

## Research Article

# Physicochemical Principles of Synthesis and Modification of Unsaturated Polyester-Polyvinyl Chloride Composites and the Properties of Materials Derived from Them

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The influence of the polymeric modifier of polyvinyl chloride on the structuring of unsaturated polyester resins has been investigated. It is established that the introduction of 2–5 parts by weight of polyvinyl chloride into a polyester composite accelerates the process of gelation and shortens the time of microgelation of the polyester. The influence of polyvinyl chloride on the structure coefficient, surface hardness, and strength of adhesive bonds and technological shrinkage of modified polyester composites has been revealed.

## 1. Introduction

Unsaturated polyester resins (UPR) are widely used for the manufacturing of filling compounds that are binders in the production of press materials, fiberglass, and other polymer composites [1–3]. The wide application of these resins is due to their relatively low cost, good wetting ability, high corrosion resistance, and resistance to aggressive media, as well as improved physicochemical and deformation properties [4, 5]. To eliminate the weaknesses inherent in polyester, namely fragility, shrinkage, and structural heterogeneity, it is modified using additives of a different nature [6–8].

Among the methods for modifying polyester resins, physical methods based on the combination of polyester with oligomers of a different nature or high-molecular compounds are technologically and economically feasible [9–11]. However, such a modification is featured by the influence of many physical and physicochemical factors, which are primarily related to the compatibility of components due to the different chemical and physical structures

of polymers, interphase system characteristics, intermolecular interactions, etc. [12].

One of the effective modifying methods for the thermosetting of binders, in particular polyesters, is the introduction of thermoplastic polymers into a compound. In contrast to oligomeric and rubber-based additives, thermoplastics may increase the resistance of polyester composite materials to blow stress without significantly reducing heat resistance. The following polymers of different structures can be used as thermoplastic additives: polymethyl methacrylate, polystyrene, polysulphone, polyester sulphone, polyesterimide, polycarbonate, etc.

It is also expedient to use a thermoplastic polymer modifier of polyvinyl chloride (PVC), which is characterized by high intermolecular and interphase interactions, as well as processability during treatment both in the presence of solvents and in the viscous-fluid state. Due to its peculiar properties, additional opportunities are offered for the improvement of modern technologies, creation of new functionalized materials, and the expansion of their application field [13].

The modification of polyester binders by thermoplastic additives should be considered as a transition to a multicomponent system, as a way of creating a certain phase of the supramolecular structure of the material and a method of directed regulation of the operational properties of materials and their products.

Besides the nature of the thermoplastic modifier, the significant influence on morphology, properties, and technological peculiarities of manufacturing modified polyester materials has the kinetics of curing the polyester binder [14].

The rate of physical, physicochemical, and chemical processes that take place during the formation of modified polyester materials has a significant and even decisive impact on the morphology and properties of structured polymers. The role of kinetic factors is especially important in the formation of structured polymers on the basis of multicomponent systems, when the curing process is accompanied by phase transformations, relaxation of the free volume, evaporation of the solvent, interactions between binders and fillers, etc. The technology of binder production or modification, the gel time, the conversion degree, and the final performance depend on the specificity of the structuring process [15].

In order to establish the physicochemical and technological patterns of the formation of polyester-polyvinyl chloride composites, the investigation of the interphase and intermolecular interactions between a polyester matrix and a macromolecule of a polymer modifier-polyvinyl chloride and physicochemical factors will be conducted. Basing on the obtained data, polyester-polyvinyl chloride binders will be developed, which will be characterized by the advance technological compatibility of components and the possibility of directive control of their operational properties. At the same time, the determination of the rheological properties of modified polyester composites will substantiate the formation of semi-interpenetrating networks in the composite, which goes through the stage of formation of local ordering regions, namely through the step of microgel formation.

## 2. Materials and Methods

The following unsaturated polyester resins were used for research: Estromal 11LM-01, Estromal 11LM-02, and Estromal A023 ("LERG," Poland). The polyvinyl chloride of the brand Lacovyl PB1156 (LLC "Karpatnaftokhim," Kalush, Ukraine) was used to modify unsaturated polyester oligomers.

The curing of the polyester resin was carried out in the presence of the initiator of methyl ethyl ketone peroxide in dibutyl phthalate (Oxytop Ltd., Poland) and the accelerator of cobalt naphthenate (CAS No.: 61789-51-3) at room temperature.

The investigation of polymer modifier influence on the curing of unsaturated polyester resins was carried out on the basis of rotational viscometry. The change in the viscosity of polyester composites was investigated by the rotary viscometer "Rheomat-30" at a constant shear rate of  $28.5 \text{ sec}^{-1}$  using a coaxial cylinder system according to ISO 3219.

For the characterization of physical and chemical interactions in polyester-polyvinyl chloride composites and the derived materials, the IR spectroscopic analysis method on the spectrophotometer SPECORD 70 over the range from 400 to  $4000 \text{ cm}^{-1}$  was used.

