

고속전단가공에서 PC의 분자량에 따른 PC/ABS 블렌드의 열적 물성 변화 영향 연구

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Effects of Molecular Weight of PC on Thermal Properties of PC/ABS Blends Using High-Shear Rate Processing

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초록: ABS(acrylonitrile-butadiene-styrene)와 분자량이 다른 2종의 PC(polycarbonate)를 블렌딩하고, 고속전단압출성형기를 사용하였을 때 고속 전단에 의한 PC 분자량에 따른 열적 물성의 변화를 연구하였다. DSC(differential scanning calorimetry)와 TGA(thermogravimetric analysis)를 이용하여 유리전이온도와 열분해온도를 각각 측정하였다. 가해지는 전단력을 증가시킬 때에는 PC1(MW=13700)/ABS와 PC2(MW=9700)/ABS 두 가지 경우 모두 유리전이온도가 감소하는 동일한 경향을 보였다. TGA의 경우 전단력을 가하지 않은 경우 명확한 두 단계의 분해곡선을 나타내고, 고속 전단 가공을 한 경우 분해곡선이 선형으로 변화하는 경향을 보였다. 또한 고분자량의 PC를 사용한 PC/ABS 블렌드의 경우 저분자량의 PC를 사용한 경우보다 높은 유리전이온도와 열분해온도를 나타내었다. 이를 통하여 고속 전단 압출을 이용하여 상용성을 향상시킬 수 있으나 3000 rpm 이상의 고속전단을 가하면 블렌드 내의 열화가 발생한다는 것을 알 수 있었다.

Abstract: Each of the two polycarbonates (PC) of different molecular weights was blended with acrylonitrile-butadiene-styrene (ABS) to afford PC/ABS which was processed at several high-shear rates in order to study thermal behaviors. Changes in glass transition temperatures (T_g s) and thermal degradation behavior were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. T_g s of both PC1 (MW=13700)/ABS and PC2 (MW=9700)/ABS gradually decreased as high-shear rate increased. T_g of PC1/ABS was higher than that of PC2/ABS at each condition of high-shear rate. PC/ABS without shear processing showed two TGA peaks which coalesced into one as high-shear rate was increased. The results indicated that high-shear rate processing could be utilized to improve compatibilities between blending mixtures but suffered from the disadvantages of thermal degradations above 3000 rpm and 20 s of high-shear rates.

Keywords: polycarbonate, acrylonitrile-butadiene-styrene, high-shear rate processing, differential scanning calorimetry, thermogravimetric analysis.

Introduction

Blends of different polymers can provide a material of new and much improved properties by reinforced synergism.^{1,2} In

our laboratory, blends of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) were studied under high-shear rate processing to study the effects on the thermal properties of PC/ABS blends.¹ PC/ABS blends have been widely used such as in electrical/electronics, telecommunications, and automotive applications.³ However, use of PC/ABS blends showed some drawbacks due to poor compatibilities between constituents.⁴⁻⁸ In this regards, we had PC/ABS processed at high-shear rates

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to solve the problems arisen by poor compatibilities between PC and ABS.¹ We confirmed that high-shear rate processing had afforded much smaller sizes of dispersed phases of ABS in PC/ABS. Besides we observed that glass transition temperatures (T_g s) and mechanical properties of PC/ABS were decreased and changed, respectively, at high-shear rates,^{1,9,10} conforming to the general phenomena observed in incompatible blends as compatibilities being improved. However, thermal degradation of PC arisen by high-shear force under high-shear rate processing was also observed to deteriorate the properties of PC/ABS.^{1,9}

In this regards, the purpose of this work was aimed to study any influences of PC, in terms of its molecular weight, on its blend with ABS in order to improve the impaired properties as was mentioned above. As is generally known, increase in molecular weight of polymer makes its processing rather difficult. However, it also provides some advantages in that smaller amounts can be used due to much improved properties of PC/ABS such as providing thinner layers. For the purposes two polycarbonates (PC) of different molecular weights were chosen to study influences exerting on the properties in PC/ABS under high-shear rate processing and hopefully to find out optimum conditions to develop a blended material of new and much improved properties.

