Role of the interphase in the interfacial flow stability of multilayer coextrusion of compatible polymers

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Role of the interphase in the interfacial flow stability in coextrusion of compatible multilayered polymers

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Keywords: interdiffusion, interphase, multilayer coextrusion, interfacial flow stability

Abstract: The role of interphase triggered from interdiffusion process at neighboring layers on controlling the interfacial flow instability of multilayer coextrusion have been highlighted in this study using a compatible bilayer system. The polymers used are based on poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF). The interdiffusion kinetics and the rheological and geometrical properties of the generated interphase have been modelized in real experimental conditions of the coextrusion process. Polymer chain orientation in coextrusion process was demonstrated to decelerate the interdiffusion coefficient. Furthermore, the interfacial shear stress was able to promote mixing and homogenizing process at the vicinity of the interface, which favors the development of the interphase. The convective mixing was evidenced by performing a pre-shear mode on PMMA/PVDF multilayer structures. The rheological and morphological properties of the interphase are related to a lot of parameters like contact time, processing temperature, interfacial shear stress and compatibility of the polymers, etc.

Some key classical decisive parameters concerning the interfacial instability phenomena such as viscosity ratio, thickness ratio and elasticity ratio, etc. were highlighted during the coextrusion process. These key factors which are significant for the interfacial stability of coextrusion of incompatible multilayered polymers seem not that important for the studied compatible systems. The coextrusion of PMMA/PVDF compatible bilayers appears to be more stable. This would be attributable to the presence of the interphase generated from interdiffusion and favored from convective mixing. The interfacial flow instability of coextrusion can be reduced (or even eliminated) despite of the very high viscosity ratio and elasticity ratio of PMMA versus PVDF, especially at low temperatures. Overall, apart from the classical mechanical parameters, we have demonstrated that the creation of diffuse interphase that favors the homogenization should be taken into consideration as an important factor to remove the interfacial instability properties.

Introduction

In general, owning the advantage of combining separate features of different individual polymers together in a facile way, technology of coextrusion has been widely used to fabricate multilayered composite sheets or films for various applications ranging from food packaging products to optical reflective films[1-4]. By this strategy, the synergic properties of oxgen barrier, mechanical propereties and cost lost, etc. could be obtained. The processing technology of coextrusion is realized by a combination of two or three extruders using a multimanifold die or a feedblock within which polymer melts are brought together and a specific multilayer assembling is created. However, in this kind of processing, the contrast in rheological and physicochemical properties of polymers, and the variations of experimental conditions of processing (like coextrusion designs, flow rate, die geometry, etc.) may cause defects at the interface of neighbouring layers, which may bring severe detrimental defects on the extrudate products. Two main defects that have been commonly observed are the interfacial instability (wave-type distortion or zig-zag defect) [5] and the encapsulation phenomena that occur due to the tendency of the lower viscous polymer to encapsulate the higher viscous polymer[3,4,8].

To date, a large number of literatures have come up reporting on the theoretical and experimental advances regarding the interfacial defects of coextrusion and the underlying origins both from mechanical and numerical approaches. Following the numerous studies published, a series of crucial parameters determining the interfacial defects have been found: layer depth ratio, viscosity ratio, elasticity ratio, die geometry, etc. Recently, Wilson and Khomami [6-7] have published a series of comprehensive works on the interfacial instabilities in multilayer flow of viscoelastic fluids. They investigated the linear stability of coextrusion processing from a mechanical viewpoint. They pointed out that the linear stability in the compatible polymer systems was related to the interphase (a non-zero thickness physicochemical zone as opposed to a purely geometrical plane interface) resulted from the diffusive and convective mixing in the vicinity of the interface [7]. In comparison to the high growth rate in the cases of PP/HDPE incompatible system, the growth rate for the LLDPE/HDPE compatible system is significantly less despite the fact that the viscosity ratio for the LLDPE/HDPE system is higher. This suggested an idea for this phenomenon that the interphase triggered from interfacial diffusion may improve the interfacial stability of coextrusion.

Despite the interesting nature of this kind of research, it is of no help in understanding either the generation of instabilities or its connection with the properties of the present interphase and the resulting final properties of multilayer polymers. In our knowledge, few studies have, with regard to fundamental and experimental aspects, been dedicated to the physical modeling of the present interphase and its effect on the flow stability. After presenting an upstream rheological study of neighboring layers based on incompatible reactive mulitlayered structures, Lamnawar and Maazouz [4] demonstrated the importance of the interphase on interfacial instabilities for reactive functionalized incompatible polymer multilayer systems using a reactive system (RS) of polyamide (PA6)/polyethylene-grafted with glycidyl methacrylate (PE-GMA) and a non-reactive system (NRS) of PE/PA6. However, the systems they used were very complex with regard to the high polydispersity and reactivity. To have a better understanding, it would be preferable to work firstly with model polymers in order to probe the effects of the diffuse interphase in the flow stability during coextrusion.

In the previous studies of this series of publications [9-10], rheology has been demonstrated to be a reliable and feasible method for monitoring the diffusion process at a polymer/polymer interface based on both symmetrical and asymmetrical bilayer structures using PVDF and PMMA model polymers; rheological modelling has been realized to describe the kinetics of the interdiffusion (self-diffusion, mutual diffusion) and to express the developments (thickness, rheology) of the interphase triggered between the neighbouring layers. Furthermore, microscopical tools like SEM-EDX, TEM, etc. have been used to confirm in terms of interphase thickness and concentration profile the validity of the rheological modeling of the interfacial phenomena. These upstream studies render us to understand the interphase at polymer/polymer interface generatedin compatible and/or reactive systems.

The complexities in analysing the role of interphase in coextrusion of two incompatible, reactive polymers are considerably reduced by using a compatible pair. This is because in the incompatible, reactive polymer system, the amount of the triggered interphase is limited during the short contact time of the two melt streams in the coextrusion while in the compatible ones, the interphase are more considerable as interdiffusion can occur in a rapider rate [3,4,8,11]. The main objective of this paper is to probe the interdiffusion and the interphase triggered in the approx real experimental conditions of the coextrusion process before disclosing role of the interphase in the interfacial flow instability of coextrusion.

