

<연구논문>

PC/SAN 블렌드의 분산혼련 작용기구에 관한 연구

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A Study on the Mechanism of Dispersive Mixing in Blends of PC and SAN

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요 약

폴리카보네이트와 스티렌-아크릴로니트릴 공중합체의 블렌드를 이축 압출기에서 용융혼련할 경우의 분산혼련 작용기구를 연구하였다. 분산상 형성에 관계되는 지배적인 과정은 sheet, lace 및 ligament 생성에 이어 Rayleigh 형태의 불안정성에 기인한 구형의 분산상(droplet) 형성으로 확인되었다. 분산상과 연속상의 점도비와 분산상의 크기에 대한 상관관계의 조사에서는 주어진 점도비의 범위에서 점도비 약 70인 경우를 제외하고는 거의 무관한 관계를 나타내었으며, 이는 이축 압출기의 강력한 혼련 요소인 kneading 부위에서 주어지는 연신 흐름장에 의한 영향을 반영한 것으로 해석되었다. 분산상의 최종 크기는 오히려 분산상들간의 coalescence 정도에 크게 영향을 받았으며 연속상의 점도가 상대적으로 낮은 경우에 동일한 분산상에 대한 coalescence 정도가 심화되어 분산상의 크기가 증가되었다.

Abstract—The mechanism of dispersive mixing during melt compounding of polycarbonate(PC) and styrene-acrylonitrile (SAN) copolymer in a twin screw extruder has been investigated. It was found that size reduction is mostly accomplished during the softening process and the mode of breakup follows the sequential formation of sheet, lace and ligaments, which in turn lead to droplets via Rayleigh type instability. The domain sizes in blends with various combination of PC and SAN appear to be little affected by the viscosity ratio of domain to matrix except the case of viscosity ratio around 70, which is explained by the strong influence of elongational flow field in kneading section. Instead of the viscosity ratio, the motion induced coalescence plays an important role in determination of the final domain size; matrix having relatively low viscosity facilitates the coalescence and yields larger domain size.

Keywords: dispersive mixing, viscosity ratio, domain size, blends, coalescence

1. Introduction

Multicomponent polymer blends are mostly produced by melt mixing of component polymers in a twin-screw extruder or batch intensive mixer. Such materials provide an effective route to expand the applicability of polymers by satisfying the diversified needs in industrial utilization. Mixing of various polymeric materials involves the disp-

ersion of the phases into ever smaller domains. In case of an incompatible system, molecular diffusion or mixing to molecular level is not possible; dispersive mixing rather than distributive mixing prevails. The dispersion is achieved by the breakup of the minor components in the matrix and the degree of mixing is associated with the final size of these microscopic domains. It is widely recognized that the formation of the dispersed phase in incompatible polymer blends are influenced by numerous factors including type of imposed flow field (shear or elongation), in-

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terfacial tension, and the viscosity ratio of the components [1-3]. Since the final morphology greatly affects the macroscopic properties of the blend, it is of great importance to properly control and generate the desired morphology for the expected performance of the material.

The primary focus of the present work is to investigate the mechanism of dispersive mixing in binary blend of polycarbonate(PC)/styrene-acrylonitrile(SAN) copolymer. In addition, the effect of viscosity ratio on the domain size of the blend is another purpose of this study. Prior to more comprehensive study on the PC/ABS(acrylonitrile-butadiene-styrene) blend, this study is intended to provide a fundamental insight on the morphology development and properties of the blend where PC and SAN is incompatible and the phase structure is characterized as a three phase system consisting of butadiene rubber, SAN and PC. Blend of PC and ABS is a commercially important material in fabrication of various parts for automobiles and appliances, providing excellent toughness and heat resistance. Although desirable combination of mechanical properties is possible because of the adequate adhesion between the components[4], practical problems relating to non-uniform state of dispersion and unstable morphologies are often encountered in injection molding [5], which lead to deterioration of quality in molded articles. Due to the commercial importance and academic interest, numerous studies have been conducted to understand the underlying principles in the performance of PC/ABS blends. It is however found that most of the studies were focused on the structure-property relationships[6] and unfortunately, little work has been reported on how the dispersion occurs and phase morphology develops in compounding of PC, SAN, and ABS. Understanding of the dispersion mechanism and morphology evolution would be useful for the design of processing equipment with improved mixing capability.