The structure coefficient of polyester materials was investigated according to the method in [16] that relied on the module-deformation calculation method based on the introduction of a conical penetrator loaded in the research sample.

The maximum curing temperature of an unsaturated polyester resin in the presence of a polymer modifier was determined in accordance with State Standard (GOST) 21970-2015.

Scanning electron microscopy was performed on a REM-106I scanning electron microscope. Copper was used as a conductive material for sample coating. A comprehensive thermal analysis was carried out on the derivatograph Q-1500D of the system "F. Paulik-J. Paulik-L. Erdely" with the registration of the analytical signal of mass loss and thermal effects (heating rate of  $5^\circ\text{C}/\text{min}$  in the air).

The determination of the coating hardness by a pendulum instrument was carried out in accordance with ISO 1522-73. The investigation of the hardness of the polymer coatings was performed using a type M-3 pendulum instrument. The strength of the adhesive bonds of the polyester composite to the metallic substrate (St3) was determined by measuring destructive stress during the uniform separation of the coupled samples in accordance with ISO 4624: 2002. The technological shrinkage of the samples was determined by comparing the size of the molded sample at 293 K to the form size according to ISO 2577.

## 3. Results and Discussion

In general, the curing process of unsaturated polyester oligomers in the presence of polymer modifiers can be divided into two stages: the first one is characterized by the growth of branching of macromolecules, but there is no general network covering the entire material; the second is the network formation, which goes mainly after the gel point.

It is known [17] that up to the gel point the system can be investigated by a viscometry method, namely rotational, that gives the opportunity to register a change in the rheological properties in a wide range of viscosities.

The change in the rheological properties of the thermo-setting systems, namely polyester, depending on the time of curing ( $\tau$ ) is described by the following exponential equation [18]:

$$\eta = \eta_0 \cdot \exp(k_\eta \cdot \tau), \quad (1)$$

where  $\eta_0$  is the initial viscosity (Pa·s) and  $k_\eta$  is the kinetic constant of the viscosity increment ( $\text{s}^{-1}$ ).

The results of the viscometric investigation of modified polyester materials showed that for all tested composites, regardless of the nature of the unsaturated polyester resin, there is a rapid viscosity increase of the system after 75–

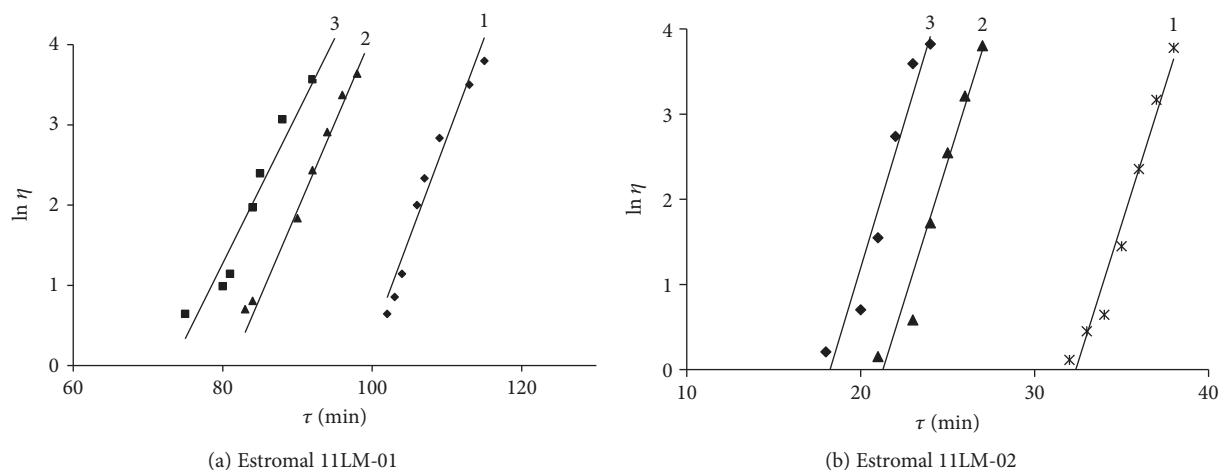


FIGURE 1: Kinetics of the logarithmic viscosity number of polyester composites. PVC content (pts.wt.): 1—0; 2—2; 3—5.

120 minutes of curing. The introduction of PVC into a polyester composite leads to an accelerated increase in the viscosity of the tested systems.

The value of the viscosity increment constant for the tested systems with the different contents of the polymer modifier can be determined graphically by the angle of inclination of the curve from dependence (1) in a semi-logarithmic scale:

$$\ln \eta = \ln \eta_0 + k_\eta \cdot \tau. \quad (2)$$

The dependence of the logarithmic viscosity number on the curing time of polyester composites containing PVC is shown in Figure 1.