Experimental Section

Materials

The polymers used in this study were supplied by Arkema. Poly (methyl methacrylate)(PMMA)/poly(vinylidene fluoride) (PVDF) were used as a compatible system and PMMA/ polyethylene(PE) were used as an incompatible system for comparison purpose. The main characteristics of the polymers are listed in Table 1. For clarity purpose, the rheological properties of the studied polymers are provided in ref.[4,9,10]. Two poly (methyl methacrylate) (PMMA)s of different molar mass, namely PMMA-1, PMMA-2 were included to allow us to vary the viscosity and elasticity ratios. The zero shear viscosity ratio and elasticity ratio of PMMA versus PVDF at different temperatures are ploted in Fig.1. It should be noted that here the elasticity ratio is expressed by the average relaxation time ratio of PMMA versus PVDF. They were determined from the Cole-Cole curves during their rheological characterizations.

Table 1 Characteristics of the investigated polymers

Samples	Trademark/Supplier	Tc(^{o}C)[a]	Tg(^{o}C)[a]	T_m(℃)[a]	M_w[b](g/mol)	M_w/M_n[b]	Ea(KJ/mol)[c]
PVDF	Kynar 720/ARKEMA	136.40	-42	170	210,000	2.0	59

PMMA-1	V825T/ ARKEMA	——	112	——	100,000	1.9	160
PMMA-2	V046/ ARKEMA	——	102	——	137,000	2.0	157
PE	Lacqtene/ARKEMA			114	207,000	9,9	53

[a] measured in our laboratory by a TA Instruments Q20 DSC at a heating and cooling rate of 10 ℃/min under N_2.
[b] determined in our laboratory by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent for PMMA and dimethyl formamide(DMF) for PVDF.
[c] energy of activation of the viscous flow (Ea) obtained from a master curve at a reference temperature of 220 ℃.

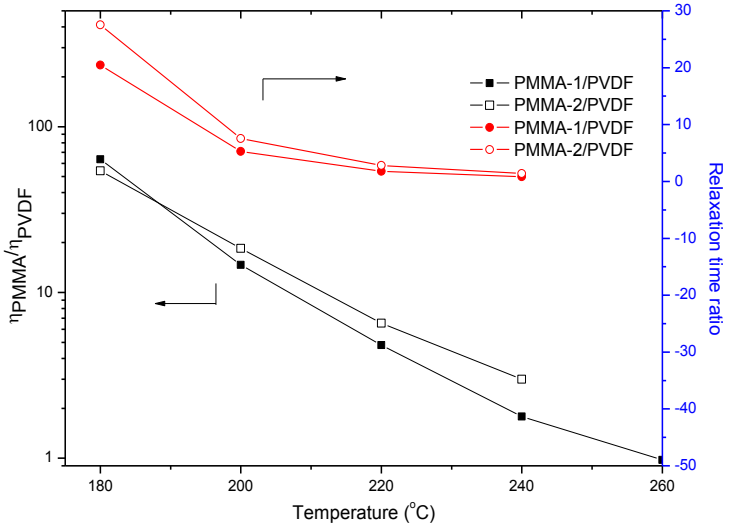

Fig.1. *Zero shear viscosity ratio and Relaxation time ratio versus temperature (viscosity ratio=30.86@190°C)*

Experimental Procedures

The interdiffusion process and interphase development occurred at asymmetric polymer/polymer interface of bilayer or multilayer assembly were monitored in small amplitude oscillatory shear measurements and a steady shear measurement using a ARES(advanced Rheometrics Expansion System) (parallel-plate, Φ=25 mm, gap=1.2 mm). The bilayer and multilayer assembly (total thickness=1.2mm) was prepared by bringing round disks of PMMA (upper layer) on top of PVDF (lower layer) alternately into intimate contact at room temperature before loading them between the plates and annealing them in the oven at a given temperature. More details about the experimental procedures are referred to our previous studies[10].

Coextrusion of mulilayer sheets were performed via a laboratory instrumental setup of coextruder especially designed in a home mode which was equiped with a feedblock system connecting three extruders and a hanger die. For clarity purpose to investigate the interfacial stability of coextrusion, the present work first considered only an AC bilayer configuration as an example (see schametic in Fig.2). In the coextruder setup, extruder A (Φs=18mm, L/D=25) was used for PMMA and extruder C (Φs=15mm, L/D=25) for PVDF in order to fabricate mono and bilayer structures.

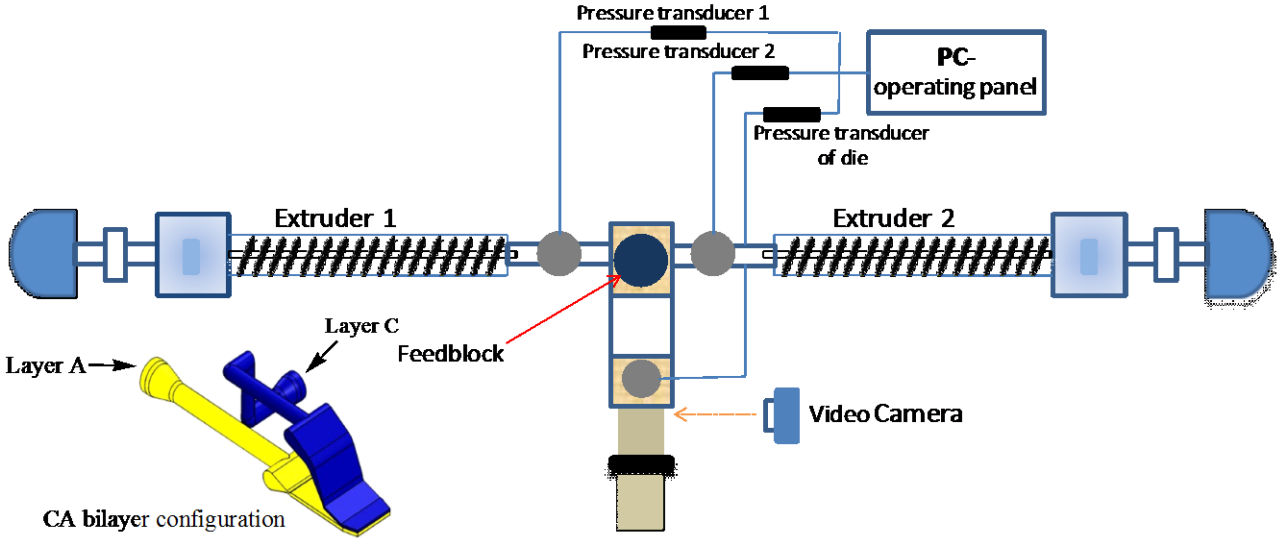

Fig.2 Schematic of experiment apparatus: laboratory device of coextruder with a CA bilayer configuration

After exiting the die, the bilayer film was passed over a water-cooled double chill roll and quenched to room temperature. Both the extrudates at the die exit and the quenched ones were visualized to examine the interfacial defects (flow stability, encapsulation, etc.) at the fluid interface.