Experimental

Material. Polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) were commercially available from LG Chem. Co. Ltd. (Korea). Two kinds of PC were used, i.e. PC1 (MW 13700) from Samyang Co. Ltd. (Korea) and PC2 (MW 9700) from LG Chem. Co. Ltd.. Acrylonitrile-butadiene-styrene (ABS) resin consisting of SAN (85%) and polybutadiene (15%) was used. All the resins were dried in an oven (100 °C) for 15 h prior to use. In a thermal degradation experiments under high-shear rate processing, bis(2,4-dicumylphenyl)penterythritol diphosphite (Dover Chem. Corp.) with which we had satisfactory results in our previous studies was used as an antioxidant.¹¹

High-Shear Rate Processing. In order to investigate the effects of high shear rate processing on thermal properties of PC/ABS blends, high shear rate processing machine (Niigata Machine Techno. Corp. Ltd., NHSS2-28) was employed. Figure 1 shows a schematic diagram of the internal structure of a high-shear rate processing machine which consists of a screw (28 mm in diameter), four heating parts and three cooling

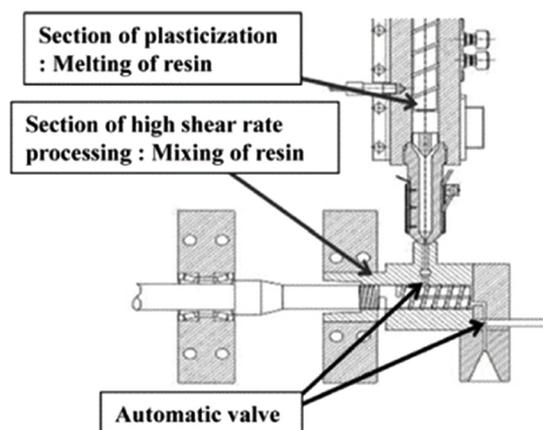


Figure 1. Schematic view of internal structure of high shear rate processing machine.¹

Table 1. Blending Ratio and Experimental Conditions under High-shear Rate Processing

PC1 or PC2 (wt%)	ABS (wt%)	High-shear rate (rpm)	Processing time (sec)
			10
		1000	20
			30
70	30		40
		2000	
		3000	20
		4000	

parts. Unlike regular machine in which the raw material is melted and kneaded simultaneously, the high shear rate processing machine is divided into plasticization section and high shear rate section. In plasticization section materials are melted and injected constantly into the high shear rate part. In high shear rate section, molten materials are processed under arbitrary rotation speed and time.^{1,11} Experimental conditions under high-shear rate processing are shown in Table 1. In order to study the thermal behaviors of blends under shear processing, experiments were carried out at various high-shear rates, i.e. at 1000, 2000, and 3000 rpm for a fixed shear rate processing time of 20 sec. And to study the effect of shear time on thermal behaviors of blends, experiments were carried out for 10, 20, 30, and 40 sec of shear time, respectively at fixed shear rate (1000 rpm). A melting process of blends was carried out at 180-220 °C and higher-shear rate than 1000 rpm was processed at 220 °C.

Analysis of Morphology. In order to observe the surface of blends, the sample was fractured after cooling it for 5 min under liquid nitrogen. Fractured surface was etched with aque-

ous chromic acid solution (H_2O 30 mL, H_2SO_4 120 mL, and Cr_2O_3 5 g) at 80 °C for 5 min. The surface was Pt-coated for 80 sec. Fractured surface of either PC1/ABS or PC2/ABS was subjected to scanning electron microscopy (SEM, JEOL-JSM-7000F) to observe surface morphologies.

Analysis of Glass Transition Temperatures (T_g s). These analyses were carried out to study thermal behaviors of PC/ABS under high-shear rate processing. Glass transition temperature (T_g) of PC was measured by DSC (Perkin-Elmer, Pyris 6), in which a specimen (about 2-3 mg) was placed in the pan and thermal behaviors were measured at a temperature range from 20 to 260 °C by heating rate of 10 °C/min.

