

Study of Some Properties of Polymer Composition

Tavashov Shakhzod Khuzhakhmatovich

Associate Professor of Karshi State Technical University

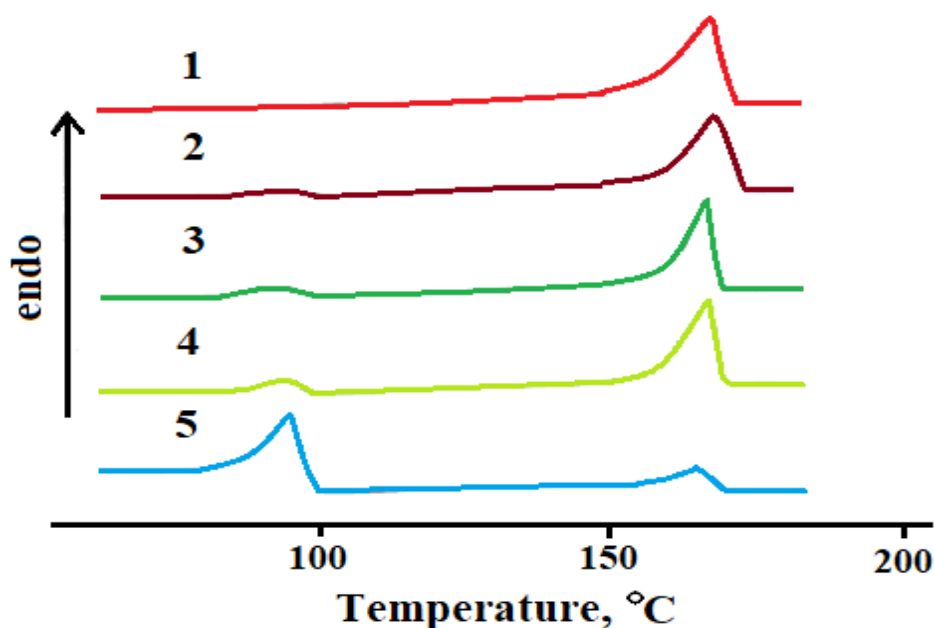
The unique physical, mechanical, chemical and electrical properties of polymers allow these materials to be used in various fields of technology. In order to rationally use polymers as dielectrics, semiconductors or electrically conductive materials, it is necessary to deeply study their electrical properties and understand the patterns of change in such properties as polymer structure and operating conditions [1].

The thermophysical properties of PP/ vinyl acetate composites were studied using differential scanning calorimetry, by analyzing melting and crystallization thermograms. The heating and cooling rate was 10°C/min. Scanning was performed in air. Figure 1 shows the crystallization and melting thermograms of PP and polymer composites.

As can be seen from the DSC curves, pure PP has a single thermal effect in the range of 165 - 185 °C, which is usually characteristic of PP homopolymers. When a copolymer is introduced into the composite, a new thermal effect is observed in the range of 85-95 °C, which is characteristic of melting low-melting polymers. It is known that vinyl acetate containing long sequences of ethylene units can form PE crystallites. Further increase in the vinyl acetate content is accompanied by a significant increase in the thermal effect in this region. A similar picture is observed on the crystallization curves of these systems. Based on these results, it can be said that these polymers form a heterophase structure when mixed.

When calculating the degree of crystallinity, the specific heat of melting of PP crystallites was taken as 145 kJ/kg; and for vinyl acetate 290 kJ/kg.

Based on the DSC data, it can be said that when vinyl acetate is introduced into PP, there is a slight shift in the melting temperature of PP to a region of lower temperatures, which indicates a change in the structure and the appearance of lower-melting crystallites (Figure 2).



a)