Main Results and Discussions

Interdiffusion kinetics and Interphase development

In our prvious work[9,10], the interdiffusion kinetics and interphase development have been comprehensively investigated by annealing PMMA/PVDF bilayer assembly in the oven of the rheometer at a given temperature and online tracking the variation of the viscoelastic functions versus time. Indeed, quantification of the interdiffusion kinetics and the diffusion coefficient in polymer melts, is quite a tremendous task since a great number of parameters are needed upon modellings. For interdiffusion occurs at an asymmetrical bilayer, recently we made an attempt to modify the primitive model of Qiu-Bousmina [12] to determine the mutual diffusion coefficient (D_m) by taking into account rheology of the interphase (complex modulus of interphase $G_I^*(t)$) rather than using rheolgy of the total sandwich structure ($G_{s,t}^*$). The modified model is as follow:

$$D_m = \left[\frac{(2/3)^{1/3}\, p}{\left(9q + \sqrt{3}\sqrt{-4p^3 + 27q^2}\right)^{1/3}} + \frac{\left(9q + \sqrt{3}\sqrt{-4p^3 + 27q^2}\right)^{1/3}}{2^{1/3}3^{2/3}} \right]^2 \quad (1)$$

with

$$p = \frac{8\delta\omega G_N^0}{\pi^2}\left(\frac{\varphi_A}{G_{A,0}^*} + \frac{\varphi_B}{G_{B,0}^*}\right) \quad (2)$$

$$q = \frac{8\delta\omega G_N^0}{\pi^2}\frac{H}{2t^{1/2}}\left(\frac{1}{G_{s,t}^*} - \frac{1}{G_{s,0}^*}\right) \quad (3)$$

$$\text{where } \delta = \frac{N_b^e N_b^3 b_b^4}{\pi^2 e_b^2}\left(\frac{\varphi_B}{N_A} + \frac{\varphi_A}{N_B}\right)\left(\frac{\varphi_B}{N_A} + \frac{\varphi_A}{N_B} - 2\chi\varphi_A\varphi_B\right) \quad (4)$$

In the equations, φ_i,, N_i denote volume fraction and repeat unit number of composition i, i=A or B; N_b^e, N_b, b_b, e_b and $G_{N,b}^0$ are the average number of repeat units between entanglements, the repeat unit number, the effective bond length, the step length of the virtual tube and the plateau modulus of the interphase (or equivalent blend), which is also a function of the composition. In the modification, the complex modulus of interphase $G_I^*(t)$ is seperated from the sandwiched structure according to an expression of mulitlayer:

$$\frac{1}{G_{s,t}^*} = \frac{\varphi_{A,t}}{G_{A,t}^*} + \frac{\varphi_{B,t}}{G_{B,t}^*} + \frac{\varphi_{I,t}}{G_{I,t}^*} = \frac{h_A^{'}/H}{G_{A,t}^*} + \frac{h_B^{'}/H}{G_{B,t}^*} + \frac{h_I^{'}/H}{G_{I,t}^*} \quad (5)$$

where $G_{i,t}^*$ .and $\varphi_{i,t}$ represent respectively the complex modulus and volume fractions of layer i at a diffusion time t>0 with an initial complex modulus of layer i as $G_{i,0}^*$ at t=0; $h_i^{'}$ represents the thickness of layer i developing with the elapsed time, and H is the total thickness of the sandwich (1.2 mm for the PMMA/PVDF assembly used in their work). After integrating the expression of interphase thickness derived from mutual diffusion coefficient as follow:

$$h_I^{'} = 2(D_m t)^{1/2} \quad (6)$$

into eq.5, $G_I^*(t)$ is obtained as

$$\frac{1}{G_I^*(t)} = \frac{H}{2(D_m t)^{1/2}}\left(\frac{1}{G_{s,t}^*} - \frac{1}{G_{s,0}^*}\right) + \left(\frac{\varphi_A}{G_{A,0}^*} + \frac{\varphi_B}{G_{B,0}^*}\right) \quad (7)$$

The modified model of eq.1 is derived by integrating the eq.7 into the primitive model of Qiu-Bousmina reported in ref. [12]. Indeed, the original modification of the model consists on the calculation and the modeling of the friction coefficients of each polymer in the multiphase systems and correlates it to the diffusion quantifications. The rheology method, Lodge−McLeish model, and test of the time-temperature superposition (tTS) principle were employed to probe the thermorheological complexity of this polymer couple. The monomeric friction coefficient of each species in the blend has been examined to vary with composition and temperature and to be close in the present experimental conditions, and the failure of the tTS principle was demonstrated to be subtle.

Fig.3 portrays a typical plot of the evolution of apparent mutual diffusion coefficient (D_m) (calculated from complex modulus G* via the modified model) with time for a PMMA-1/PVDF asymmetrical bilayer at T=220 ℃. w=1.0 rad/s (an angular frequency at the terminal zone of both components). At the first beginning of diffusion, the dynamics is dominated by short chains or segmental motions in a Rouse behavior with a higher diffusion coefficient, then more and more long chains participate into the diffusion, resulting in a decrease of D_m to a plateau stage where is a sum of contributions from species of different chain lengths. It is worthy noting that the D_m given here was determined based on a concept of the interphase. Moreover, the model of D_m proposed in our early work [10] allows us to gain insight the feature of the triggered interphase. For example, a typical figure of the resulting thicknesses of the interphase triggered at a PMMA-1/PVDF assembly at 220 ℃. w=0.1 rad/s is also shown in Fig. 3. We can observe that the interphase can own a thickness of several dozens' microns after diffusion for 45 min, which is similar with the literatures. Thus, the thickness of the interphase could be monitored versus time during the interdiffusion by rheology.