Analysis of Thermogravimetric Behaviors. Thermal behavior of PC/ABS was observed by TGA (thermogravimetric analysis) and DTG (derivative thermogravimetric analysis) (Mettler-Toledo) under high-shear rate processing conditions. Analysis was conducted by measuring changes in mass at a temperature range from 20 to 600 °C by heating rate of 10 °C/min under nitrogen atmosphere.

Results and Discussion

Analysis of Morphology. Morphological changes in PC/

ABS blends under high-shear rate processing were characterized by SEM images. Figure 2 shows changes in domain sizes of the PC1/ABS morphologies depending on the high-shear rates when PC1 (higher molecular weight) was used. Figure 2(a) shows the SEM image from ‘compounded’ specimen which is processed with conventional compounding of PC1/ABS blending before high-shear rate processing.

SEM images shown in Figure 2(b)-(d) were obtained at several shear rates, i.e. at 1000, 2000, and 3000 rpm. Figure 2(b) obtained at high-shear rate of 1000 rpm clearly shows that dispersed phases of PC1 and ABS are mixed well as in Figure 2(a), and are connected each other phase. In Figure 2(c) obtained at 2000 rpm, more effectively dispersed phases, thereby with decreased domain sizes, are observed.

SEM image in Figure 2(d), obtained at high-shear rate of 3000 rpm, is quite different to those of Figure 2(b) and Figure 2(c). We could conclude that some shear-induced degradations had occurred in parts, which was supported by additional experiments.¹⁰ Figure 3 shows the average dispersed phase size of PC1/ABS, measured from SEM images by using Image J software, depending on shear rates. As was observed from SEM images, average size of the dispersed phase decreased as shear rates increased from 1000 to 2000 rpm. However, mor-

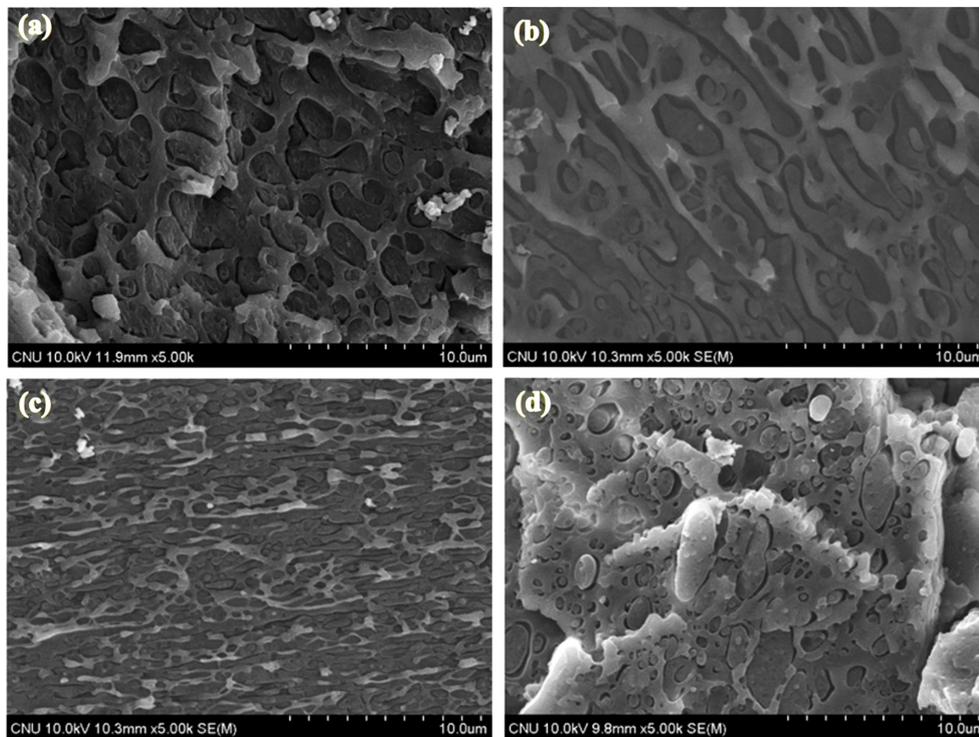


Figure 2. SEM image ($\times 5000$) of PC1/ABS blends at a fixed processing time of 20 sec at high-shear rates; (a) ‘compounded’; (b) 1000 rpm; (c) 2000 rpm; (d) 3000 rpm.

phology of the phase and its size at 3000 rpm are quite different to those at either 1000 or 2000 rpm.

