

Effect of the Interface with Solid on the Interfacial Region in the Blends of Linear Polymers Formed *In Situ*

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ABSTRACT: Blends of polyurethane and poly (methyl methacrylate) of various compositions were synthesized *in situ* in presence of various amounts of nanoparticles (fumed silica). From thermo-physical measurements it was found that the reaction is accompanied by the phase separation and evolution of two phases. The temperature transitions in the systems and their positions depend on the blend composition and on the filler amount. Using scanning differential calorimetry, the fraction of an intermediate region between two main phases has been estimated from the changing of heat capacity increments. It was observed that in filled polymer blends in

the temperature region between two main relaxation transitions, there appears the third transition. This transition is supposed to be the result of the formation of adsorption layer at the interface with solid. The appearance of such an intermediate regions increases essentially the total fraction of an interfacial region in the system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4646–4651, 2006

Key words: blends of linear polymers; formation *in situ*; glass transition; interface; fumed silica; fraction of interfacial region; scanning differential calorimetry

INTRODUCTION

Introducing filler into the blends of linear and cross-linked polymers [interpenetrating polymer networks (IPNs)] gives rise to the essential change in the physical properties of filled polymers due to the formation of interfacial layers at the polymer–filler interface. The properties of such multicomponent systems are determined by the processes of the surface segregation of components at the interface and physical interaction of each component with the surface.^{1,2} The surface segregation by IPN formation proceeds in a nonequilibrium conditions being dependent on the kinetic parameters of the reaction.³ Earlier it was established that introducing filler into the reaction system forming IPNs leads to the slow down of the phase separation in the course of reaction.⁴ The principle of IPNs formation, as is known, is based on the simultaneous reactions of two polymer formation proceeding according to different mechanism. The typical phenomenon for phase-separated IPNs is the formation of extended interfacial region as the result of incomplete phase separation during reaction. The latter is determined both by the crosslinking of the reaction system and by high increase in its viscosity.

Introducing fillers into the reaction systems slows down the phase separation and increases the fraction of an interfacial layer.

The principle of IPNs formation may also be applied to obtain the blends of two linear polymers. It may be supposed that in such a case, when crosslinking of components during reaction is absent, the degree of phase separation should be higher. In our previous work,⁵ we have investigated the formation of the blends of two immiscible linear polymers [polyurethane (PU) and poly(methyl methacrylate) (PMMA)]. It was found that two immiscible polymers formed are phase-separated at a definite conversion degree. The conditions of the phase separation in the system are determined by the kinetics of two simultaneously proceeding reaction. At the initial stages of the reaction the interconnected periodic structures are formed, which are due to the spinodal mechanism of phase separation. Preliminary study has shown the effect of filler on the reaction kinetics and phase separation. It was observed that increasing of filler concentration accelerates MMA polymerization and diminishes the rate of PU formation. Simultaneously the onset of phase separation is delayed, whereas its rate diminishes.

The appearance of the incompatibility in the course of reaction also strongly depended on the ratio of polymer components. It was also established that the mutual effects of the reaction kinetics and phase separation determine the thermophysical properties of the filled blends.^{2,4}

The aim of the present article is to estimate the effects of the ratio of components and the amount of

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filler on the thermophysical properties of phase-separated system and their role in the formation of an intermediate region between these two phases.

EXPERIMENTAL

For the experimental study, the blend of poly(methyl methacrylate) (PMMA) and polyurethane (PU) was chosen. Such a blend is characterized by the upper critical solution temperature in the region of 373 K.

All initial reagents were dried and purified. Methyl methacrylate (MMA) was washed clean from stabilizer, dried and distilled at $T = 373$ K, $n_d^{20} = 1.1414$. Hexamethylene diisocyanate (GMDI) was distilled in vacuum, the boiling point $T = 394$ K at $P = 3$ mmHg, $n_d^{25} = 1.4516$. Oligotetramethylene glycol (mol. mass 1000) (OTMG) was dried under vacuum at 353–358 K during 5 h and stored under dry argon. Diethylene glycol (DEG) was dried under molecular sieves and distilled in vacuum at boiling point $T = 366$ K and $P = 1$ –2 mmHg; $n_d^{20} = 1.4445$. Initiator of radical polymerization, α, α' -azobisobutyronitril (AIBN), was recrystallized from ethanol and dried in vacuum (1–2 mmHg) at the room temperature up to the constant weight.

Nanoparticles of fumed silica (aerosil) (trade mark A-175) with particle size ≈ 16 nm and specific surface 175 m²/g were used as filler. Aerosil was heat treated at 1073 K for 6 h.