2. Experimental

The materials used in this study are all commercially available polymers. They are supplied in the form of powder or granule and their details are summarized in Table 1. All the blends were compounded on the Twin Screw Mixing Element Evaluator(TSMEE)(see Fig. 1) which retains the main geometric features of a Werner & Pfleiderer ZSK-30 co-rotating twin screw extruder. In addition to various useful features including on-line measurements of rheological property, pressure, and temperature, TSMEE

Table 1. Polymers used in this study

Polymer	Abbreviation	Source (Grade)	Molecular weight	Copolymer composition (Wt.%)
Poly-carbonate	PC-1	Teijin (Panlite L1250W)	$\overline{M}_n = 15,000$ $\overline{M}_w = 27,000$	-
	PC-2	Samyang (Trirex 3020)	$\overline{M}_n = 12,000$ $\overline{M}_w = 19,000$	-
Poly (styrene-co-acrylonitrile)	SAN-1	Cheil Ind. Inc.	$\overline{M}_n = 42,000$ $\overline{M}_w = 69,000$	25% AN
	SAN-2	Cheil Ind. Inc.	$\overline{M}_n = 53,000$ $\overline{M}_w = 96,000$	24% AN
	SAN-3	Cheil Ind. Inc.	$\overline{M}_n = 91,000$ $\overline{M}_w = 17,000$	26% AN

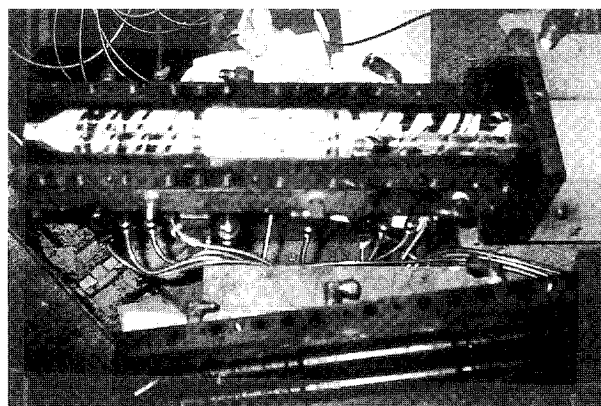


Fig. 1. W&P TSMEE with split barrel shown in fully open positions.

offers a facilitated route for carcass experiments which are essential for the study of phase morphology development during melt compounding of polymer blends. The details of TSMEE is given elsewhere[7]. In each case, the components were first dry blended and fed simultaneously to the hopper at a rate of 36 g/min using a loss-in-weight feeder. The barrel was maintained at a temperature of 250°C except the feed zone where the barrel temperature was set at 180°C. The screw speed was set at 120 rpm, which correspond to an average shear rate of 326 sec⁻¹. After reaching steady state, the machine was brought down to a stop. The device was then fast cooled by circulating cooling water to a temperature of 80°C to freeze the material. The time required for cooling was about 60 sec after stopping. It is important for the study of morphology development to minimize the cooling time since melt blend morphology can change significantly during annealing at elevated temperature or slow cooling[8-10]. Within the accessible cooling time of this experiment, one might expect morphology change like breakup of elongated cylinder[10]. Nevertheless, the analysis given here should at least provide a reliable rationale based on the fixed sampling re-

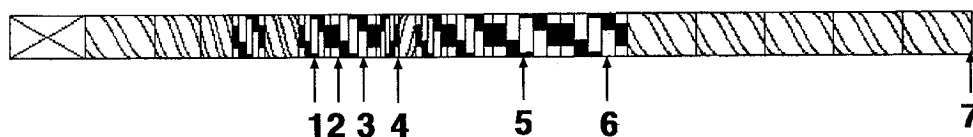


Fig. 2. Sampling positions in TSMEE.

gime for all cases. Once the machine was sufficiently cooled, the top portion of the barrel was opened, and sampling was made at various points along the mixing section. The extruded strands during the steady state operation were directly put into cold water to eliminate possible morphology change. The schematic illustration of configuration and sampling positions is shown in Fig. 2.

