

Thermophysical Properties of Modified Polyvinyl Chloride Compositions

¹Lenar Nurgaleevich Shafigullin, ¹Andrey Ivanovich Shveyov,
¹Azat Florovich Gumerov, ¹Marat Irekovich Gumerov and ²Engel Rafikovich Galimov

¹Naberezhnochelninsky Institute of Kazan Federal University,
Russian Federation, 423814, Naberezhnye Chelny, Mira av., 68/19, Russia
²Tupolev Kazan national research technical university, Russian Federation,
420111, Kazan, K. Marx street, 10, Russia

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Abstract: This paper reports the investigation results for thermophysical properties of rigid and plasticized particle reinforced polyvinyl chloride composites. The thermophysical characteristics and behavior of modified compositions for different constituent ratios are established.

Key words: Polyvinyl chloride • Modification • Thermophysical properties

INTRODUCTION

The investigation of polymer thermophysical properties in wide temperature range is dictated by the necessity to study their temperature dependence anomaly during relaxation and phase transitions. The findings in thermophysical properties of polymer compositions including those based on such large-scale polymer as polyvinyl chloride (PVC) make it possible to define optimum temperature-time conditions of composition processing into products and predict their physical chemical behavior in the operation, storage and transportation conditions [1-3].

Main Part: The investigation object was rigid (unplasticized) and plasticized specimens based on PVC grade PVKh-C7059-7058I which was heat stabilized with the mixture of calcium stearate and dibasic lead silicate (3 mass fractions per 100 polymer mass fractions). The plasticizer was dioctyl phthalate (DOP) with the content changed from 10 to 50 mass fractions in the compositions. The mineral filler for formulations of rigid and plasticized compositions was investment casting waste (ICW). The organic fillers were chemical wood processing waste – hydrolised lignin (HL) and also the products of its chemical treatment: chlorinated hydrolised lignin (CHL) and oxidized hydrolised lignin (OHL). First, the fillers were subjected to drying and mechanical milling followed by

dispersion with planetary mill “Activator-2SL”. Particle size distribution was determined using diffraction analysis with laser analyzer “AnalyzeTre-22”. Filler particle size was maximum 20 μm and their concentration was changed from 1 to 30 mass fractions. The compositions were made by mixing specific combinations and ratios of polymer, heat stabilizers, fillers and plasticizer in the laboratory blender. First, the plasticized compositions were gelatinized during 24 hours at room temperature. Then the mixtures were heat softened in the friction lab mills in temperature range 140-160°C during 10-15 minutes till 0.1-0.2 mm films.

The composition thermomechanical properties were investigated using three-channel automatic unit PTB-I-IIZh. The pelleted specimens (10 mm dia x 5 mm high) were made by hot pressing the films in the metal mold at temperature 150-170 °C, pressure 0.2-10 MPa and dwell time 5-7 minutes depending on the composition content. The pellets were cooled in the closed mold under molding pressure with rate 15-20° C/min. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were made by multifunctional programmable derivatograph Q-1500D with temperature scan rate 10°C/min. The start temperature of intense degradation and 5% and 50% loss in mass of the specimens investigated were used as evaluation criteria for thermal properties of PVC compositions. Differential scanning calorimetry (DSC) was made by Setaram calorimetric unit DSC-111 with temperature scan rate 5° C/min.

Corresponding Author: Lenar Nurgaleevich Shafigullin, Naberezhnochelninsky Institute of Kazan Federal University, Russian Federation, 423814, Naberezhnye Chelny, Mira av., 68/19, Russia.

Table 1: Composition thermomechanical behavior

		Plasticizer content, mass fractions											
		0			10			30			50		
		filler content, mass fractions											
Filler	Characteristic, °C	0	10	30	0	10	30	0	10	30	0	10	30
HL	T _c	80	80	83	55	55	55	40	38	40	35	34	35
	T _T	160	153	160	150	145	150	125	122	122	113	113	115
CHL	T _c	82	79	80	56	56	57	41	40	41	36	36	37
	T _T	162	155	161	152	146	151	126	120	126	116	112	116
OHL	T _c	82	79	80	56	57	57	41	41	40	36	37	37
	T _T	162	156	162	152	146	152	126	121	125	116	113	117
ICW	T _c	83	80	81	57	57	58	42	42	42	37	37	38
	T _T	163	158	165	153	148	153	127	120	126	117	112	117

The integrated investigation methods were used due to the required qualitative and quantitative evaluation for processes in the modified compositions exposed to heat.

The analysis of thermomechanical curves of rigid and plasticized compositions showed that they are typical for amorphous thermoplastic materials with regions corresponding to glassy, rubberlike and viscous-flow states. Table 1 represents the summarized findings in thermomechanical behavior of rigid and plasticized PVC compositions depending on modifier content.