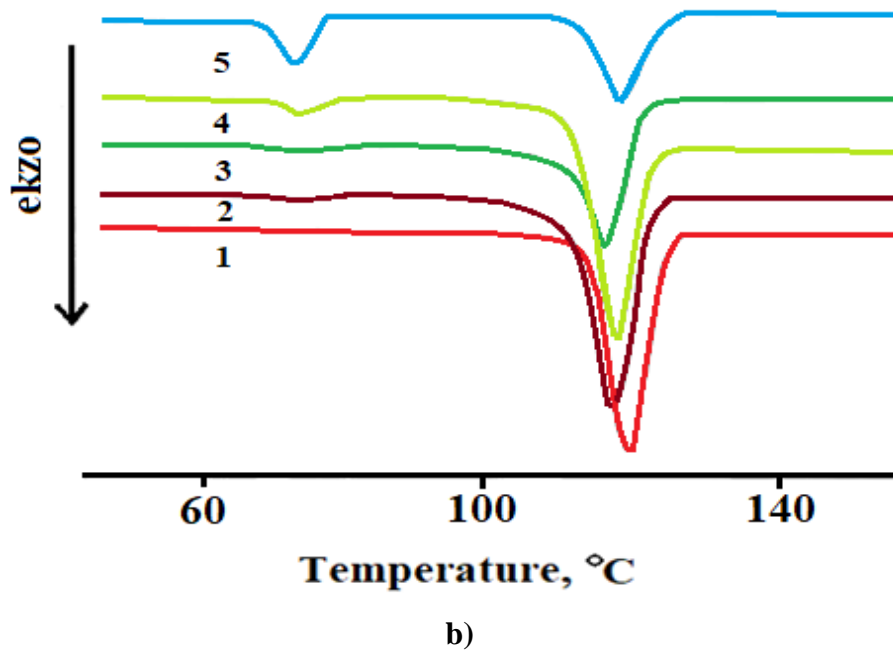


Figure 1 - Thermograms of melting (a) and crystallization (b) of PP/vinyl acetate composites: 1 - 100/0; 2 - 90/10; 3 - 80/20; 4 - 70/30; 5 - 60/40.

In addition, with an increase in the vinyl acetate content, in general, the enthalpies of melting decrease, and consequently the degree of crystallinity of PP (Figure 3). This indicates its partial amorphization. The observed slight increase in X_{10} PP may be due to the fact that at low concentrations, vinyl acetate can act as a crystallization nucleator. The lowest degree of crystallinity is characterized by the 60/40 composition.

The main thermophysical properties of PP/vinyl acetate polymer composites are presented in Table 1.

Table 1. Results of DSC data processing of PP/vinyl acetate composites

Polymer composition	T _{max . mel} , °C		Δ H _{mel} , kDj / kg		X _k , % (PP)*	X _k , % (vinyl acetate)	X _k , % (composite)
	pp	vinyl acetate	PP	vinyl acetate			
100/0	166	-	62	-	41	-	43
90/10	168	94	65	1	45	1	45
80/20	167	93	66	3	44	2	48
70/30	166	92	59	9	40	3	40
60/40	165	91	21	24	16	8	25
50/50	164	93	36	18	27	6	29
40/60	163	92	29	22	19	8	27
30/70	163	92	23	29	17	11	25
20/80	162	91	4	28	10	10	14
10/90	162	91	3	27	3	8	12
0/100	-	90	-	38	-	12	13