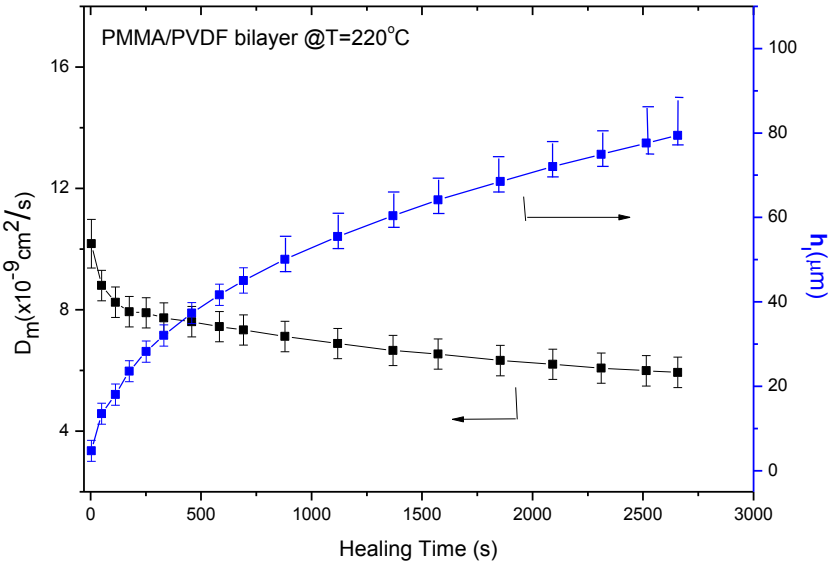

Fig.3 Evolution of mutual diffusion coefficient (D_m) and corresponding interphase thickness (h_I) versus time for PMMA-1/PVDF bilayer determined from the modified model [10]

In the practical conditions of a coextrusion system, the situation is more complicated considering that the orientation of polymer chains in shear flow field may pronouncedly influence the rate of interdiffusion [13]. According to the work of Kim et al [13], it is necessary to take into account the effect of the orientation by introducing an orientation factor, α, into the calculation of the diffusion coefficient. It is supposed that when there is no flow, the polymer chains have an average orientation angle of 45 degrees whereas the average orientation angles in the respective phases will be greater than 45 degrees when they are under a shear field. In a shear field, the orientation factor can be described by an expression as follow:

$$\alpha_i = \frac{\cos\left\{(\pi/4)+\left[\tan^{-1}\left(3\sigma_{\text{int}}(\overline{M}_{wi}/\overline{M}_{ni})^3/G^0_{Ni}\right)\right]/2\right\}}{\cos(\pi/4)} \quad (1)$$

where σ_{int} is the interfacial stress at the interface. To determine the σ_{int}, firstly we assume that the velocity distribution for the multilayer flow of incompatible non-Newtonian fluids is also valid for the case of PMMA/PVDF in this study. The σ_{int} and velocity profile could be calculated by solving the equation of motion:

$$-\partial P/\partial z+\partial\sigma_{yz}/\partial y=0 \quad (2)$$

assuming the viscoelastic behavior of polymers being described by power law. Based on these, the σ_{int} can be determined as follow:

$$\sigma_{int}=-\zeta(\delta-\lambda) \quad (3)$$

in which ζ is the pressure gradient defined by $\zeta=-\partial P_A/\partial_z=-\partial P_B/\partial_z=const.$; δ is the position of interface and λ is the position at which the maximum in velocity (and hence. the minimum in shear stress) occurs, which could be obtained from the velocity profile. For a given volumetric flow ratio in experiments, with the pressure gradient detected by the transducers, the important variables such as δ, λ, σ_{int} and thus the orientation factor, α,could be avaible. For clarity, here we only take the case of 220 °C as an example, some important involved parameters obtained at different flow rate ratios are listed in Table 3.

Table 3. *Some important calculated parameters at the interface of PMMA/PVDF bilayer in a coextrusion die at T=220°C*

Q ratio	**Q_{PMMA}** (kg/h)	**Q_{PVDF}** (kg/h)	**contact time**(s)	**pressure gradient** ξ(×10⁴Pa/mm)	**Interfacial position**[a]	**position of υ_{max}, λ**	**interfacial stress** σ_{int}(×10⁴Pa)	$\dot{\gamma}_{PMMA}$ (s^{-1})	$\dot{\gamma}_{PVDF}$ (s^{-1})	α_{PMMA}	α_{PVDF}	$\alpha_{average}$	$\tilde{D}_m$ (×10⁻⁹ cm^2/s)	**h_I**(um)
0.3	0.6	0.18	91,36	2,73	0,77	0,65	0,655	0,00810	1,94614	0,806	0,875	0,840	7,105	16,11
0.6	0.6	0.36	77,67	2,62	0,68	0,64	0,210	0,00044	0,21741	0,939	0,961	0,950	8,127	15,89
1.0	0.6	0.6	64,52	3,48	0,6	0,66	0,418	0,00255	0,81846	0,876	0,921	0,898	7,782	14,17
1.6	0.6	0.96	51,32	2,32	0,53	0,64	0,510	0,00427	1,20390	0,848	0,903	0,876	7,674	12,55
2.6	0.6	1.56	38,19	3,5	0,45	0,62	1,190	0,03743	6,13175	0,662	0,773	0,717	6,545	9,99

[a]*the interfacial position is expressed as δ/h; total thickness h=2mm in the studied die.*

According to the results of orientation factors and the kinetics of the interdiffusion evolving with time at static condition as shown in Fig.3, the mutual diffusion coefficient in a shear flow field of the coextrusion conditions can be estimated as follow:

$$\tilde{D}_m=\alpha_{av}D_m \quad (4)$$

The results are given in Table 3 and also given are the interphase tickness which are calculated by a similar way as in static conditions. Obviously, the orientation factors are below 1, which results in lower diffusion coefficient during coextrusion process than that in the static condition. This means that the polymer chain orientation in the shear flow field during coextrusion has a decelerating effect on the interdiffusion process between neighbouring layers. Among the different flow rate ratios (Q_{PVDF}/Q_{PMMA}) ranging from 0.3 to 2.6 as shown in Table 3, one can see that when Q_{PVDF}/Q_{PMMA}=0.6, the δ is closest to the λ, with the interfacial stress and the interfacial shear rate being the smallest and the orientation factor close to 1. The larger deviation of the Q_{PVDF}/Q_{PMMA} from 0.6, the higher the value of the interfacial shear stress and the greater the orientation effect. Indeed, a shear flow is able to induce a local pressure drop at the interface between two fluids and thus gives rise to fractal structure and hence convective mixing[14],as schemed in Fig.4.