Various microscopy analyses were performed on samples collected along the axial position. Hot Stage Microscopy(HSM) was used to explore the mechanism of dispersive mixing. The HSM method is particularly useful in such purpose since it allows focusing at various depths providing a pseudo 3-D image[11]. The morphology of the blends was characterized by transmission electron microscopy(TEM) using a Jeol JEM-2000EX. For improved contrast, two stage staining method was applied: First, specimen blocks broken from the carcass samples at liquid nitrogen temperature were stained in a 2% solution of OsO_4 for 48 hours. Ultrathin slices were cut using a Reichert-Jung Ultracut Microtome at room temperature. Then, the thin sections were further stained by the vapor of a 0.5% RuO_4 solution for 30 minutes[12]. Average domain sizes were calculated from SEM photomicrographs by using an image analyzer. Samples for SEM were sputter

coated with a thin layer of Au and observations were made using a Jeol JSM-840A.

The rheological characterizations were performed using a Rheometrics RMS 800 rheometer with parallel plate fixtures for shear rates less than 100 s^{-1} and a capillary viscometer for the range of higher shear rates. The measurements were made at a temperature of 250°C and the results are presented in Fig. 3.

3. Results and Discussion

Fig. 4 shows the effect of viscosity ratio(p) of the domain to the matrix on the phase size of PC/SAN(10/90) blends. The viscosity ratio was calculated from the viscosities at the specified shear rate above. Since the AN contents of SAN copolymers used in this study are close to the range which exhibits optimum thermodynamic interaction with PC[4], we can minimize the possible influence caused by different interfacial activities. For the given processing environment, the phase size shows weak dependency on the available range of viscosity ratios except the case when the ratio is around 70. In compounding of immiscible polymer blends in a twin screw extruder, it has been reported and widely recognized that the phase size of the minor component is minimum at a

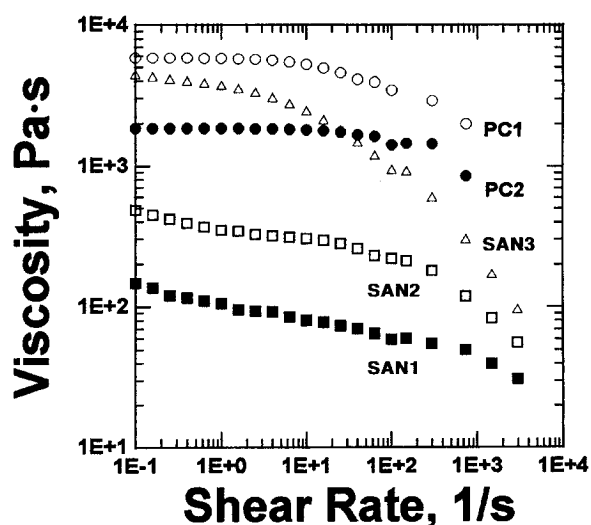


Fig. 3. Viscosity at 250°C as a function of shear rate for polymers used in this study.