It should be noted that the introduction of polyvinyl chloride into an unsaturated polyester resin regardless of its brand leads to an acceleration of the curing process, which is evidently induced by the influence of the polymer modifier on the nature of intermolecular interactions between the components of the system.

The values of the kinetic constants of the viscosity increment depending on the content of the polyvinyl chloride polymeric modifier are given in Table 1.

It was found that the viscosity increment constant of composites based on the UPR of the brand Estromal 11LM-01 decreases with an increase of the polymer modifier content. Obviously, it is caused by a significant increase in the viscosity of the system after polyvinyl chloride introduction into the composite. However, polyester compositions based on Estromal 11LM-02 demonstrate a slightly different dependence—the increase of PVC content leads to the slight increase of the viscosity increment constant. Obviously, it is caused by the fact that the polyvinyl chloride polymeric modifier physically interacts with the polyester oligomer, affecting the kinetics of the cross-linking reaction. Such a mechanism of the modified polyester binder structuring can also be caused by the copolymer formation and a decrease in the molecular weight of the polymer for the subsolution of PVC in a polyester oligomer.

TABLE 1: Dependence of the kinetic constant of viscosity increment on the content of the polymer modifier.

No.	PVC content (pts.wt.)	Viscosity increment constant ( $k_\eta$ ), ( $s^{-1}$ )	
		Estromal 11LM-01	Estromal 11LM-02
1	0	0.0042	0.0108
2	2	0.0036	0.0109
3	5	0.0031	0.0113

The gel time ( $\tau_{gel}$ ) was determined from the dependence of the inverse viscosity on time in the final stages of the curing process by approximating the straight line to the abscissa (Figure 2).

The results of determining the gel time depending on the nature of the polyester resin and the polymer modifier content are given in Table 2.

The results indicate that the introduction of polyvinyl chloride in amounts of 2–5 pts.wt. in the UPR-based composite of the brand Estromal 11LM-01 and Estromal 11LM-02 accelerates the gelation of the system. Such structuring process regularities are obviously caused by the different nature of polyester oligomers and the significant increase in system viscosity during the introduction of polyvinyl chloride, as well as the specificity of intermolecular interactions between components.

During the modification of polyester materials by polyvinyl chloride, according to the structural theory of gelation [19], the formation of a three-dimensional network goes through the stage of the formation of local ordering regions, which is a result of intermolecular interactions. The existing ordered arrangement of oligomeric macromolecules makes the inhomogeneous curing of polymer systems possible during the reaction of the phase separation processes of the components. The three-dimensional network that formed in the region of gel formation is characterized by the uneven distances between the nodes of structuring. At the same time, the structuring of aggregates

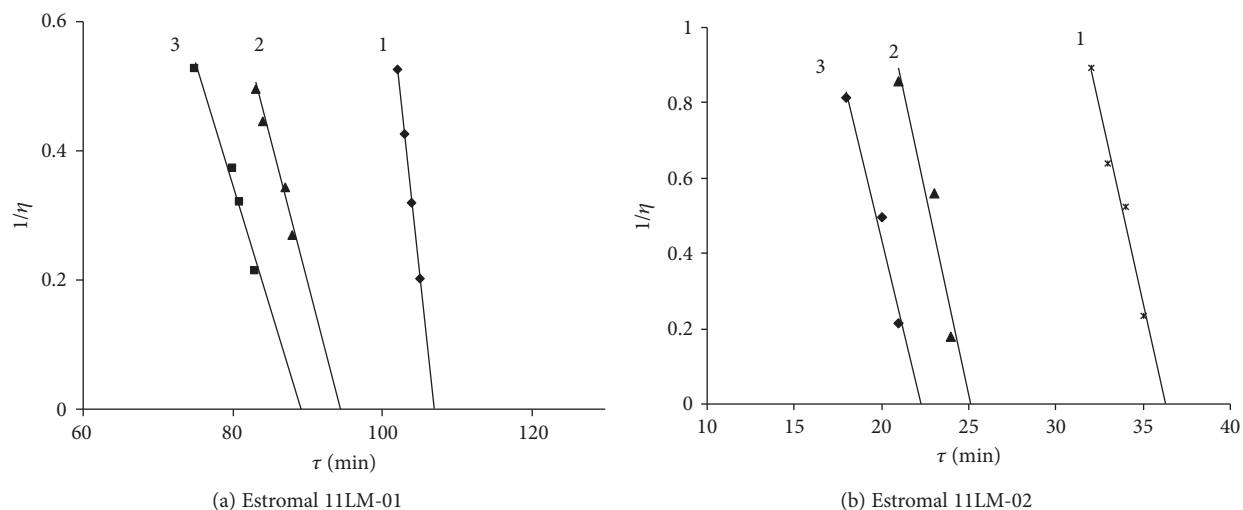


FIGURE 2: Dependence of the inverse viscosity of polyester composites on the curing time. PVC content (pts.wt.): 1—0; 2—2; 3—5.

