groups which can undergo radical formation leading to cross-linking. PO is similar to CDER in this respect, while it contains oxirane as well as peroxy groups.

PVC Mixtures

For preparing of PVC mixtures we use the PVC powder, the Ca/Zn thermal stabilizer, and a mixture of plasticizers: ditiodecyl phthalate (DTDP) and triisononyl trimellitate (TINTM) in the 2:3 ratio. We have used PCOS, CDER, CPO and PO as modification agents. For cross-linking we have chosen PEPA. The chemical structures of all components are shown above. The PVC mixtures were prepared in accordance to the method described above; their compositions are given in Table 2. The TGA diagrams of PVC samples are presented in Figure 2 and the respective numerical values in Table 3.

It is known that adding plasticizer to PVC reduces the degradation temperature. This is confirmed by our results in Figure 2b and Table 3. For un-plasticized PVC (Figure 2a), the first degradation peak is at 618 K but for the mixture PVC + plasticizer (mixture II)

(Figure 2b) we find it at 609 K. The second peaks for these two compositions are closer (763 and 769 K, respectively). Pure PVC powder starts to degrade at 573 K (Figure 2a) but mixture II at 543 K. When we add the epoxy resin to the mixture (mixture III), we observe a further reduction of the degradation peak until 598 K (Figure 2c). Simultaneously, the second peak remains almost the same (766 K). At the same time we observe increasing temperature of the beginning of degradation of the mixture with epoxy resin in the amount 2.5 mass parts (mixture III) (548 K) as compared with the beginning of degradation for the mixture PVC + plasticizer (533 K) (mixture II) (Figure 2c and 2b and Table 3).

Adding to the mixture the crosslinking agent PEPA (mixture IV and mixtures VI – IX) results in lower beginning degradation temperatures in comparison to the control sample I; closest to that control sample is sample VII which contains both PEPA and PCOS. Sample VII, however, has the highest weight loss, namely 70 %, in the first degradation region; the control sample I has 63 % weight loss. An increase of the epoxy resin content to 4.5 mass parts with simultaneously addition of the crosslinking agent PEPA leads to a significant decrease of the temperature of the beginning of degradation of mixture IV (Figure 2d and Table 3). Incorporation into mixture of modified epoxy resin which contain in their structure carboxy groups (CDER) instead of the epoxy resin (mixture V) shows almost the same results (first and second degradation

Table 2.
composition of PVC formulations.

Component	Component content in g								
	I	II	III	IV	V	VI	VII	VIII	IX
PVC	100	100	100	100	100	100	100	100	100
Ca/Zn	–	1	1	1	1	1	1	1	1
Plasticizer	–	25	25	25	25	25	25	25	25
Epoxy resin	–	–	2.5	4.5	–	3.1	3.1	3.1	3.1
CDER	–	–	–	–	2.5	1.4	–	–	–
PCOS	–	–	–	–	–	–	1.4	–	–
PO	–	–	–	–	–	–	–	1.4	–
CPO	–	–	–	–	–	–	–	–	1.4
PEPA	–	–	–	0.4	–	0.4	0.4	0.4	0.4