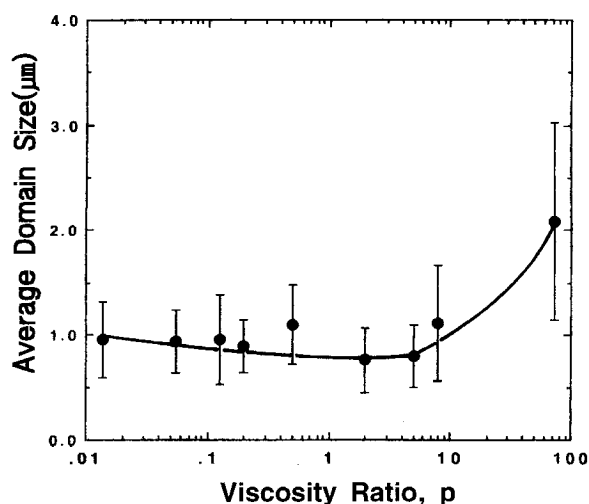


Fig. 4. Effect of viscosity ratio on the average domain size of blends base on PC and SAN (Minor/Major=10/90 in wt.).

closely matched viscosity ratio[1]. In contrast, present data reveal comparable level of dispersion even in the mismatched viscosity ratios. This result considered to be attributed to the intensive elongational flow field imposed by kneading blocks of twin screw extruder[13], which is well known to be very efficient in break-up mechanism regardless of the viscosity ratio[14]. In order to delineate the interfacial and the rheological effects on the size of dispersed phase, it is useful to plot critical Weber number(We^c) versus the viscosity ratio; the critical Weber number is expressed by

$$We^c = \dot{\gamma} \mu_m R / \Gamma \quad (1)$$

where " $\dot{\gamma}$ " represents shear rate, " η_m " represents viscosity of the matrix, "R" the radius of the domain and " Γ " the interfacial tension. When the interfacial tension and shear rate are fixed, such plot indicates the relative ease or effectiveness of dispersion for various viscosity ratios. Fig. 5 was constructed based on the data shown in Fig. 4 with constant values of shear rate and interfacial tension as 326 s^{-1} and 4.0 dyne/cm [15], respectively. In Fig. 5, in addition to the result of present work, various curves obtained by previous studies are compared together. It is worthwhile to note that the trend found in this study is close to the case of Newtonian fluids in elongational(hyperbolic) flow field, which reflects the long Newtonian plateaus of all the resins used in this study(see Fig. 3) and dominant influence of elongational flow imposed by the given mixing environment. In comparison of various cases in Fig. 5, it

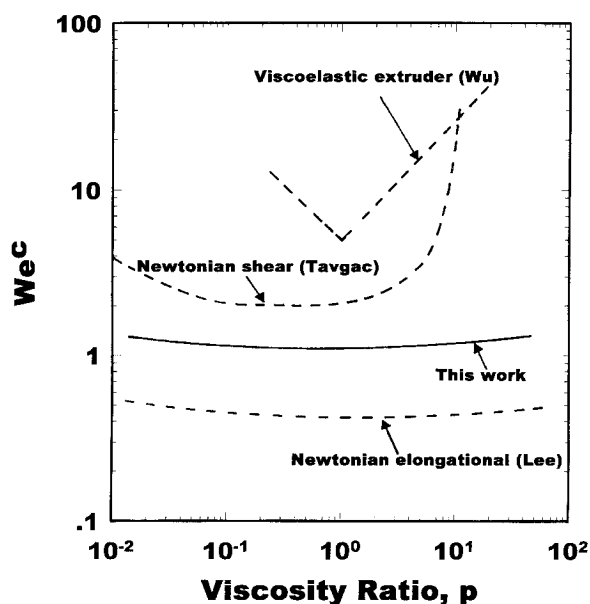


Fig. 5. Critical Weber number as a function of viscosity ratio.

is again emphasized that dispersion occurs much more easily in elongational field than in shear field. As previously mentioned in Wu's report[1], it has been claimed that drop breakup is easiest when the viscosities are matched. It is noted, however, that due to the different nature of materials used and processing conditions, comparison with other studies should be made with some cautions and the general consideration of minimum domain size at $p=1$ is not universally true. As will be addressed in the later discussion, the state of dispersion and the final size of domain are more relevant to the issue of coalescence which is mainly influenced by the matrix viscosity.