It is seen that as the content of organic and mineral fillers increases glass transition temperature (T_g) of rigid and plasticized compositions does not change significantly. It depends on relatively low mobility of globular polymer textural features connected by passing chains in the regions of composition transition temperature from glassy to rubberlike state in the thermomechanical analysis conditions. In this temperature region, due to adsorption interaction between polymer macromolecules located directly on the filler surfaces, boundary layers are formed in the constituent interfaces limiting the mobility of PVC textural paTerns [4]. When filled with organic and mineral fillers the flow temperature behavior (T_f) differs significantly, especially for rigid and conditionally rigid compositions containing relatively small amount of plasticizer (up to 10 mass fractions). In such compositions the effect of small additives manifests itself distinctly and flow temperature decrease rate is higher when filled with mineral filler inert to PVC which incorporation causes the cleavage of passing chains bonding polymer textural paTerns and increase in their

mobility in thermomechanical analysis conditions. When filled with organic fillers containing a large amount of different functional groups (carbonyl, carboxyl, hydroxyl, eTc.) the degree of molecular interaction between polymer macromolecules and surface of filler particles increases resulting in mobility decrease of polymer textural paTerns and flow temperature decrease. For the compositions with higher plasticizer content (30 and 50 mass fractions), when filled with mineral or organic fillers, the rate of change T_f decreases due to decreasing filler influence on the mobility of polymer textural paTerns as a result of the dispersed particles being blocked by plasticizer. Therefore, the effects which manifest itself as different behavior of thermomechanical values when rigid and plasticized compositions are filled with organic and mineral fillers are caused by heterogeneous globular structure remaining unchanged during PVC processing and having different molecular interaction in the constituent interface and change in mobility of polymer textural paTerns [3].

There are two main peaks in DTA curves of investigated PVC compositions with different ratios of modifying additives. The first exothermic peak characterizes thermal oxidative process and the second endothermic peak corresponds to PVC dehydrochlorination process [1, 2]. Moreover, as the content of modifying additives increases the position, height (depth) and areas of exothermic and endothermic peaks change significantly that is the evidence of active modifier influence on thermal degradation and dehydrochlorination processes on PVC exposure to heat.

Figure 1 shows as an example DSC curves of rigid and plasticized PVC compositions.

Table 2: The modifier influence on the composition thermal behavior

		DOP content, mass fractions								
		0			10			50		
		Filler content, mass fractions								
Filler	Value, °C	0	10	30	0	10	30	0	10	30
HL	Peak of endo effect	280	290	305	290	315	325	280	290	295
ICW		284	292	305	292	318	328	285	295	300
HL	Degradation start	210	230	240	190	200	205	180	190	202
	5% loss in mass	250	270	290	265	270	280	270	275	285
	50% loss in mass	290	310	320	300	310	320	290	295	308
ICW	Degradation start	215	235	243	193	204	207	192	194	205
	5% loss in mass	255	274	293	267	270	280	272	276	287
	50% loss in mass	292	312	320	303	313	323	295	295	310

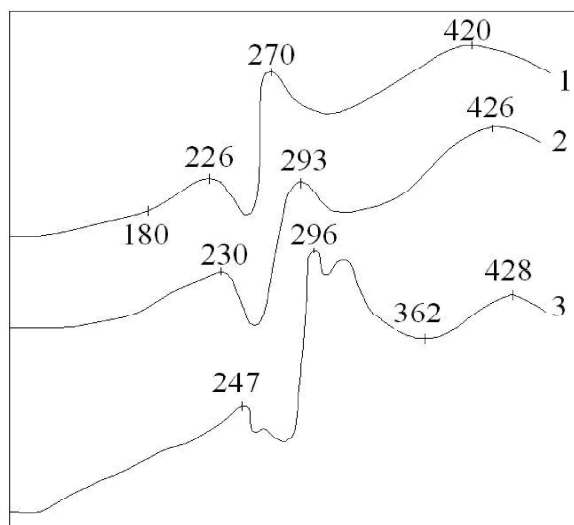


Fig. 1: DSC curves: PVC (1), PVC-10 CHL (2), PVC-50 DOP-10 CHL (3)

It is seen that when filler is incorporated into rigid and plasticized PVC compositions DSC curve behavior remains much the same, only exothermic peaks shift in the direction of higher temperatures and their intensity changes slightly. For PVC only with heat stabilizers the peak shows at 226°C and for maximum plasticized composition filled with 10 CHL mass fractions the peak shows at 247°C. By putting together the shifting of exothermic peaks and PVC dehydrochlorination the conclusion can be made that filler incorporation suppresses this process at the earlier degradation stages and improves the composition heat stability in the region of moderate temperatures (180-250 °C) which are significantly higher than melt processing temperatures of rigid and plasticized compositions.

Table 2 shows the summarized findings in changes of main thermal characteristics of rigid and plasticized PVC compositions modified with fillers.

CONCLUSION

It is seen from the given data that the position of endothermic peaks, start of thermal degradation and mass loss of investigated specimens shift in the direction of higher temperatures as filler content increases. When the specimens are heated till 220-230 °C slight mass loss is observed and when heating up to 350 °C intense degradation occurs with approximately 55% loss in specimen mass. And the filled compositions lose the same mass at higher temperatures that unfilled ones that is the evidence of heat stabilizing effect of modified additives [4].

Summary: These experimental investigations made it possible to establish that the fillers used have the significant effect on the temperatures of relaxation transition from one physical state to another and thermal degradation of PVC compositions.

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