The mixture of two polymers, PU and PMMA, was obtained by simultaneous formation of both polymers proceeding *in situ* according to various mechanism: radical polymerization (PMMA) and polyaddition (PU). PU was synthesized from macrodiisocyanate based on oligotetramethylene glycol and hexamethylene diisocyanate (ratio 1 : 2) using diethylene glycol as chain extender. The catalyst concentration for PU formation (dibutyl stannum dilaurate) was 1×10^{-5} mol/L; the initiator concentration was taken 0.005 mol/L. Aerosil was introduced into the reaction mixture and thoroughly mixed for 20 min. At such conditions no sedimentation of filler was observed more than 8 h. Also, aerosil particles were distributed in the mixture uniformly (Fig. 1). It was mentioned above that the size of filler particles is about 16 nm. However, when particles are introduced into the reaction mixture, we can observe some aggregation of particles (a very well known fact). These aggregates can be seen in optical microscope (Fig. 1) situated between elements of interconnected structures of the cured system, these structures being the result of the spinodal mechanism of phase separation. The reagents for synthesis of both polymers were mixed and reactions were performed at 333 K.

The films of blends were obtained between two glass covers with coating from the poly(ethylene

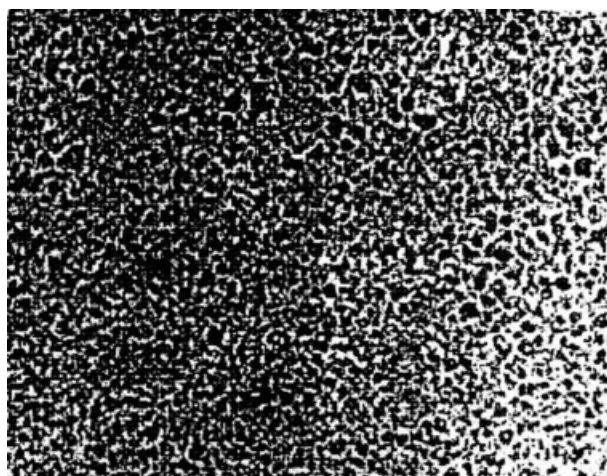


Figure 1 Microscopic structure of the PU/PMMA blends (50/50) containing 2% of filler (magnification 400).

terephthalate) (like a sandwich) applying hermetic protection on butt ends. The films were stored at 333 K during a month up to full disappearance of reaction active groups. IR-spectra of samples did not reveal the absorption bands of NCO-groups (2270 cm⁻¹) and C=C bonds (1610 – 1640 cm⁻¹). Figure 2 shows fragments of IR-spectra of starting reaction mixture and cure blends PU/PMMA = 70/30. Samples for IR-spectra registration were prepared either in tablet form with KBr or reaction mixture was spread onto the KBr plates. IR spectra were registered on the spectrophotometer Specord IR-75.

Calorimetric measurements were done using differential scanning calorimeter of Perkin-Elmer type with diathermic shell in the temperature interval 133–473 K at the heating rate of 2 grad/min. Glass transition temperature was determined from thermograms as a temperature corresponding to the half-increment of heat capacity.

RESULTS AND DISCUSSION

Figure 3 presents the temperature dependence of the heat capacity, C_p , and its temperature increment, dC_p/dT , for the 30/70 PU/PMMA blend containing various amount of the filler. Such dependencies are typical of all the component ratios. As is seen, the thermograms for unfilled blends have two inflection points for C_p and correspondingly two maxima of dC_p/dT . This effect is due to the coexistence in the blend of two phases—low temperature jump in C_p corresponds to the phase enriched in PU, whereas the high temperature jump relates to the PMMA enriched phase. In present study, for the first time, the presence of additional increment C_p and corresponding dC_p/dT maximum on the thermograms for all filled blends was discovered. We related this