The mechanism of phase breakup during dispersive mixing of PC and SAN is demonstrated in Fig. 6. When the materials are fed into the extruder and forwarded along with the axial positions at the early stage of mixing, they are softened and/or melted to become viscoelastic liquids. As the phase transition occurs from solid to melt, it was found that most of size reduction is accomplished during the softening process and the mode of breakup follows the sequential formation of sheet(Fig. 6(a)), lace(Fig. 6(b)) and ligaments(Fig. 6(c)), which in turn lead to droplets (Fig. 6(d)). The observed behavior in the dispersion of SAN in PC matrix is in accordance with the proposed mechanism of Scott and Macosko[16] which has been based on model experiments in a batch mixer with five different matrix polymers having various T_g 's(glass transition temperature). Their experiments suggested a mechanism of morphology development for the initial stage of polymer blending where a particle is dragged against a hot surface. This hot surface could be the mixer wall and the mixing blades in a batch mixer or the surface of kneading blocks and barrel in an extruder. Such contact causes the formation of a sheet of the phase. Owing to interfacial and shearing forces, holes form in the sheet and grow until a lace structure is formed. This lace is then broken down into thin ligaments, which eventually break into drops by Rayleigh-type instability[17,18].

The mechanism of dispersive mixing in polymer blends is certainly associated with various factors including relative softening or melting rates of the blend components, type of deformation during softening and nature of flow field, etc.. Among these variables, the relative softening rate which is mainly dependent on the molecular weight and T_g of the component polymer is critical in determining the order of softening. In fact, for systems such as dispersion of rubbers in thermoplastic matrices where the T_g of the minor phase is significantly lower than that of the