TABLE 2: The initial viscosity ( $\eta_0$ ) and gel time ( $\tau_{gel}$ ) dependence on the polymer modifier content.

No.	UPR	PVC content (pts.wt.)	Characteristics $\eta_0$ (Pa·s)	$\tau_{gel}$ (min)
1		0	0.45	106.9
2	Estromal	2	1.12	94.4
3	11LM-01	5	1.34	89.1
4		0	0.47	36.3
5	Estromal	2	0.56	25.1
6	11LM-02	5	0.67	22.3

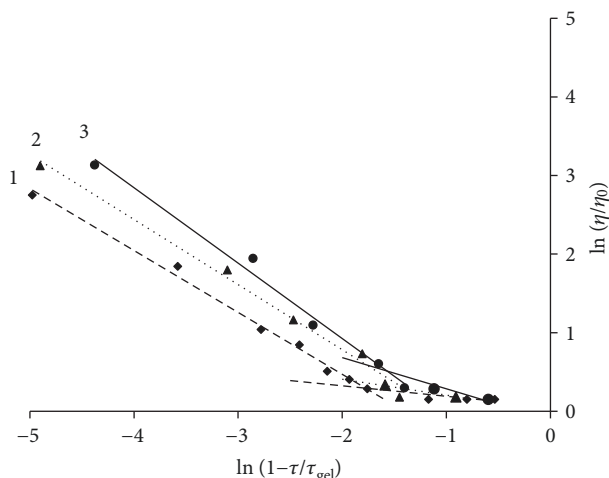


FIGURE 3: Dependence of  $\ln(\eta/\eta_0)$  from  $\ln(1 - \tau/\tau_{gel})$  for modified polyester composites based on Estromal 11LM-02. PVC content (pts.wt.): 1—0; 2—2; 3—5.

of branched macromolecules takes place first and only in the deeper gelation stages do they form a continuous three-dimensional network due to the interconnection of the transfer chain.

Thus, the curing of thermosetting oligomers occurs with the formation of microgel particles in the system. In this case, particles of the microgel can be formed from the very beginning of the reaction, and at a certain moment. So, we may consider systems with a microgel as filled systems, which give an opportunity to use known rheological concepts to describe the dependence of viscosity on the curing time.

The process of structuring near the gelation point is described by the following scaling (percolation) equation [20]:

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\tau}{\tau_{gel}}\right)^{-b}, \quad (3)$$

where  $\tau_{gel}$  is gelation time (s);  $\eta_0$  is initial viscosity (Pa·s);  $\eta$  is viscosity (Pa·s);  $\tau$  is time (s); and  $b$  is “scaling” coefficient that is theoretically equal to  $0.7 \pm 0.07$ .

The microgel formation in the system during structuring is confirmed by a break on the kinetic viscosity dependence in the logarithmic coordinate  $\ln(\eta/\eta_0)$  from  $\ln(1 - \tau/\tau_{gel})$ . The graphic representation of the microgelation process for polyester composites based on Estromal 11LM-02 is shown in Figure 3.

It should be noted that viscosity dependencies in logarithmic coordinates for composites based on the unsaturated polyester resin Estromal 11LM-01 are of the same nature.

It has been established that for the investigated systems, the viscosity change in the percolation equation coordinates (3) is described by two straight lines with different angles of inclination [20].

The type of the above dependencies shows that the curing of polyester composites occurs inhomogeneously through the stage of microgel formation.

The values of “scaling” coefficients  $b_1$  and  $b_2$  that characterize the inclination angle and microgel formation time ( $\tau_m$ ) from the content of the polymer modifier are given in Table 3.



TABLE 3: The dependence of the coefficients  $b_1$  and  $b_2$  and the time of microgel formation ( $\tau_m$ ) from the content of the polymer modifier.

No.	UPR	PVC content (pts.wt.)	Characteristics		
			$b_1$	$b_2$	$\tau_m$ (min)
1		0	0.9	0.43	92.03
2	Estromal 11LM-01	2	1.03	0.27	80.25
3		5	1.24	0.58	78.79
4		0	0.79	0.13	30.37
5	Estromal 11LM-02	2	0.84	0.2	19.9
6		5	0.96	0.39	17.91