In Figure 4, SEM images of PC2/ABS obtained with the use of PC2 (lower molecular weight) are shown in order to compare phase morphologies of PC2/ABS with PC1/ABS.^{1,9,10} It is

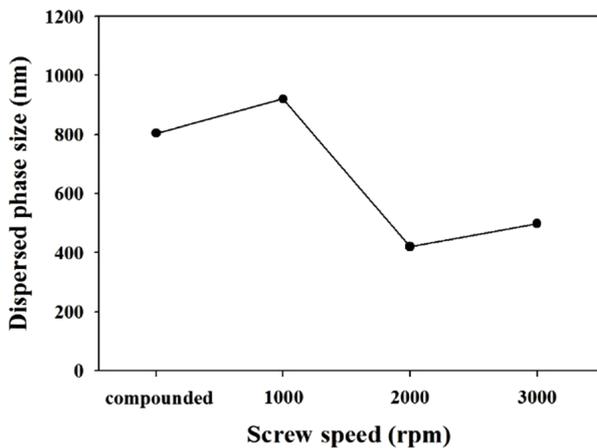


Figure 3. Average size of dispersed phase in PC1/ABS blends at various shear rates for a fixed processing time of 20 sec.

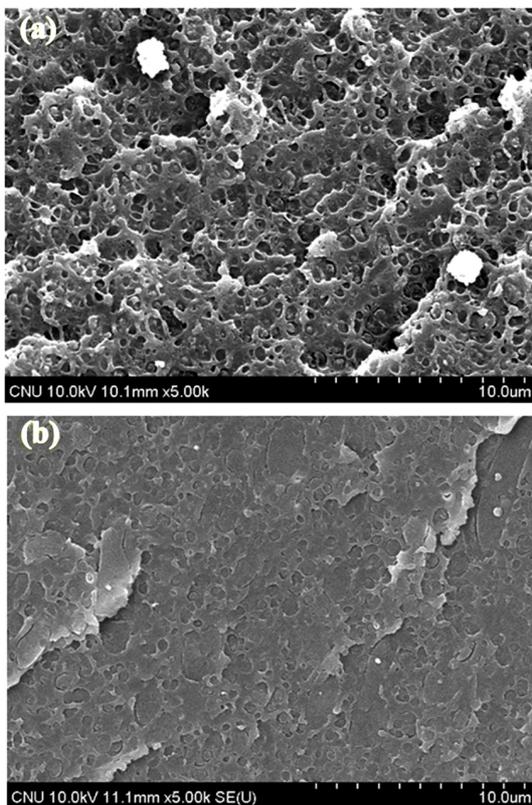


Figure 4. SEM image ($\times 5000$) of PC2/ABS blends at various shear rates: (a) 1000 rpm; (b) 2000 rpm for a fixed processing time of 20 sec.¹⁰

noted in Figure 2(b) that dispersed phases in PC1/ABS are well connected each other, while only phase sizes in PC2/ABS became smaller (Figure 2(a)) at 1000 rpm. The results provided a piece of information that better mixing would be achieved by using PC of higher molecular weight in PC/ABS blends. Similar phenomena were observed by comparing SEM images of Figure 2(c) and Figure 4(b), both obtained at 2000 rpm. In addition it was seen that phase sizes at 2000 rpm were smaller than those obtained at 1000 rpm for both cases.