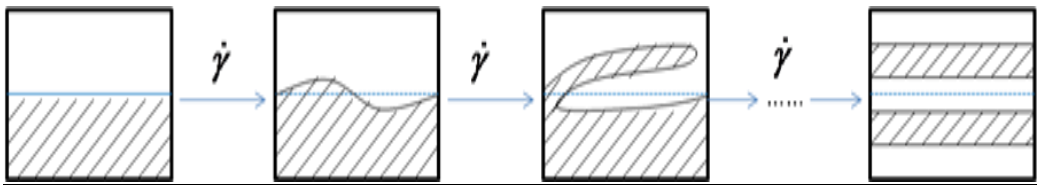

Fig.4. *Schematic of interfacial morphology variations when it is subjected to a certain steady shear*

Due to the high complexity of probing this problem in the real shear flow field of processing conditions in coextrusion, it is of interest to introduce a pre-shear mode in the dynamic rheological measurements of multilayer structures. By this way, one could simulate the effect of shear flow on the diffusion process/convective mixing in the practical situation in coextrusion in a more closely manner. A given amount of steady shear flow $\dot{\gamma}(t)=\dot{\gamma}*t$ was introduced to the multilayer assembly, by rotating the lower plate of the parallel-plate rheometer before following a time sweep test. To examine the change of interfacial structure, once the pre-steady shear was given, we removed immediately the specimens out of rheometer and quenched them in liquid nitrogen before observing their cross-section morphology under SEM.

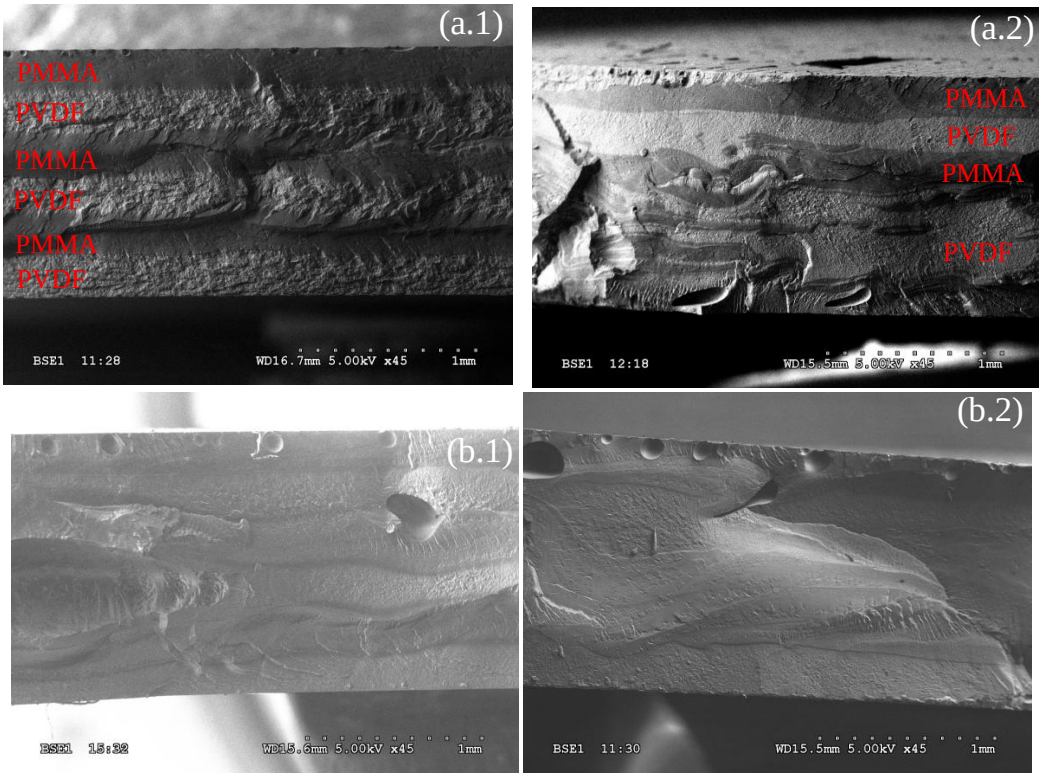

Fig.5. *Micrographs of PMMA/PVDF multilayers: (a) specimens quenched immediately after the accomplishment of pre-shear. due to the different index of refraction. both phases are clearly distinguished. darker layers are PMMA, whiter ones are PVDF: (a.1)-6layers.no pre-shear; (a.2)-6layers.* $\gamma=4s^{-1}\times60s$*; (b) specimens quenched after the healing process for 1.5h at 200 °C. 0.1rad/s: (b.1)- 6layers. no pre-shear; (b.2)-6layers.* $\gamma=4s^{-1}\times60s$.

Obviously, the convective mixing provoked from certain mounts of pre-shear is well demonstrated in Fig.5. Compared to the uniform sandwich structure of the 6-layers assembly without pre-shear in Fig.5-a.1, the assembly experienced fractal branched structures at the vicinity of the interface after being subjected to pre-shear ($4s^{-1}\times60s$) as shown in Fig.5-a.2. This convective mixing caused by pre-shear greatly promotes the interdiffusion process and the homogenizations. This is evidenced from the non-boundary homogenous morphologies observed in specimen subjected to pre-shear (Fig.5-b.2) as opponent to the visible light boundary of two phases observed in that not subjected to pre-shear (Fig.5-b.1) after a healing process of 1.5h in the oven of the rheometer.