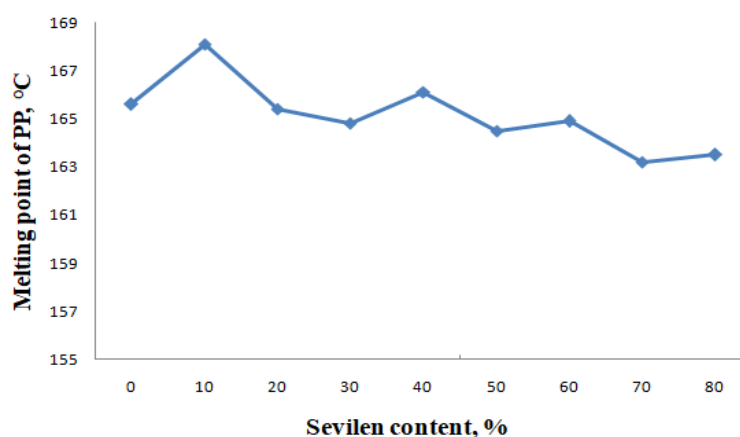


Figure 2 - Dependence of PP melting temperature on vinyl acetate content

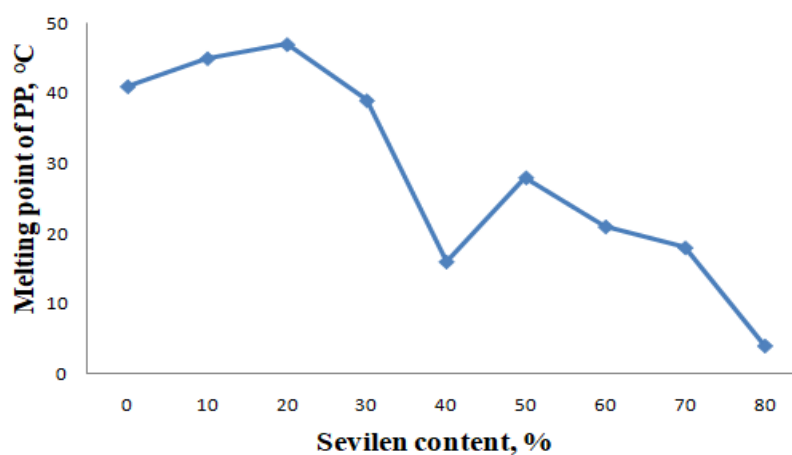


Figure 3 - Dependence of the degree of crystallinity of PP on the content of vinyl acetate

Rheological properties and detailed analysis of crystallization parameters of PP/vinyl acetate composites are presented in Table 2.

Table 2. Rheological properties and crystallization parameters of PP in PP/vinyl acetate composites

Polymer composition	MFI, g/10 min	$T_{max. cry.}$, °C	$T_{init. cry.}$, °C	$\Delta H_{cry.}$, kDj / kg	$t_{1/2}$, sec	K, kDj / kg/sec
100/0	5, 1	121	125	88	26	1.8
90/10	6, 3	119	124	77	30	1,1
80/20	5, 4	118	123	78	28	1.5
70/30	5.0	118	122	63	30	1
60/40	3.7	117	113	37	29	0.5
50/50	2.9	118	124	39	34	0.5
40/60	2.7	112	115	25	30	0.5
30/70	1.6	107	112	6	29	0.04
20/80	1.0	102	110	3	22	0.01
10/90	0.2	100	107	-	21	-

The crystallization process patterns indicate the structural features of PP/vinyl acetate mixtures. The rate of crystallite formation was determined by the time it takes for half of the crystallites to form (crystallization half-life):

$$t_{1/2} = (T_{\text{init. cry}} - T_{\text{max. cry}}) / V_{\text{cool.}}$$

where $T_{\text{init. cry}}$ is the initial crystallization temperature; $T_{\text{max. cry}}$ is the maximum crystallization temperature (peak); $V_{\text{cool.}}$ is the cooling rate.

The rate of crystallization was estimated by the rate of heat release during this process, which was calculated as the ratio of enthalpy to crystallization time:

$$K = \Delta H_{\text{mel}} / 2 t_{1/2}$$

As is known, the rate of formation of polymer crystallites in the mixture is determined by the rate of nucleation and the rate of diffusion of macrochains from the melt to the surface of the crystallization nucleus. Vinyl acetate does not have a significant effect on nucleation. It has a significantly greater effect on the growth of crystallites. In this case, the determining factor is apparently the chemical structure of vinyl acetate. Being mostly an amorphous polymer, as well as the content of polar acetate groups, determines the nature of interaction with the polymer matrix. A looser structure is formed due to an increase in the amorphous part. In this case, an interphase layer may form, which hinders the movement of PP macromolecules to the crystallization center, which is also evidenced by an increase in the viscosity of the melt. This is accompanied by an increase in the half-period of crystallization, i.e. a slowdown in the rate of crystallite growth and a decrease in the degree of crystallinity.