Comparative Analysis of Glass Transition Temperatures (T_g s) Depending on High-Shear Rates. T_g s of PC in PC/ABS blends at several high-shear rates were determined and shown in Figure 5. Under the conditions described in Table 1, measurements were carried out for shear time of 20 sec at high-shear rates. Here, T_g s of PC in PC1/ABS blends were decreased to 144.2, 141.2, and 136.7 °C when high-shear rates were 1000, 2000, and 3000 rpm, respectively. It was investigated that T_g s of PC gradually decreased from 148.4 °C, T_g of PC in 'compounded' which is a simply blended PC/ABS without any shear. The similar trends of decreasing T_g s were also observed for PC of PC2/ABS, i.e. 141.0, 138.7, and 133.6 °C at high-shear rates, such as, 1000, 2000, and 3000 rpm, respectively. Here, T_g of PC in 'compounded' was 143.2 °C.

In general when two incompatible polymers are mixed, two T_g s are measured independently and when compatibilities of mixing polymers are improved, then T_g would approaches to a middle value of the two polymers.^{8,12,13} As a matter of fact the compatibility of PC/ABS blends increases, T_g of PC shifts to that of ABS, which is difficult to be measured by DSC. But it is noticed that PC1 of higher molecular weight changes more

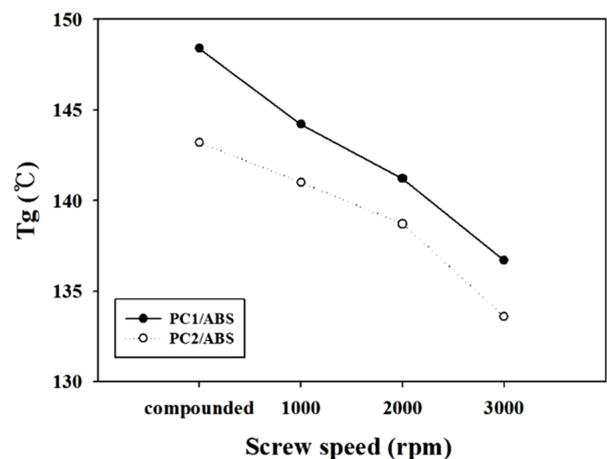


Figure 5. Correlations of glass transition temperatures of PC1/ABS and PC2/ABS as a function of high-shear rates.

declined than PC2 of lower molecular weight does.

In other words, decreased values of T_g s can be expected as compatibilities are improved. The phenomena might be considered to be attributed to phase changes under high-shear rate processing. Noteworthy at high-shear rate of 3000 rpm (Figure 5) was that T_g of PC2/ABS was 133.6 °C, which value was more steeply decreased. The results could be understood that thermal degradations had proceeded as was confirmed by SEM images.^{1,9,10}

Comparative Analysis of Glass Transition Temperatures (T_g s) Depending on Processing Times at High-Shear Rate. At fixed a high-shear rate of 1000 rpm, T_g s were determined depending on processing times and are shown in Figure 6. Herein, T_g s of PC1 and PC2 in PC/ABS blends had decreased considerably as high-shear processing time increased to 40 sec as follows, i.e. from 148.4 to 142.2 °C and from 143.2 to 139.4 °C, respectively.

Behaviors of Thermogravimetric Behavior Depending on High-Shear Rates. Mass losses were measured by TGA from room temperature to 550 °C by heating rate of 10 °C/min under nitrogen atmosphere in order to analyze the thermal degradations of PC/ABS depending on high-shear rates. The correlations of the residual weights versus heating temperatures for PC1/ABS in Figure 7(a) and for PC2/ABS in Figure 8(a) were shown.

We researched in Figure 7(a) that the degradation temperatures gradually decreased upon increasing high-shear rates. Also in Figure 7(a) two steps of thermal degradations in TGA were observed at about 400 and 450 °C for ‘compounded’. However, at high-shear rate process above 1000 rpm, only one