Theoretically, when the multilayer structure was subjected to a steady shear flow $\dot{\gamma}(t)=\dot{\gamma}*t$, the fractal undulated structures appeared can be described by the reduction of the initial striation thickness. r_0, with time in a term of [15]:

$$r(t)=r_0/(1+\dot{\gamma}*t) \quad (5)$$

and consequently the reduction of the characteristic diffusion time in a term of

$$t_D(t)=r^2(t)/D_m \quad (6)$$

These investigations give us a clear idea that even though the polymer chain orientation in the shear flow field of processing may slow down the D_m, the intervention of the convective mixing arise from the shear behaviour could shorten the striation thickness to a level where the interdiffusion process can easily occur, thus effectively accelerate the homogenization rate of the liquid-liquid phase. We can take the case of Q_{PVDF}/Q_{PMMA}=1.0 at 220°C given in Table 3 as an example, assuming an interfacial shear rate $\dot{\gamma}_{int}$ being averaged from $\dot{\gamma}_{PMMA}$ and $\dot{\gamma}_{PVDF}$ to be 0.411 s^{-1}, with contact time of 64.52s, one can obtain $r(t)=r_0/26.52$ from eq.25, even $\tilde{D}_m$ =0.898 D_m, the characteristic diffusion time $t_D(t)$ can be lowered by a fold of 1.6×10^{-3}. This greatly indicates the fact that the convective mixing in the shear flow field significantly decrease the time for interdiffusion and would broaden the interfacial zone.

Coextrusion Process

i) Interfacial flow stability of different polymer bilayer systems

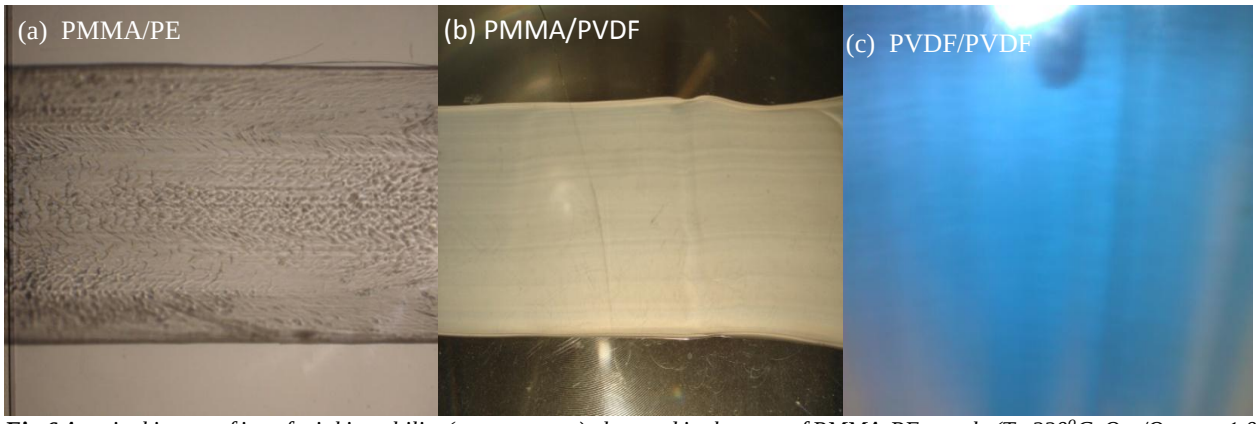

Fig.6 *A typical image of interfacial instability (wave pattern) observed in the case of PMMA-PE couple (T=220°C. Q_{PE}/Q_{PMMA}=1.0) (a) and typical images of stable interface of PMMA/PVDF couple (T=220°C. Q_{PVDF}/Q_{PMMA}=1.0) (b) and PVDF/PVDF couple (c).*

For the purpose of disclosing the role of the interphase in controlling the flow instability, different bilayer systems were considered, one is incompatible polymer pair composed of PMMA/PE; the other two are compatible polymer pairs composed of PVDF and PMMA with varying molecular weight and those symmetrical bilayers of same polymers as reference. Bilayer coextrusion of these three systems was carried out at 220 °C by varying flow rate ratio from 0.3 to 2.6 and comparisons were given with regard to the interfacial flow stability. Typical samples obtained at a theoretically interfacial stability favorable condition of flow rate ratio=1 are illustrated in Fig.6. A severe wave-like distortion at the interface can be obviously observed in the case of PMMA/PE incompatible bilayer co-extrudates (Fig.6a) whereas coextrusion of PMMA/PVDF (Fig.6b) and PVDF/PVDF (Fig.6c) compatible bilayers exhibits a stable interfacial flow at the exit of the die under this condition. Indeed, for PMMA/PE pair, in addition to the wavelike form at the interface, the solid co-extruded bilayer could be easily delaminated by hand since there is no adhesion between neighboring layers, on the contrary, no sharp interface can be found and good adhesion is formed in the cases of PMMA/PVDF and PVDF/PVDF or PMMA/PMMA pairs.