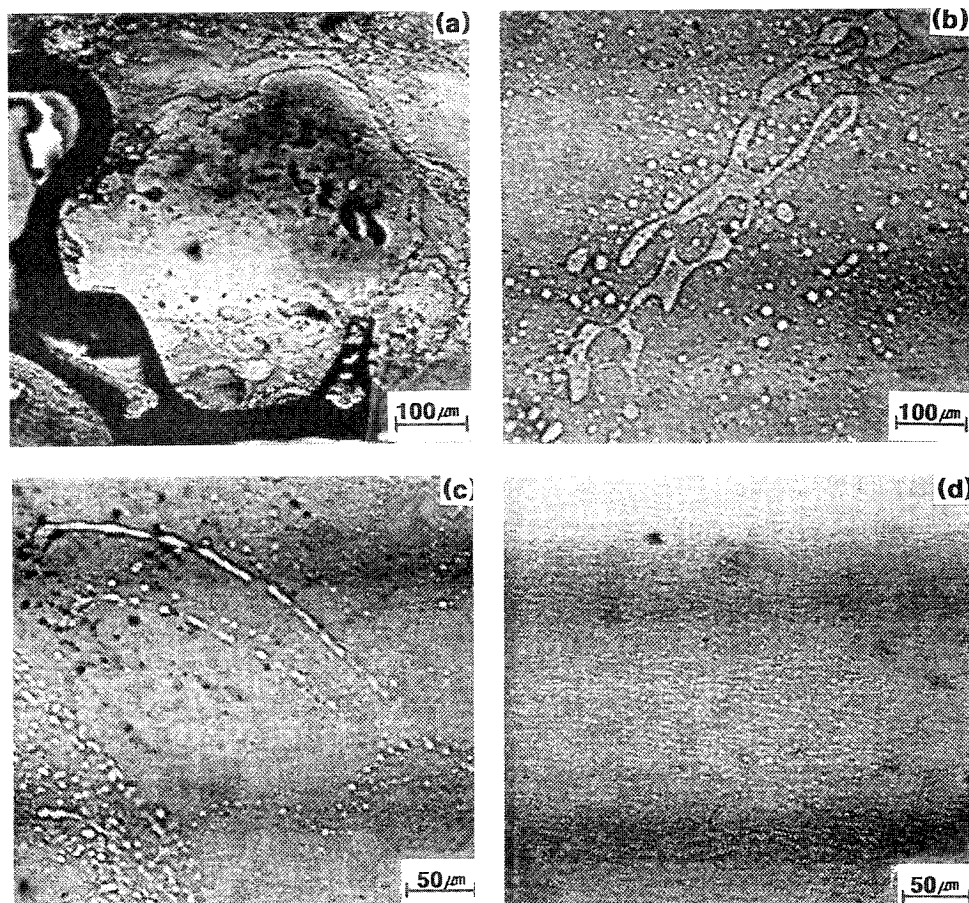


Fig. 6. Morphology images illustrating the mechanism of phase breakup in SAN-3/PC-1(10/90) blend. (a) position 1, (b) position 2, (c) position 3 and (d) position 4.

major, a phase inversion is expected to be part of the mechanism as described by Shih et al.[19]. In this case, the minor phase softens first and initially becomes the continuous phase, provided the heating rate is very slow. After melting or softening of the major phase, phase inversion occurs so that the major phase becomes the continuous phase. A similar argument may be pertinent here since the T_g of the minor(SAN) is about 50°C lower than that of the matrix(PC). Throughout the work reported here, however, such morphological transition was not observed; since the solid mixture is typically fed into a relatively cold feeding zone and then quickly conveyed into a hot barrel zone where the temperature is kept higher than those of the polymers. In other words, the heating rate applied in this study is much faster and immediate heating of both phases above T_g is expected to eliminate the possibility of phase inversion. A similar mode of breakup mechanism has been also observed in the system where the matrix is SAN instead of PC. Owing to the large number of variables in the entire process of dispersive

mixing, cautions should be taken in comparison of mechanism between different blends and mixing environments. For example, abrasion of solid or partially softened pellets against the mixer wall may constitute another potential mechanism, as suggested by Plochocki et al.[20]. Nevertheless, the common features obtained from the works conducted here and by Scott and Macosko[16] add confirmation on the generality of the proposed mechanism at least in blending of high molecular weight polymers under the typical conditions of a batch mixer or an extruder. One important issue remains to be addressed here is the fact that the disintegration of ligaments into droplets arises within such a short period throughout the entire mixing process. Regarding the time scale and effectiveness of breakup process, a reasonable interpretation can be made by rigorous analyses on breakup time conducted by Tomotika[17] and Sundararaj et al.[10] along with understanding the characteristics of kneading action in a twin screw extruder: At the early stage of melt-mixing, where affine deformation of the minor phase prevails with large

Weber number, interfacial forces cannot resist the stresses imposed by the flow field in an extruder; however, once sufficient decrease in local radii of threads (order of 1 μm) is achieved, the interfaces should become active especially in relatively low stress region[21] and breakup initiates simply because the interfacial tension tends to minimize the interface between the two phases. Accordingly, it is important to accommodate the alternative level of high and low stresses to facilitate the dispersion process, which is essentially imposed by cyclic movements of compression and expansion in kneading blocks[22]. When those thin threads are ready to breakup into droplets, the required breakup time can be estimated by Tomotika's theory which was originally developed for breakup of a viscous fluid cylinder in a viscous matrix, in which the breakup time is given:

$$t_b = \frac{\mu_m R_o}{\Omega \Gamma} \ln(\alpha_b / \alpha_o) \quad (2)$$

where t_b is the breakup time; η_m is the matrix viscosity; R_o is the initial cylinder radius; Ω is a mathematical function that depends on the viscosity ratio and the disturbance wavelength; Γ is the interfacial tension; α_b is the distortion at breakup; and α_o is the initial distortion. As shown in equation (2), it is critical to develop the thinnest possible threads to minimize the required breakup time in

a given mixing environment; since the required breakup time is proportional to the thread diameter. Compared to the original prediction of Tomotika in which the initial distortions are purely induced by Brownian motion, however, Sundararaj et al.[10] suggested that much faster breakup