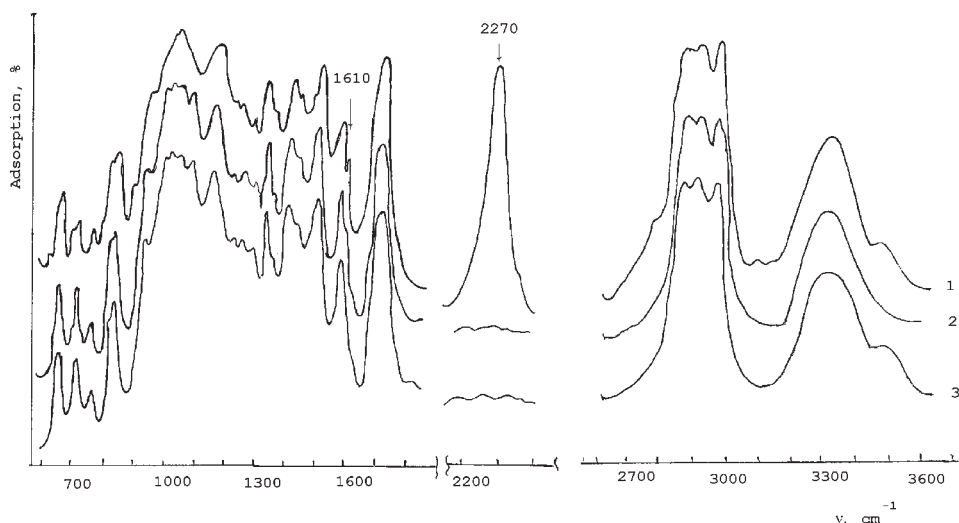


Figure 2 IR spectra of the reaction mixture (1), and unfilled (2) and filled (5% mass) (3) polymer blend PU/PMMA of ratio 70/30 (by mass) after completing reaction.

phenomenon to the thermal transition in the adsorption (or surface) layers of the blends at the interface with solid. According to the results of the investigation of the surface segregation in blends on the solid surface,⁶ the composition of such a layer differs from the composition of the polymeric matrix. In Figure 3, it can be seen that in unloaded blends, the interphase does not become a separate phase. Similar effect was also observed by Song et al.⁷ In the presence of filler an additional surface layer characterized by its own transition temperature is formed at the interface with solid.

From the experimental data, the increments ΔC_p and corresponding transition temperatures (T_g) were defined. The determined error of ΔC_p and T_g did not exceed 1%. Using the data on ΔC_p and T_g and using Couchman equation,^{8,9} the compositions of the two phases evolved in the course of the reaction blending were estimated.

Mass fraction of component 1, W_{11} , in phase 1 was calculated as

$$W_{11} = \frac{\Delta C_{p2}^0 \ln \frac{T_{g1}^0}{T_{g2}^0}}{\Delta C_{p1}^0 \ln \frac{T_{g1}^0}{T_{g2}^0} + \Delta C_{p2}^0 \ln \frac{T_{g1}^0}{T_{g2}^0}} \quad (1)$$

Mass fraction of the same component in the phase 2, W_{12} , was determined as

$$W_{11} = \frac{\Delta C_{p2}^0 \ln \frac{T_{g2}^0}{T_{g1}^0}}{\Delta C_{p1}^0 \ln \frac{T_{g2}^0}{T_{g1}^0} + \Delta C_{p2}^0 \ln \frac{T_{g2}^0}{T_{g1}^0}} \quad (2)$$

where ΔC_{p1}^0 and ΔC_{p2}^0 are the increments of heat capacity at the transition temperature for pure components, T_{g1}^0 and T_{g2}^0 are their transition tempera-

tures, T_{g1} and T_{g2} are transition temperatures of PU- and PMMA-enriched phases of the blend.

Mass fraction of component 2, W_{21} , in phase 1 was calculated as

$$W_{21} = 1 - W_{11} \quad (3)$$

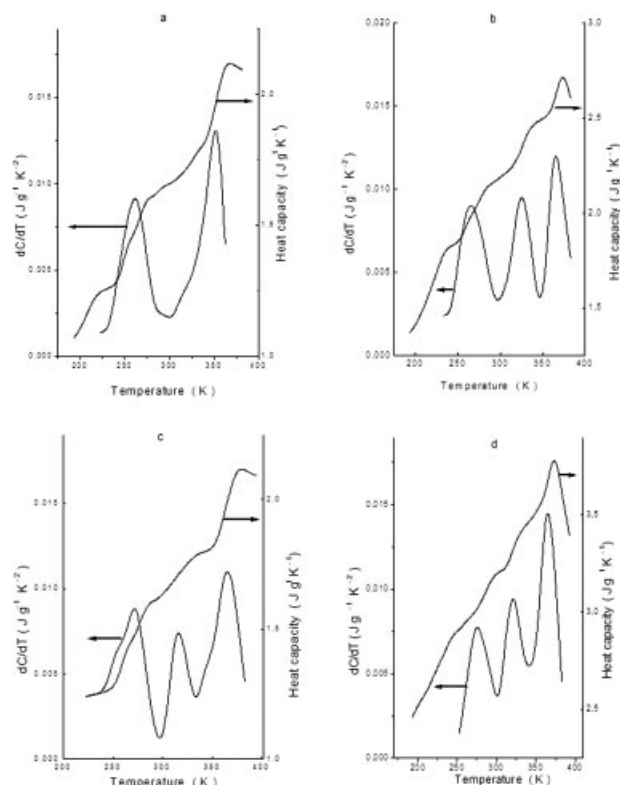


Figure 3 Integral and differential DSC curves for the PU/PMMA blends (30/70) at various amount of filler: (a) without filler, (b) 1, (c) 2, (d) 5 mass % filler.