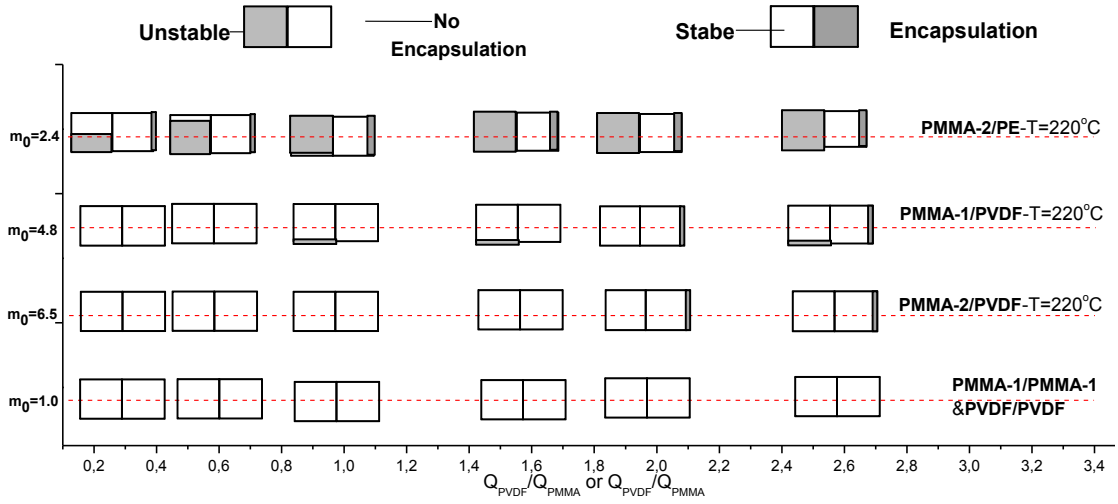

Fig.7 *Map of stability/instability and encapsulation/un-encapsulation observed experimentally for different couples of coextruded bilayers versus flow rate ratio: PMMA-2/PE; PMMA-1/PVDF; PMMA-2/PVDF.m_0 in y axis denotes the zero viscosity ratio of PMMA/PE or PMMA/PVDF.*

In the analysis, to compare the interfacial flow stability between different experimental conditions, we construct a stability map by listing the situation of the flow stability obtained at different conditions in a same figure, as shown in Fig.7. Here, the x-axis indicates the varying flow rate ratio employed in the experiments from 0.3 to 2.6. In this stability map, two types of interfacial defects are considered, flow instability (wavy shape, etc.) and encapsulation. The empty and wavy small rectangle in the left part of the symbol indicates stable (or smooth interface) and unstable (or wavy interface) of the bilayer systems, respectively; and the empty and hachured small rectangle in the right part of the symbol represents the state of no encapsulation and the state of high encapsulation.

Hence, based on this analysis guide-line and the experimental results obtained for the various bilayer systems summarized in this stability map (Fig.7), we can see that even though we changed the flow rate ratio,

the PMMA/PE bialyer system still experienced severe flow instability though the encapsulation is few within the range of the flow rate ratio measured, with the flow instability a bit better only when Q_{PE}/Q_{PMMA}=0.3. In comparison to the severe flow instability of the coextrusion products of PMMA/PE incompatible bilayer, those of PMMA/PVDF compatible bilayer appears to be smooth without apparent interfacial flow instability at the similar conditions of 220°C, with only some subtle encapsulation observed at high Q_{PVDF}/Q_{PMMA}. Likewise, the symmetric bilayers of PMMA/PMMA and PVDF/PVDF at the same conditions have good flow stability. These greatly indicate that the flow instability encountered under certain conditions in the coextrusion of incompatible polymer systems could be removed in compatible systems due to the presence of the interphase at polymer-polymer interface triggered from interdiffusion. Even so, the underlying mechanisms of this result are still not well understood and it will be the hope of the present paper .

Certainly, by varying other parameters like temperature, flow rate etc., the amount of the interphase would be comparatively changed as the diffusion coefficient and/or the contact time allowed for interdiffusion are different at varying experimental conditions. For the aim to have an idea about the degree of the interdiffusion and the development of the interphase during the coextrusion process, it is necessary for us firstly to analyze the velocity distribution during the flow and calculate the diffusion coefficient.

ii) Interfacial flow stability of PMMA/PVDF bilayer at different temperatures

To study the effect of the temperature on the flow stability of PMMA/PVDF bilayer, we established a new stability map as shown in Fig.8 by listing together the situation of flow stability obtained at different temperatures varying from 190°C to 260°C and different flow rate ratio Q_{PVDF}/Q_{PMMA} ranging from 0.3 to 2.6. In the figure, the y axis is the zero shear viscosity ratio of PMMA-1 versus PVDF (i.e. η_{PMMA}/η_{PVDF}). We can see that even at the condition of high viscosity ratio at low temperatures, eg. η_{PMMA}/η_{PVDF}=30.8 at 190°C, the interfacial flow was still stable, with few interfacial waviness observed during the flow exiting the die. This is quite distinct from the viscous instability reported in the literature for incompatible polymer pair which says that high viscosity ratio of the fluids may destabilize the interface. In fact, the tendency of severer interface instability at higher viscosity ratio also exists in the present system considering the interfacial flow stability situation is worse at lower temperature. However, the extent of the instability is apparently reduced by the creation of the interphase. Furthermore, though few interfacial waviness were observed at such a low temperatures and high viscosity ratios, a greater thickness was found at the edge of the bilayer films, i.e., the encapsulation, as shown in Fig.9. As pointed out by Wilson and Khomami [6], encapsulation phenomena occur irrespective of the stability/instability of the interface. It is noted that to observe this phenomenon more clearly, some green pigments were mixed in the PVDF layers. In the case of this study, the less viscous polymer, here PVDF, tends to immigrate to the region of high shear rate (i.e. the wall), thereby producing encapsulation, that is, the less viscous fluid encapsulating the more viscous components, and resulting in a great thickness nonuniformity in coextrusion flow which gives rise to a thick edge of the sheet. The encapsulation becomes more serious as flow rate ratio increases, as shown in Fig.8.

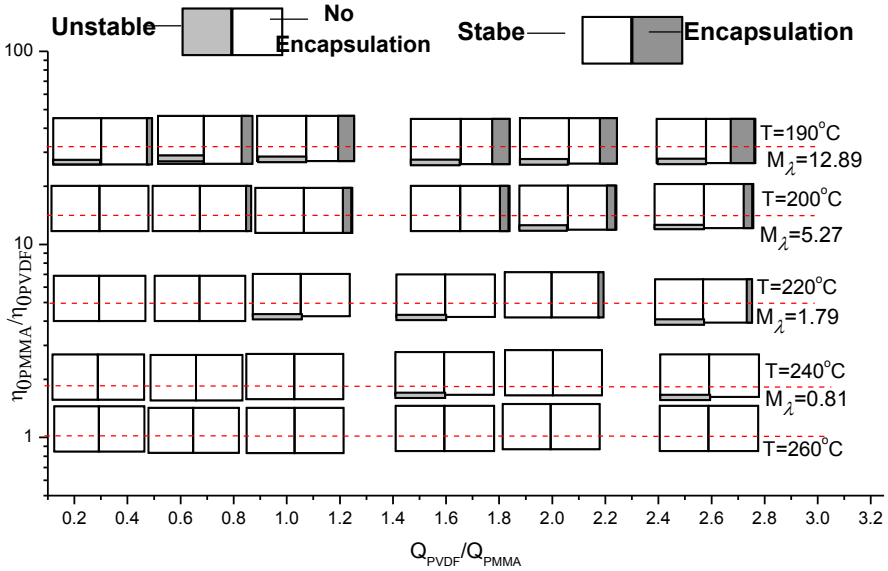

Fig.8. *Map of stability/instability and encapsulation/no-encapsulation observed experimentally for PMMA-1/PVDF coextruded bilayers (evolution of viscosity ratio vs. flow rate ratio). M_λ denotes the elasticity ratio expressed by $\lambda_{PMMA}/\lambda_{PVDF}$.*