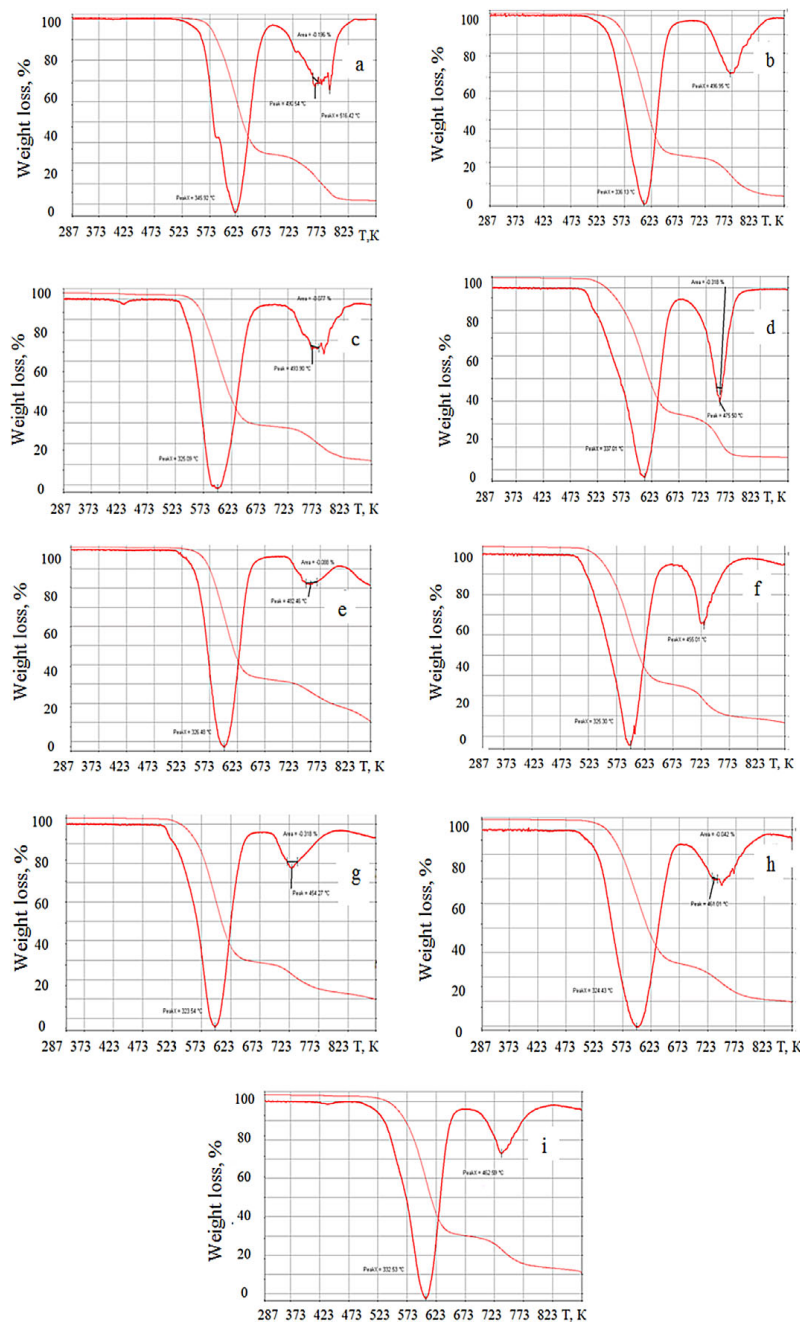


Figure 2.

Thermogravimetric curves of PVC mixtures: I (a), II (b), III (c), IV (d), V (e), VI (f), VII (g), VIII (h), IX (i) in accordance to Table 2.

peak) as mixture III (Figure 2e) and leads to small a decrease of temperature of the beginning of degradation of mixture V, in comparison with mixture II used in industry (Table 3). For mixture VI which contains PVC, stabilizer, plasticizer, epoxy resin, CDER and PEPA we observe the first degradation peak beginning at 523 K, that is 20 K lower than the value for the control sample I. Addition of

the PCOS component (mixture VII) (table 2) give almost the same first degradation peak (596 K) as in the previous case (Figure 2g) as well as unchanged second degradation peak (727 K). For mixture VIII containing as a modifying agent PO oligomer we again observe almost the same first degradation peak (597 K) and slightly higher second one (734 K) (Figure 2h). Incorporation into

Table 3.
Thermal stability of PVC mixtures.

Mixture	Weight loss temperature/K and weight loss amount/%			
	The first period of weight loss		The second period of weight loss	
	Beginning	End	Beginning	End
I	548	673/63	723	798/90
II	533	648/62	733	823/90
III	548	648/63	733	823/87
IV	508	648/67	713	773/88
V	548	648/66	733	873/89
VI	523	643/69	713	773/90
VII	543	648/70	698	773/86
VIII	523	650/68	713	793/88
IX	523	648/68	683	773/85

mixture of the CPO additive component (mixture IX) (Table 2) leads to slightly higher both first and second degradation peak (605 and 735 K, respectively).

TGA diagrams show all similar degradation peaks of PVC mixtures between 598 and 610 K (618 K for pure PVC); the second peaks are different and appear within a wide temperature range, from 728 to 763 K. The largest weight loss we can observe between 573 and 623 K for all mixtures.

As seen in Table 3, PVC materials based on mixtures III and V are characterized by better thermal stability than the commercially used mixture II at lower temperatures. The choice has to be based on the service temperature range. In the second period of weight loss the amounts of that loss are comparable: 90, 87 and 89 % respectively for compositions II, III and V.

Aging Behavior

Our materials have been investigated for aging stability. The process was carried out in accordance to the method described above. We have determined weight loss of samples kept at 422 K as a function of time in days. The results are displayed in Figure 3.

Figure 3 tells us that the incorporation of epoxy resin into PVC mixture (mixture III and IV) and also epoxy resin plus oligomers CDER, PCOS, CPO or PO (mixtures V – IX) affects the weight loss, but in the worst case

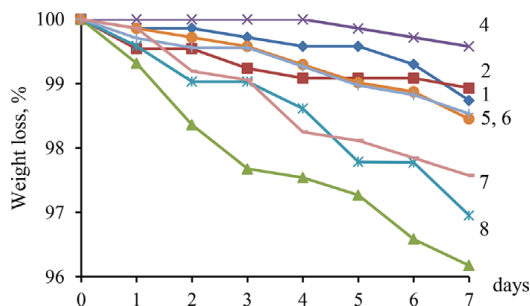


Figure 3.
Weight loss vs. time for materials based on mixtures II (1), III (2), IV (3), V (4), VI (5), VII (6), VIII (7), IX (8) in accordance with the Table 2.

the weight loss is below 4%. Analysis of curve 4 in Figure 3, which pertains to mixture V, shows that during first four days weight loss is below 1% and only later there is a slight weight loss. Results for mixture V containing oligomer CDER (curve 4) are much better than for the standard mixture (curve 1) and indicate a possibility of using synthesized oligomer CDER to improve aging stability of materials based on modified PVC mixtures containing a plasticizer and a stabilizer.

Conclusion

Our results can be summarized as follows:

1. New PVC mixtures containing functional oligomers as modification agents were developed.
2. Thermal stability of both synthesized functional oligomers and PVC materials based on them was investigated. Addition of 2.5 g of epoxy resin or 2.5 g of oligomer CDER to PVC mixture leads to higher thermal stability of the PVC material than the stability of the mixture PVC + plasticizer + Ca/Zn widely used in industry.
3. Aging stability of commercially used and our modified PVC materials was investigated. Using as a modified agent 2.5 g of oligomer CDER per 100 g PVC increases the aging stability of PVC. This material maintains its mass during 4 days at 422 K while the unmodified

- PVC material starts to lose weight from the first day of testing.
4. Incorporation of synthesized functional oligomers into PVC mixture, suggested earlier, leads to additional cross-linking which in turn causes higher thermal stability and improved aging stability.
 5. Synthesized new functional oligomers can be recommended for use as modifying agents for PVC mixtures. The incorporation of these oligomers leads to higher thermal stability and aging resistance of PVC material at high temperatures.

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