and mass fraction of the same component in phase 2, W_{22} , was determined as

$$W_{22} = 1 - W_{12} \quad (4)$$

All the results are presented in the Table I. Considering these data one has to bear in mind the approximate character of the Couchman equation. The uncertainty of calculation of the component fractions in both phases did not exceed 5%. Table I shows that T_g of all phases in unfilled and filled blends change depending on the component ratio and filler amount (for filled blends). It is natural that T_g of phases enriched in PU in all cases are higher than pure PU, and T_g of phases enriched in PMMA is lower than pure PMMA. The changes in T_g of evolved phases in unfilled blends correspond to the calculated compositions of these phases. This fact implies that the phase separation in the course of reaction begins at various stages depending on the starting component ratio and reaction rates.

Let us now consider the effect of filler on the positions of T_g . T_g of PU-enriched phase increases with increasing the filler amount for all the blend compositions. This effect may be explained by the diminishing molecular mobility in the surface layers of polymers on the surface.¹ Another reason of increasing T_g may be the enrichment of PU by PMMA upon introduction of the filler.

T_g of PMMA-enriched phase of all the filled blends increases as well. This effect may be due to the diminishing fraction of PU in PMMA-enriched phase with increasing filler amount. The enrichment of both phases in PMMA with filling may be explained by the preferential transition of PU component into the surface layer and into the interfacial region.

The most interesting effect found in the work is the appearance of additional temperature transition related to the surface layer of the blend components at the interface with the filler surface. Earlier it was established⁶ that the compositions of the surface layer in filled polymer blends differ from one in the matrix. These layers are formed due to the preferential adsorption of one of the blend components at the interface with solid and may be considered as an independent phase region. The details of the mechanism of the formation of the surface layers in filled polymers and blends are described elsewhere.¹ The molecular mobility of polymer chains near the interface is lowered, leading to the increase of T_g and average relaxation time.

T_g of the surface layer for filled blends of all the composition are situated in rather narrow temperature interval (315–325 K). This fact implies that the ratio of the starting components of reaction (DEG and MMA), adsorbing at the interface at the initial reaction stages, is almost the same for all compositions of the reaction mixture. This ratio seems to be

TABLE I
Thermophysical Properties of the Unfilled and Filled Blends of PU/PMMA

Composition of PU/PMMA (w/w)	Filler (mass %)	T_g of PU-enriched phase (K)	T_g of bound layer (K)	T_g of PMMA-enriched phase (K)	ΔC_p of PU-enriched phase (J/g K)	ΔC_p of bound layer (J/g K)	ΔC_p of PMMA-enriched phase (J/g K)	1-F	PU fraction in PMMA-enriched phase	PMMA fraction in PU-enriched phase
100/0	0	253	—	—	0.9	—	—	—	—	—
70/30	0	258	—	350	0.53	—	0.41	0.3	0.08	0.13
	1	261	313	358	0.44	0.23	0.3	0.45	0.06	0.2
	2	264	320	358	0.48	0.17	0.36	0.4	0.06	0.2
50/50	5	278	325	360	0.48	0.25	0.38	0.4	0.05	0.47
	0	255	—	353	0.5	—	0.35	0.29	0.07	0.06
	1	265	324	353	0.45	0.23	0.2	0.46	0.07	0.28
30/70	2	268	317	353	0.39	0.2	0.24	0.47	0.07	0.33
	5	273	323	354	0.36	0.23	0.25	0.49	0.07	0.4
	0	260	—	347	0.32	—	0.33	0.33	0.1	0.18
0/100	1	267	323	367	0.29	0.22	0.26	0.45	0.04	0.31
	2	273	315	368	0.3	0.17	0.25	0.44	0.04	0.4
	5	273	320	368	0.26	0.2	0.27	0.45	0.04	0.4
0/100	0	—	—	383	—	—	0.3	—	—	—

preserved when starting components transform into the polymer state. Preferential adsorption interaction of MMA and DEG with the filler surface is observed in experimental data concerning the filler effect on the reaction kinetics. It was found¹⁰ that introduction of filler lowers the rate of PU formation. Aerosil contains a small amount of OH groups and residual moisture, which can interact with the blend components. Earlier¹¹ it was shown that the presence of aerosil accelerates the formation of a linear PU from oligo (tetramethylene glycol) and tolylene diisocyanate (TDI). The authors relate this acceleration to the catalytic effect of urea, which is formed from diisocyanate and moisture adsorbed on the surface of aerosil.¹¹ We observe the reverse situation. Urethane formation may be decelerated both due to a rise in the viscosity of the starting system as a result of addition of aerosil and to a lower mobility of the oligomeric diisocyanate compared to TDI, DEG, and MMA. Therefore MMA and DEG will reach to the aerosol surface faster and interact with filler surface. Besides, IR spectra of unloaded and filled (5 mass %) PU/PMMA blends (70/30) are identical, testifying the lack of chemical interaction between NCO-groups with residual moisture at the filler surface (Fig. 2).