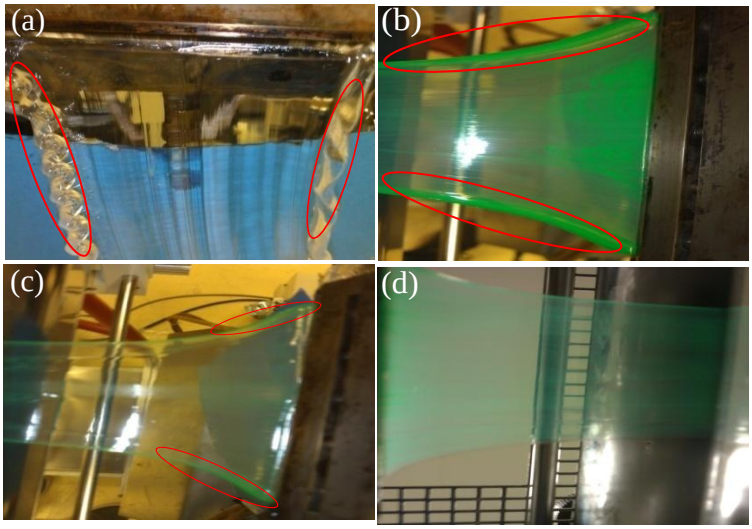

Fig.9. *Photographs of flow stability situations of PMMA-1/PVDF bilayer with Q_{PVDF}/Q_{PMMA}=2.0 obtained at different temperatures: (a) T=190°C; (b) T=200°C; (c) T=220°C; (d) T=260°C. (traces of PVDF green pigments were added to the PVDF layer)*

Furthermore, both Fig.8 and Fig.9 show that at a given flow rate ratio, as the temperature increase, the interfacial flow of the PMMA/PVDF bilayer becomes more stable and the encapsulation is also reduced, in particular, at T=260 °C, the flow is always stable irrespective of the flow rate ratio(layer thickness ratio) and no encapsulation is found. On one hand, this could be attributed to the decrement of the rheological difference between PMMA melt and PVDF melt as temperature increase, especially the $\eta_{PMMA}/\eta_{PVDF} \sim 1.0$ when T= 260°C, as indicated in Fig.1. On the other hand, as the temperature increase, the interdiffusion process between the melts and the development of the interphase are evidently mounting up, hence greatly improve the flow stability and the encapsulation situation. Apparently, this is in accord with the results obtained in our earlier studies [8] that the encapsulation appeared to be hindered by the interdiffusion process occurred in the compatible system and the formation of a certain amount of interphase.

In addition, it has been reported in the literature that for non-Newtonian fluids, the variation of the elasticity ratio could have an independent effect as viscosity ratio on the interfacial flow stability of coextrusion processing [16-17]. With an aim to examine this effect, coextrusion experiments of PMMA-2/PVDF was also performed at T=190°C to be compared with PMMA-1/PVDF system at same processing conditions. As shown in Fig.1, these two polymer pairs have similar viscosity ratio at T=190°C while PMMA-2/PVDF has a higher elasticity ratio than its counterpart. It should be noted that here the elasticity ratio is expressed by relaxation time ratio $M_\lambda=\lambda_1/\lambda_2$ and the relaxation times of the investigated polymers were determined from the Cole-Cole curves during their rheological characterizations. Unexpectedly, no significant difference was observed between these two polymer pairs with regard to their interfacial waviness and encapsulation situation. The flow is kept stable despite of the change of viscoisty and elasticity ratio. The result gives us an idea that for compatible polymer systems, the existance of sufficient interphase may weaken the elasticity instability as well as the viscosity instability.

Conclusions

An experimental study regarding the flow stability and encapsulation has been carried out based on PMMA/PVDF compatible systems. Results indicated that different from the severe flow instability observed in the PMMA/PE incompatible bilayers, the coextrusion of PMMA/PVDF compatible bilayer (and also PMMA/PMMA, PVDF/PVDF symmetrical bilayers) appears to be smooth without apparent interfacial flow instability at the similar condition. This is attributable to the presence of the interphase generated between neighboring layers during the coextrusion process of compatible polymers.

To characterize the interphase in the practical condition of coextrusion, the effect of polymer chain orientation on the interdiffusion process has been focused as well as the convective mixing in the shear flow field. The convective mixing was simulated on PMMA/PVDF laminated multilayer structures by performing a pre-shear mode before starting time sweep tests for interdiffusion. Polymer chains orientation decreases the diffusion coefficient a bit while the convective mixing greatly reduces the diffusion time by lowering the

striation thickness and increasing the interfacial area, and therefore significantly accelerate the homogenization rate in the interfacial region and the development of the interphase.

Classical parameters such as thickness ratio, viscosity ratio and elasticity ratio, etc. have been evaluated by elaborating stability charts. It is shown that despite of their decisive role in an incompatible system, the key factors seem not that important in a compatible system as they are compensated by the presence of the interphase generated from interdiffusion. In other words, the formation of the interphase weakens the viscosity instability and elasticity instability. The interfacial flow instability of coextrusion is reduced (or even eliminated) despite of the very high viscosity ratio of PVDF versus PMMA as well as the variation of elasticity ratio.

Overall, this study will be of some value on showing guide-lines for stable coextrusion of multilayer polymers since it presents us an idea that it is important to enrich the classical mechanical approach by taking into account of the role of the interphase during the optimization of the coextrusion processing conditions

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