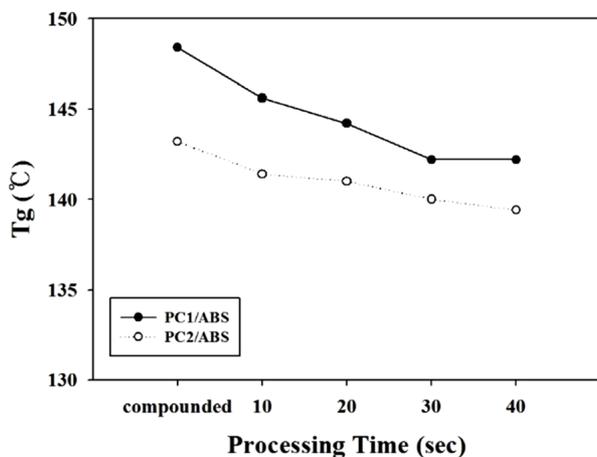


Figure 6. Correlations of glass transition temperatures of PC1/ABS and PC2/ABS as a function of processing times.

step of thermal degradations was observed, decreasing smoothly around 450 °C.

In order to study these phenomena more clearly, first derivatives of experimentally measured TGA curves (Figure 7(a)) were plotted in Figure 7(b) in which thermal behaviors of processed specimens are shown. That is, ‘compounded’ in Figure 7(b) clearly shows two peaks, on the contrary, there is only one peak at 1000 rpm for 20 sec of processing time. When two peaks in curves of thermal degradations coalesced into one, this phenomenon is the evidence due to the enhanced compatibilities.^{9,14} Therefore, it could be concluded that compatibilities would have considerably improved at high-shear rate of 1000 rpm for 20 sec. In this regards, a peak observed at both 2000 and 3000 rpm under high-shear processing might be attributed to further improved compatibilities.

Analysis of Thermogravimetric Behaviors Depending on Molecular Weight and High-Shear Processing Time. We have measured changes in masses of PC/ABS depending

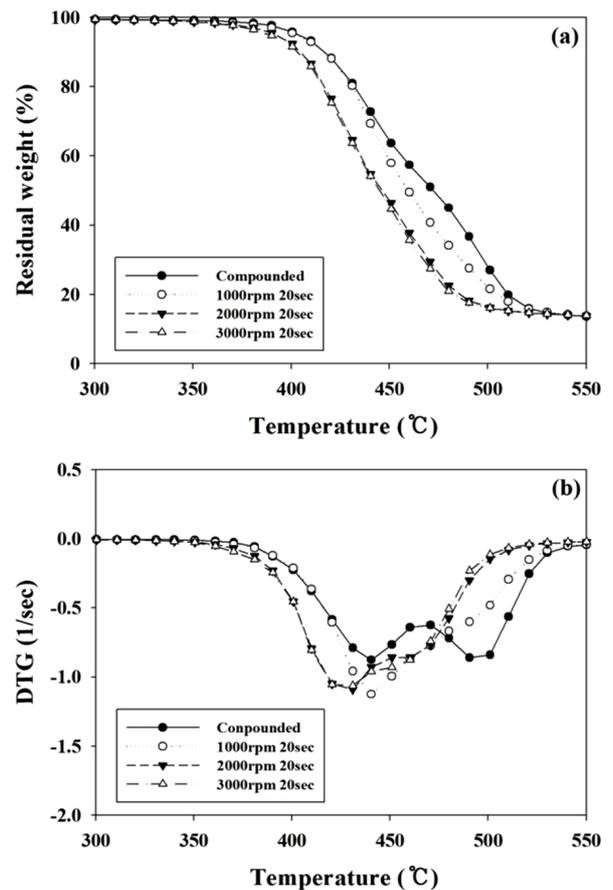


Figure 7. (a) TGA curves; (b) DTG curves of PC1/ABS blends at various high-shear rates of ‘compounded’, 1000, 2000 and 3000 rpm for 20 sec of processing time.