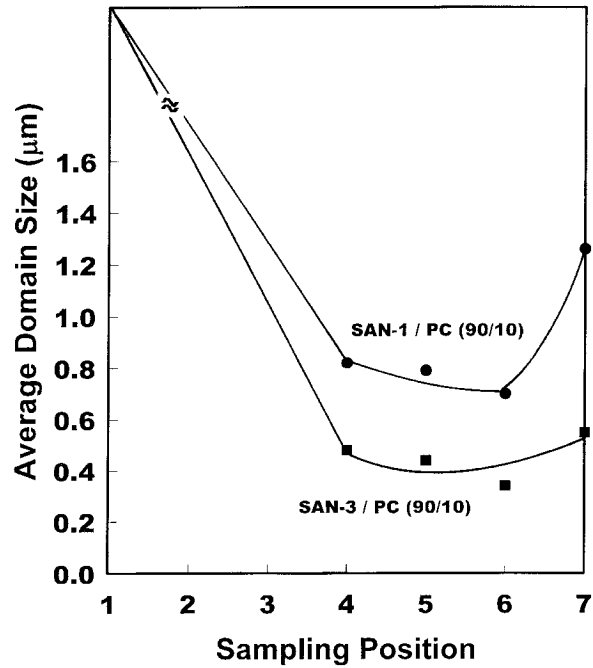


Fig. 7. Average domain size as a function of sampling position.

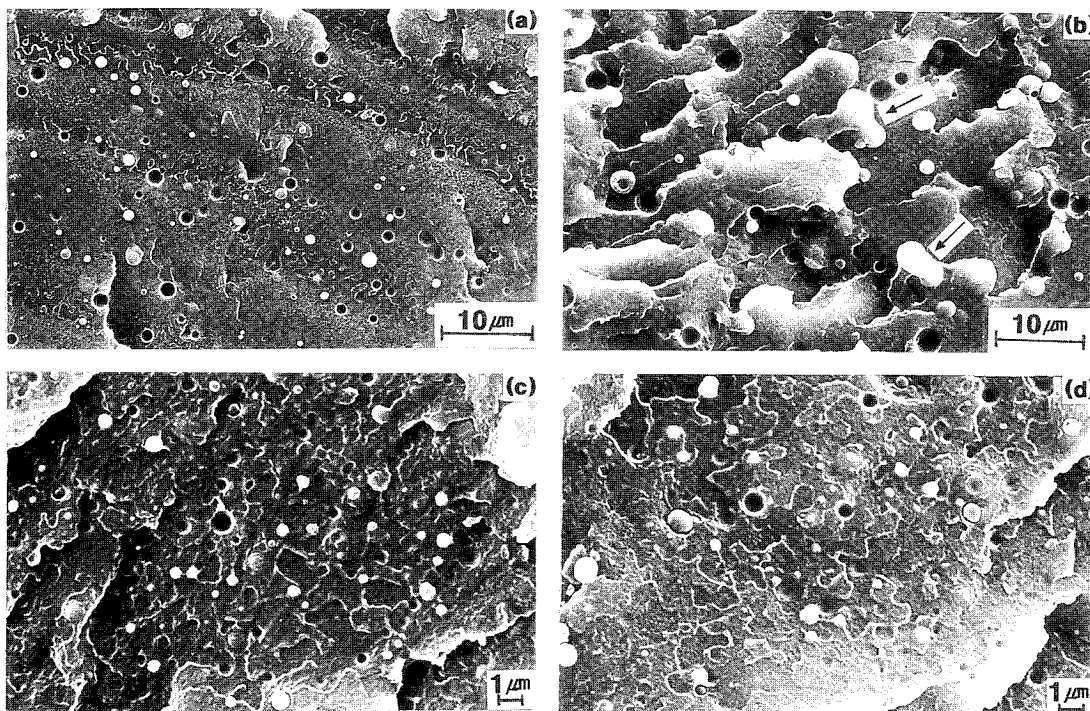


Fig. 8. SEM photomicrographs of PC-1/SAN-1((a)&(b)) and PC-1/SAN-3((c)&(d)) blends for two different sampling positions(each blend contains 10% of PC): (a),(c) position 5 (b),(d) position 7(die out).