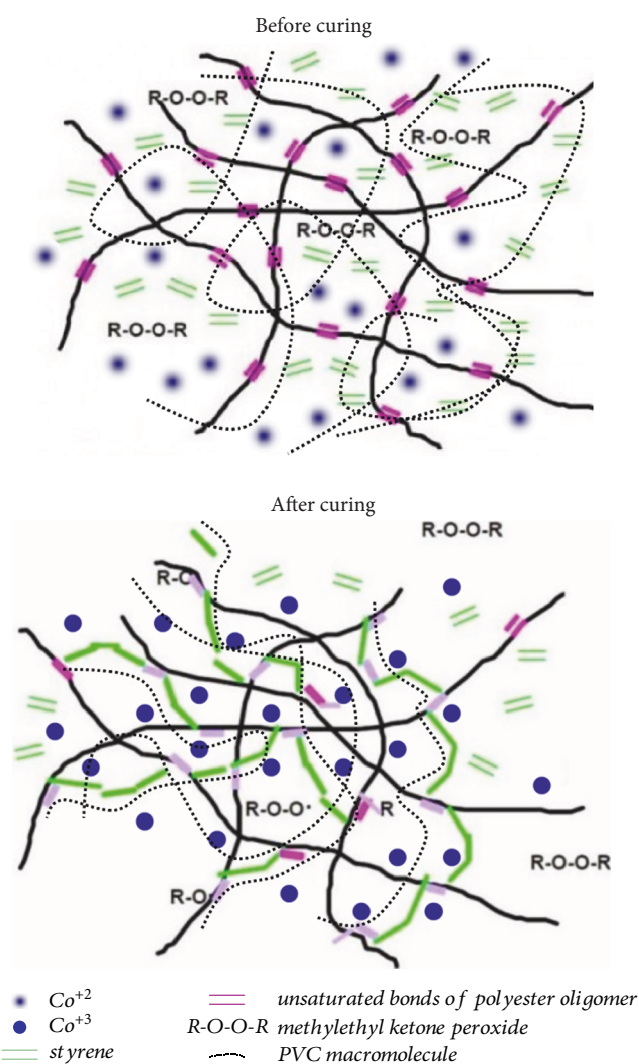


FIGURE 4: General schematic illustration of the process of polyester resin curing under the influence of cobalt naphthenate and methyl ethyl ketone peroxide in the presence of a polymer polyvinyl chloride modifier.

It has been established that the scaling coefficient is not equal to the theoretical value of 0.7. The curing of the polyvinyl chloride-modified polyester composite is characterized by an increase in the scaling coefficient  $b_1$  both for Estromal

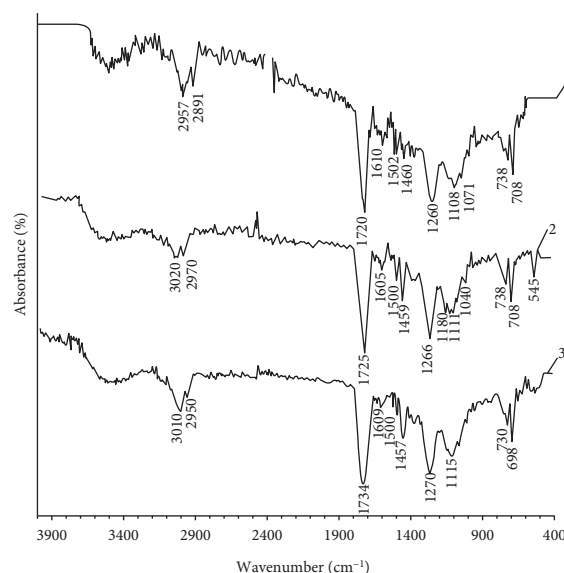


FIGURE 5: FTIR spectra of unstructured UPR (1), structured UPR (2), and structured modified UPR (3) based on Estromal 11LM-01. PVC content (pts.wt.): 1 and 2—0; 3—10.

11LM-01 and for Estromal 11LM-02. Such behavior, apparently, is caused by a change in the nature of the structuring of polyester oligomers under the action of polyvinyl chloride macromolecules. The introduction of 2–5 pts.wt. of polyvinyl chloride in a polyester composite leads to a decrease in the microgel formation time for the investigated systems.

Based on the investigations of the kinetics of the modified polyester resin structuring, a possible mechanism of unsaturated polyester resin structuring in the presence of polyvinyl chloride under the action of methyl ethyl ketone peroxide and cobalt naphthenate is proposed (Figure 4).

The regularities of the structuring of polyvinyl chloride-modified oligomer polymers are apparently caused by the nature of the interphase and intermolecular interactions in the system. The nature of intermolecular interactions between components was specified on the basis of FTIR spectroscopic analysis, the results of which are shown in Figure 5 and Table 4.

On the basis of FTIR spectroscopic studies, it was found that the introduction of polyvinyl chloride into the polymer modifier polyester matrix leads to a change in the intensity of the absorption bands, their redistribution, and the emergence of new in-between components of the reaction system.

Such changes in the intensity of the absorption bands and their displacement in the spectra of polyvinyl chloride-modified materials indicate that the polymeric polyvinyl chloride modifier influences the process of polyester oligomer structuring and the emergence of active interactions, apparently hydrophobic, between the polyester matrix and the macromolecules of the modifier.

The structure coefficient of the net materials is a characteristic of the three-dimensional network of chemical and physical origin, and also somewhat characterizes the interphase and intermolecular interactions between the components.

TABLE 4: Influence of the structuring process on the characteristic absorption wavelength of modified polyester materials.