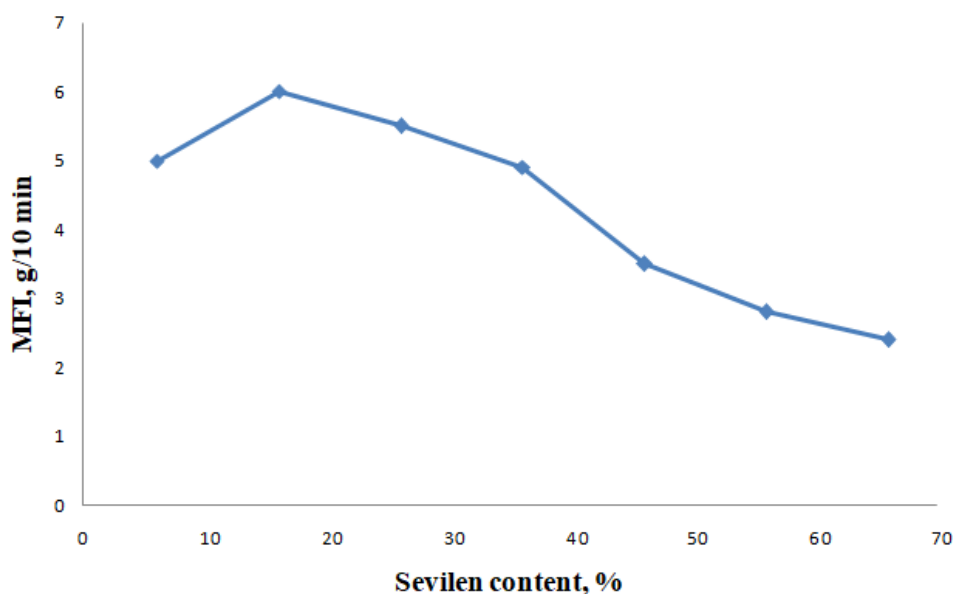


Figure 4 Dependence of the MFI of PP on the content of vinyl acetate

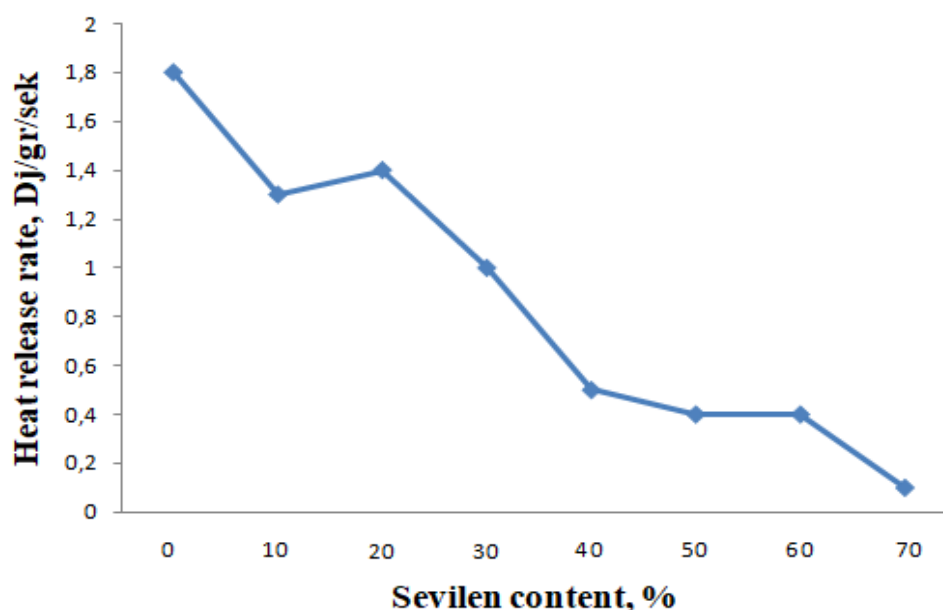


Figure 5 - Dependence of the rate of heat release during crystallization of PP on the content of vinyl acetate

It should be noted that the crystallization parameters of PP change quite monotonously with increasing vinyl acetate concentration. However, when the copolymer content reaches 40%, a clear “jump” occurs, i.e. a decrease in the specified parameters (T_{cry} , ΔH_{cry} , K - Figure 5). This is apparently due to the transition of vinyl acetate to the continuous phase and the achievement of maximum heterogeneity of the structure, where an extensive interphase layer complicates the crystallization process.

Thus, the introduction of vinyl acetate leads to a change in the structure of PP. On the one hand, at low concentrations, it can act as a crystallization nucleator, on the other hand, its high amorphousness and adhesion can cause disturbances and difficulties in the crystallization of PP macrochains.

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