(order of few seconds) is possible in polymeric fluids due to the significantly larger initial distortion which is mainly caused by polymer memory effects. Similar calculation was applied to present case and comparable order of breakup time was obtained by assuming initial distortion of 25 nm for a thread of SAN in PC matrix.

In Fig. 7, the variations of the domain(PC) size as a function of sampling location are presented for two different matrices, SAN-1 and SAN-3, respectively. In both cases, the main part of the size reduction is readily achieved around position 3 and the domain sizes are slightly further decreased until position 6 which is the end of the kneading section as described in Fig. 2. However, at the discharge of the extruder, the domain size is increased especially in the case of SAN-1/PC blend. Such variation of domain size is well demonstrated by SEM pictures shown in Fig. 8, where it is pointed out that the enlargement of domain is mainly due to the coalescence (see arrows in Fig. 8(b)).

The coalescence in immiscible polymer blends has been the subject of numerous studies performed at static or flow conditions, and several theories have been developed to interpret the coalescence effect[23-29]. Although various kinematic models were also proposed to predict the domain sizes in polymer blends, discrepancies are still inevitable due to the polymer viscoelasticity and complexity of the given flow field during melt-mixing. On the other hand, qualitative aspects of flow induced coalescence in polymer blends are rather well described by a three-step mechanism originally modeled for Newtonian liquid drops[30], where the droplets are brought close together by the flow field, and then the matrix film between the drops thins until the interface ruptures and then coalescence occurs. Of course the nature of the whole process in polymeric systems may be quite different from that of simple liquid drops; however, the collision of domains and removal of matrix phase should be maintained for both cases as a prerequisite for coalescence. Furthermore, considering the high viscosity of polymer melt, drainage of the matrix film is the rate-determining step[31]; hence, the amount of coalescence should be decreased by increasing matrix viscosity[24]. Thus, by this reason, coalescence is more active in SAN-1 matrix than the case of SAN-3.

Conclusions

The mechanism of phase breakup during dispersive mixing of PC and SAN appears to be closely related with in-

itial softening stage of component polymers. As the phase transition occurs from solid to melt, it was found that the mode of breakup follows the sequential formation of sheet, lace and ligaments, which in turn lead to droplets via Rayleigh type instability. The observed behavior in this study is in accordance with the proposed mechanism of Scott and Macosko[16]. Within the available range of viscosity ratios and the given mixing environment, the average domain size in various blends of PC/SAN was little affected by the viscosity ratios except the case when the viscosity ratio was the highest as 70. The main reason for such weak dependency on the viscosity ratio stems from the nature of the flow field in kneading section where elongational flow prevails. From the SEM observation and size analysis for samples taken at different positions, it is reported that while the phase size of each domain is in the minimum range during the intensive melt-mixing by kneading blocks, throughout the rest part of compounding process, motion induced coalescence operates and subsequently increases the domain size especially when the matrix viscosity is relatively low. It is emphasized that the condition of matched viscosity ratio around 1 is not a prerequisite for the minimum domain size in melt-mixing of polymer blends by a twin screw extruder; instead it is more important to minimize or prevent coalescence for stable phase structure. In practice, in the development of PC/ABS blends, choice of SAN copolymers can be made within the wide range of viscosity if the matrix phase is PC which usually exhibits higher viscosity than SAN does. In case that ABS forms a continuous phase, however, formulations should be established with some cautions since coalescence can be even more serious and consequently leads to significant deterioration in mechanical performance of the blend.

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