Sample	Absorption wavelength ( $\text{cm}^{-1}$ )				
	$\nu_{\text{s.v.}}$ (-CH)	$\nu_{\text{as.v.}}$ (-C=O)	$\nu_{\text{def.}}$ (-C=C-O-C)	$\nu_{\text{as.v.}}$ (-C-O-C-)	$\nu_{\text{def.}}$ (C-H)
Unstructured UPR	2957	1720	1260	1108	738 708
Structured UPR	3020	1725	1266	1111	738 708
Structured modified UPR	3010	1734	1270	1115	730 698

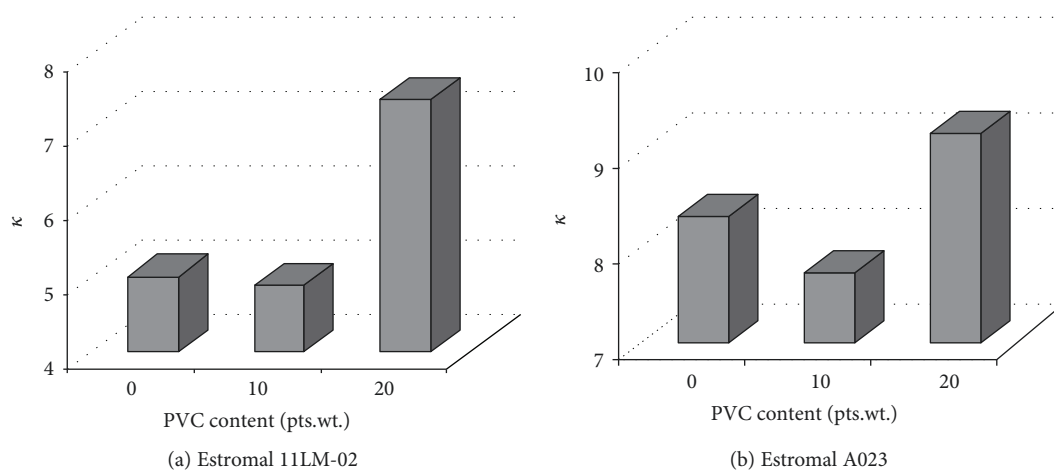


FIGURE 6: Influence of PVC on the structure coefficient of polyester materials.

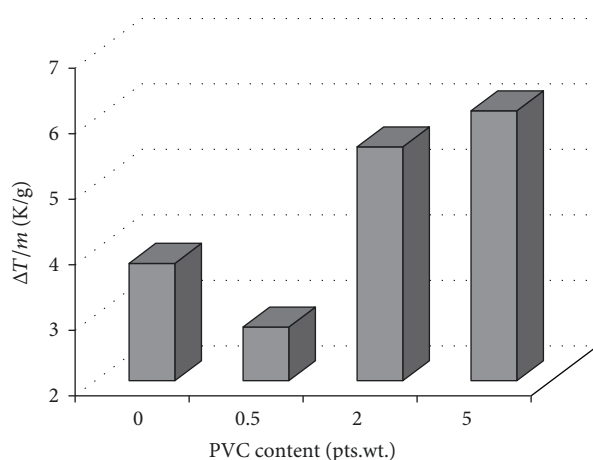


FIGURE 7: Effect of polymer modifier content on the characteristics of the curing process of the polyester resin Estromal 11LM-01.

The influence of the content of the polymer modifier on the structure coefficient ( $K$ ) of polyester materials is shown in Figure 6.

The introduction of 20 pts.wt. of polyvinyl chloride into a polyester composition results in an increase in the structure coefficient of the composite, which is obviously caused by the formation of semi-interpenetrating networks of structured polyester resin and PVC macromolecules.

The acceleration of curing of a polyester resin under the influence of polyvinyl chloride is represented by the value of the maximum thermal effect shown in Figure 7.

Such features of the polymer modifier that influence the structuring process are apparently caused by the

higher viscosity of the initial composition, as well as the matrix effect [21] on the styrene molecules involving the PVC macromolecules.

A slight slowdown in the process of curing a polyester resin was detected in the presence of a small amount of the PVC polymeric modifier (up to 0.5 pts.wt.) that is characterized by the smallest thermal effect. This, obviously, depends on an increase in the heterophasicity and the free volume of the system. Thus, the highest curing rate of the polyester resin is observed at the content of polyvinyl chloride of 5 pts.wt., which is confirmed by the highest values of the maximum thermal effect.

By scanning electron microscopy, the influence of the polymeric modifier of polyvinyl chloride on the morphological features of polyester materials has been established (Figure 8).

It has been found out that the morphological features of the material have a significant influence on the composite processibility, in particular, the previous swelling and partial dissolution of the modifier in styrene—a solvent for UPR—which contributes to the formation of modified polyester materials with less pronounced heterophasicity.

The thermal stability of modified polyester materials was determined by complex thermal analysis, the results of which are shown in Figure 9.