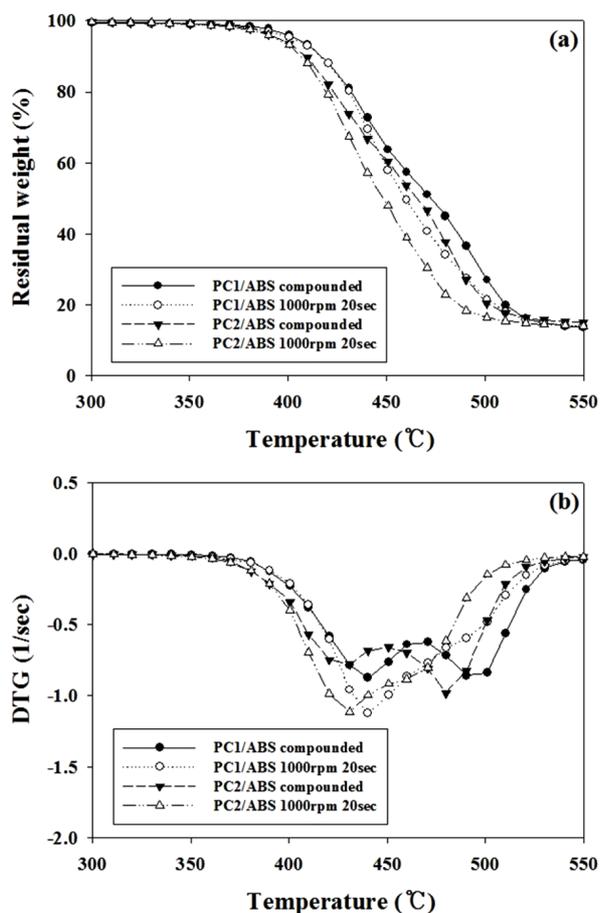


Figure 8. (a) TGA curves; (b) DTG curves of PC1/ABS and PC2/ABS at shear rates of ‘compounded’ and 1000 rpm for 20 sec of processing time.

on high-shear processing time and found out the similar behaviors. Therefore, thermal behaviors of two PC/ABS consisting of PC1 and PC2 were compared each other and are shown in Figure 8 in which changes (Figure 8(a)) and the rate of changes (Figure 8(b)) in masses of PC1/ABS and PC2/ABS before and after high-shear rate processing at 1000 rpm for 20 sec are shown. In Figure 8(b) two peaks corresponding to thermal degradations are seen for ‘compounded’ of both PC1/ABS and PC2/ABS. i.e. ca. 440 °C and ca. 500 °C for PC1/ABS; ca. 430 °C and ca. 480 °C for PC2/ABS. On the contrary, DTG peaks at high-shear rate of 1000 rpm for 20 sec show only one peak, i.e. at around 440 °C for PC1/ABS and at around 430 °C for PC2/ABS. The results revealed an information that the thermal degradation temperature was higher for PC1/ABS consisting of higher molecular weight of PC by about 10 to 20 °C. Overall we found out that the thermal stability was higher in the PC/ABS blend consisting of higher molecular weight of PC.

Conclusions

In this study we have investigated how compatibilities and thermal characteristics of PC/ABS blends would be dependent upon molecular weight of PC. For the purposes, PC1/ABS and PC2/ABS containing PC of different molecular weights have been employed. SEM images indicated that phase sizes have been decreased and then compatibilities have been improved by using high-shear rate process. Enhanced compatibilities were observed in PC1/ABS compared to those in PC2/ABS. Glass transition temperatures (T_g s) influenced by both high-shear rates and processing times were changed from 148.4 to 136.7 °C for PC1/ABS and from 143.2 to 133.6 °C for PC2/ABS, indicating phase changes. However shear-induced degradations in PC/ABS were believed to proceed at 3000 rpm under high-shear processing from the experimental results.⁹ Thermal degradations of specimens in TGA had shown much different behaviors depending on whether they were subjected to high-shear processing or not. That is, two peaks corresponding to thermal degradations were seen in ‘compounded’, a conventionally mixed specimen without high-shear processing, while only one peak was observed under high-shear processing. The results gave an information of changes in compatibilities by high-shear rate processing. Initial temperature of thermal degradation was higher for PC1/ABS than PC2/ABS. Based on the results obtained from experiments related with thermal properties of PC/ABS blends, it would be recommended to choose higher molecular weight PC for PC/ABS blends under high-shear rate processing and optimum processing conditions were found to be at 1000~2000 rpm of high-shear rates and for 10~20 sec of processing time.

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