The data of the Table I shows also that the ratio of starting components and the amount of the filler introduced affects the value of the heat capacity jump at T_g . ΔC_p of both blend phases decrease by means of increasing the MMA amount approaching to ΔC_p value of pure PMMA. Introduction of 1, 2, and 5 mass % of filler in all the compositions leads to the diminishing ΔC_p of the PU-enriched phase. We suppose this effect to be the exclusion of the part of PU macromolecules from the cooperative process due to transition into the surface layer on the filler where the molecular mobility is restricted.¹ The value of ΔC_p of PMMA-enriched phases also drops following filler as compared with unfilled blends; but increases with the increase of filler amount. The heat capacity increment of the intermediate region for all filled systems varies in a small interval (0.17–0.25), which shows its weak dependence on the filler amount and on the components ratio. The composition of an intermediate region seems to be the same for all the systems.

Experimental data on ΔC_p allows to calculate the fraction of the interfacial regions in the systems under consideration and establish the filler effect on its value. For this purpose, we have used the Fried equation,¹² which was applied by many authors:^{13,14}

$$(1 - F) = 1 - \frac{(W_1 \Delta C_{p1} + W_2 \Delta C_{p2})}{W_1 \Delta C_{p1}^0 + W_2 \Delta C_{p2}^0}, \quad (5)$$

where W_1 and W_2 are the mass fraction of components, ΔC_{p1} and ΔC_{p2} are heat capacity jumps for

evolved phases, ΔC_{p1}^0 and ΔC_{p2}^0 are the same for pure components. Value $(1 - F)$ is a qualitative measure of the amount of the interphase in polymer blend. When $(1 - F)$ is equal to 0, no interphase exists. When $(1 - F) = 1$, all the polymers are supposed to be in the interphase.

The corresponding data are presented in Table I. The accuracy of calculation of F value was about 4%. Value of $(1 - F)$ characterizes the total fraction of the surface layers at the interface and interfacial region in filled systems. Presently there are no methods allowing to estimate their fractions and their ratios separately. The broadening of the interfacial region between two phases observed experimentally seems to be the result of slowing down the phase separation in the filler presence. The existence of the surface layers at the interface with filler surface contributes additionally to the total fraction of both polymers that do not enter both phases.

Table I gives the values of $(1 - F)$ for all the systems under investigation. The reasons for the different changing in values of $(1 - F)$ in filled blends of different compositions presently are yet unclear. For unfilled systems, the fraction of interfacial region in unloaded systems increases with the growth of MMA in starting reaction system. From the Table I, it follows that introducing filler broadens the transition region between two phases, i.e., increases the fraction of an intermediate region. This effect may be connected with compatibilizing action of filler.¹ The broadening of transition region by IPNs compatibilization was observed in ref. 15.

CONCLUSIONS

In this article for the first time it was observed that in filled polymer blends in the temperature region between two main relaxation transitions, there appears the third transition, which we related to the adsorption layers formed by both components at the interface with filler during reaction. The appearance of such intermediate regions increases essentially the fraction of an interfacial region.

We suppose that in filled systems the value of $(1 - F)$ consists of two parts: of interfacial region formed as result of incomplete phase separation in the reaction mixture and of the surface layer at the interface with solid filler. The appearance of this layer is connected with adsorption effects at the interface, which create an additional region of nonuniform distribution of the system components. This region contributes to the total amount of components, which do not enter the main two phases. Value of $(1 - F)$ for all compositions increases 1.5 times when 1% of filler is introduced. Generally, increasing the total fraction of interfacial region may serve as a sign of

improving compatibility in the system. Filler prevents the phase separation and increases the uniformity of the system. Such effects were described in detail elsewhere.¹ At the same time, subsequent increase of the amount of the filler introduced does not lead to the essential changes in $(1 - F)$. The total fraction of interfacial region between two evolved phases and of the surface layers stays practically unchanged. This fraction depends neither on the component ratio nor on the filler loading.

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