It was found that polyester materials are characterized by a multistage process of thermolysis. It should be noted that for polyester materials in the temperature range up to 77–85°C at the first stage of thermolysis, the appearance of a slight endothermic effect on the DTA curve is characteristic, which obviously corresponds to the softening of the

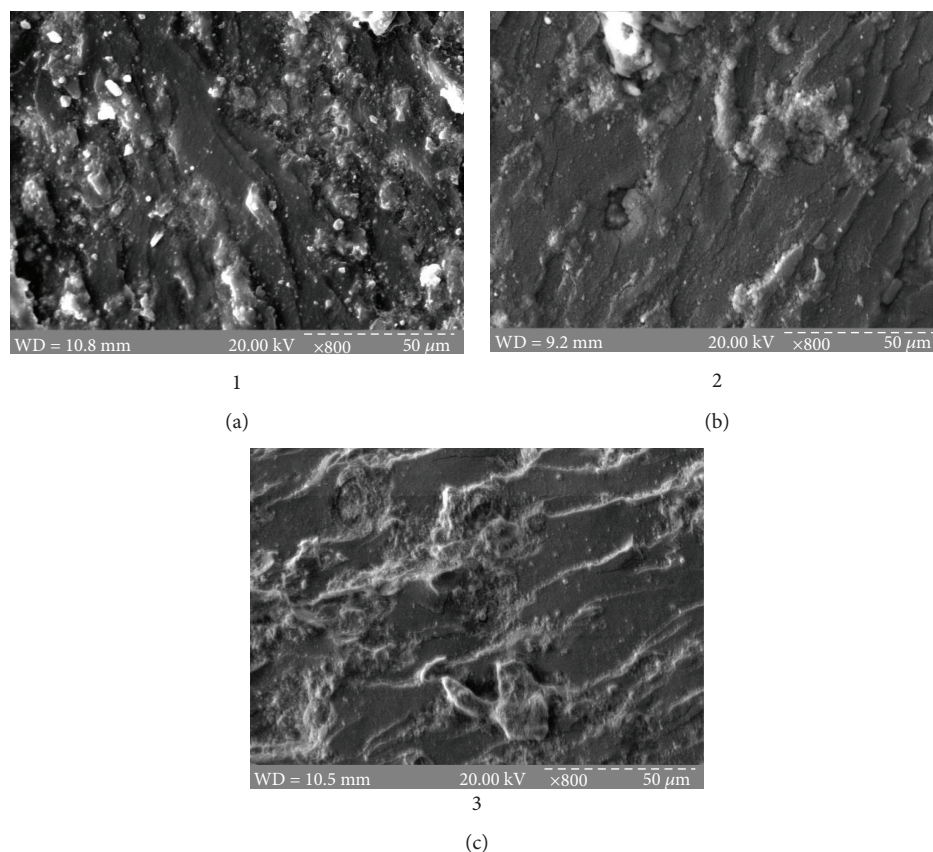


FIGURE 8: SEM micrographs of modified polyester materials. PVC content (pts.wt.): 1—0; 2 and 3—10. The time from the beginning of the PVC introduction to the beginning of curing of composition (min): (a) 0; (b) 5; (c) 90.

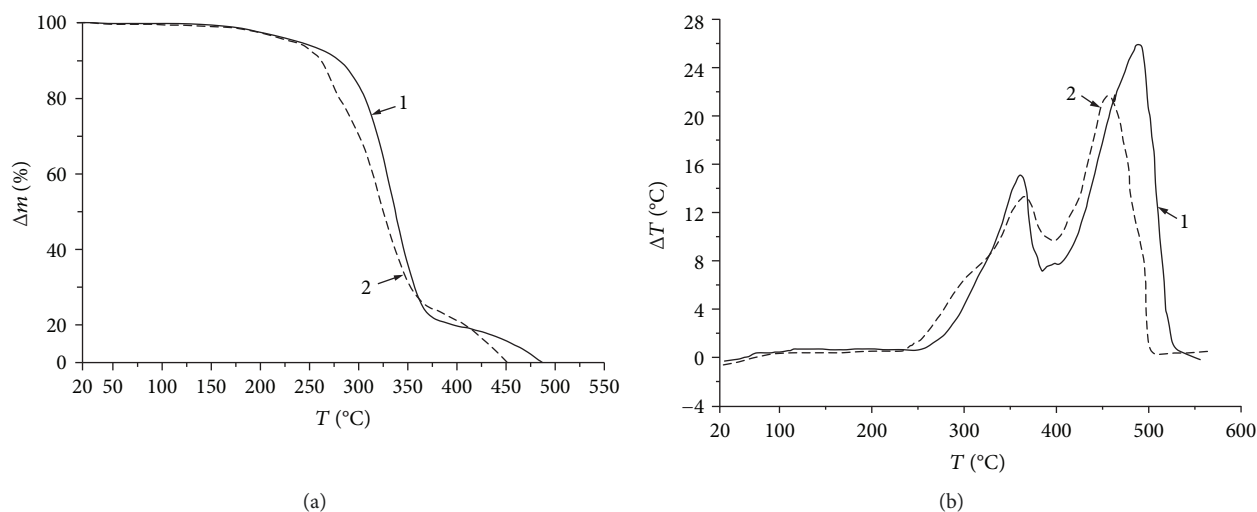


FIGURE 9: Results of complex thermogravimetric (a) and differential-thermal (b) analyses. Composite's content (pts.wt.): 1—UPR : PVC = 100 : 0; 2—UPR : PVC = 100 : 10.

samples and the increase in the mobility of the elements of the three-dimensional structure, namely polyester chains and polystyrene “cross-links” that chemically connect polyester chains [22].

The second stage of thermolysis (77–251°C) is followed by a slight mass loss and the deviation of the DTA channel into the region of exothermic effects, where the volatile

molecules are released and the additional polyester resin structuring occurs. Most likely, those volatile molecules are the molecules of styrene, which is a setting agent in this system.

It should be noted that the mass loss in this temperature range for sample 2 is smaller than for sample 1, which is obviously a result of the influence of PVC macromolecules on the

TABLE 5: Influence of modifier content on the properties of polyester materials.

No.	Characteristics	PVC content (pts.wt.)				
		0	2	5	10	20
1	Pendulum hardness	0.64 ± 0.02	0.54 ± 0.02	0.71 ± 0.03	0.70 ± 0.04	0.34 ± 0.02
2	Strength of adhesive bonding (MPa)	28.7 ± 0.5	24.4 ± 0.4	21.6 ± 0.2	26.7 ± 0.5	30.1 ± 0.3
3	Shrinkage capacity (%)	8.51 ± 0.06	8.76 ± 0.04	7.91 ± 0.07	7.32 ± 0.04	7.18 ± 0.06

All data were expressed as mean ± standard deviation obtained by at least five different experiments. The level of significance was set at  $p < 0.05$ .

acceleration and depth of the polyester oligomer structuring involving styrene molecules. On the third stage of thermolysis (temperature range 251–384°C), along with the thermooxidative destructive processes, in sample 2 in the polyester resin autocatalytic destructive processes in PVC accompanied by the release of HCl take place. The progress of these processes is largely influenced by the filler and its nature.

The introduction of polyvinyl chloride into the polyester composite can influence the process of the polyester binder structuring and, accordingly, the physical and mechanical properties of the resulting material. The influence of the polymer modifier on the properties of polyester materials is given in Table 5.

As it is seen from Table 5, the modification of polyester materials by polyvinyl chloride gives an opportunity to adjust the strength properties of the material. The introduction of 5–10 pts.wt. of PVC increases the pendulum hardness of the investigated materials. A further increase of the PVC content in the polyester composite leads to a decrease in surface hardness, which is obviously a result of changes in the surface characteristics of the material.

It should be noted that the introduction of up to 10 pts.wt. of polyvinyl chloride somewhat reduces the value of the adhesion strength of the polyester to the metal substrate. The increase in PVC content by more than 10 pts.wt. leads to an increase in the adhesion strength. This effect is obviously caused by the presence of a greater number of different polar groups in such composites, as well as by the change in the morphology of materials with the formation of a fluctuation network between a structured polyester resin and PVC macromolecules.

Polyvinyl chloride-modified polyester materials were found to be characterized by lower technological shrinkage. The introduction of polyvinyl chloride in an amount up to 2 pts.wt. somewhat increases the technological shrinkage of polyester materials. This is caused by a greater number of different polar groups in such composites. However, a further increase in PVC content leads to a decrease in the value of technological shrinkage from 8.51% to 7.18%. The established mechanisms are connected with the specificity of intermolecular interactions between the macromolecules of the polyester oligomer and the modifier, and with the changes in the morphology of the modified materials.

#### 4. Conclusions

It has been established that polyvinyl chloride influences the kinetic patterns of unsaturated polyester resin curing, i.e., the introduction of 2 to 5 pts.wt. of the polymer

modifier accelerates the process of unsaturated polyester oligomer structuring, namely, the constant of viscosity increment changes, the initial viscosity of the system increases, and the gel time decreases.

Based on the results of FTIR, photocolometric, and SEM investigations, the change in the nature of intermolecular interactions, their redistribution, and the emergence of new interactions between components of the reaction system were established, as well as the formation of semi-interpenetrating polymer networks through the formation of regions of local ordering.

Developed polyester-PVC materials are characterized by 10% more pendulum hardness, 5% more strength of adhesive bonding, and 10–15% less shrinkage capacity; they can also be effectively used as a polymer base for composite materials of various applications.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article. This research was performed as part of the employment of the author at the Lviv Polytechnic National University and at the Ministry of Education and Science of Ukraine.

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