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Effect of the matrix plasticization behavior on mechanical properties of PVC/ABS blends

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Abstract: Acrylonitrile-butadiene-styrene (ABS) grafted copolymer prepared by emulsion polymerization was used to modify different molecular weight poly (vinyl chloride) (PVC) resins. The effects of the molecular weight of the PVC resins on dynamic mechanical analyses (DMA) of PVC/ABS blends and matrix plasticizing behavior on the impact mechanical properties and the morphology were investigated. The tan δ peaks of PVC/ABS blends occurred at the same temperature obtained by DMA, indicating that miscibility of PVC/ABS blends was independent of the molecular weight of PVC. The notched Izod impact test results indicated that the amount of polybutadiene (PB) rubber needed for the brittle-ductile transition (BDT) increases together with the molecular weight of PVC when milled at 165°C. Increasing the operation temperature and adding the plasticizer dioctyl phthalate (DOP) could change the matrix plasticizing extent and the BDT. At a milling temperature of 165°C, the BDT was reached only with 3.6 wt% PB when DOP was added, in contrast to the addition of 7.2 wt% PB in the absence of DOP. The morphology of different plasticized degree of PVC/ABS blends was studied by transmission electron microscopy (TEM) showing that the PVC-1/ABS blends milled at 165°C showed a larger unstained area than the other series of PVC blends.

Keywords: ABS; miscibility; molecular weight; plasticizing; PVC.

1 Introduction

Poly (vinyl chloride) (PVC) is a commercial engineering plastic material which has been widely used in construction, transportation, packaging, and many industrial productions due to its chemical resistance, nonflammability, and low cost [1–3]. However, unmodified unplasticized PVC possesses some disadvantages such as low toughness and heat-softening temperatures are scarcely applied in these fields. In the application process of PVC, some modifiers are usually added to improve the toughness of the PVC resulting in modified PVC called PVC/modifier blend. The commercial modifiers for toughening PVC can be divided into two categories: traditional core-shell modifiers such as methacrylate-butadiene-styrene (MBS), and acrylonitrile-butadiene-styrene (ABS) made up of a rubber core, and a plastic shell; and plasticizing polymers such as chlorinated polyethylene and ethylene-vinylacetate [4–6].

Recently, much attention has been paid to the modification of PVC by the addition of core-shell modifiers in order to improve the impact resistance. For example, Chen et al. [7, 8] investigated the effect of the shell thickness of MBS core-shell impact modifiers on toughening PVC, and considered that the shell thickness of MBS played an important role in determining the dispersion of the MBS modifier particles in the PVC matrix. When the shell thickness was too thin, the MBS particles tended to aggregate in the PVC. On the contrary, the toughening efficiency of MBS was reduced if the shell thickness was too thick. Si et al. [9] investigated the effect of the internal structure of core-shell particles of MBS on toughening PVC, and indicated that sub-inclusion of the core of the rubber phase promoted voids that occurred in the blends of PVC/MBS. To our knowledge, only a few papers have discussed the effect of the matrix composition or the processing conditions on the mechanical properties of the PVC/modifier blend.

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However, the molecular weight and agglomerated state of PVC has great influence on the mechanical properties of plastic materials. It is well known that PVC polymer with an average of 1000 vinyl chloride monomer units is termed PVC DP 1000 (mid molecular weight) and normally used for extrusion molding. PVC DP 800 is used for injection molding. PVC with high molecular weight is hard to use because of its high processing viscosity [10]. In addition, the melt plasticizing behavior of PVC is relative to both processing conditions and additive materials, and further affects the physical and mechanical properties of the blends [11]. Taking into account these observations, we think that the processing temperature and the addition of plasticizers into the matrix can play important roles. Suspension-polymerized PVC particles are built up by primary particles with diameters of 0.1–2 µm. During polymerization, the primary particles agglomerate to larger particles named secondary particles with diameters in the 20–250 µm range [12]. The addition of a plasticizer, such as dioctyl phthalate (DOP), would decrease tensile strength, modulus and other mechanical properties except flexibility and the ease of processing [13].

Engineering issues, such as the matrix plasticization behavior, have gradually attracted the attention of engineers because of the close relationship between the mechanical properties of the matrix/modifier and the matrix plasticization behavior. However, only a few articles have discussed this relationship, which limits the development of polymer blends. In this manuscript, we try to claim this relationship, and discuss the effect of the processing conditions on the mechanical properties of the matrix/modifier blend. PVC and ABS were chosen as the matrix material and organic modifier, respectively. The compatibility between PVC and ABS, and the dispersion of the ABS modifier particles under different processing conditions are mainly presented.

2 Materials and methods

2.1 Materials

Suspended general (SG) PVC powders with different molecular weights were supplied by Qilu Petrochemical Corp (Zibo City, Shangdong Province, China), and were used as the matrix. The physical characteristics of the material are listed in Table 1. The ABS impact modifier was synthesized by grafting styrene and acrylonitrile monomers onto polybutadiene (PB) latex rubber particles by seed emulsion polymerization. The ABS modifiers exhibited a PB latex particle diameter of 300 nm and a grafting degree of the styrene-acrylonitrile (SAN) copolymer of 45%. The weight ratio of PB to SAN was 60/40, and the weight ratio of styrene to acrylonitrile in the SAN here-prepared was 75/25. The SAN copolymer was supplied by Jilin Petrochemical Corp (Jilin City, Jilin Province, China). The preparation of the ABS modifier is described in detail in our previous published article [14]. The average molecular weight (M_w) and the average molecular number (M_n) for the SAN copolymer were 148,000 and 49,400 g/mol, respectively. DOP was produced by the Ningbo East Chemical Co., Ltd. (Ningbo City, China). Processing aids used in this work were all commercially available products and are listed in Table 1.

Table 1: The physical characteristics of poly (vinyl chloride) (PVC) resins adopted in this work.[a]

Sample[b]	K value	DP	M_w ($\times 10^{-3}$g/mol)	M_n ($\times 10^{-3}$g/mol)
PVC-1(SG-1)	76	1500	117	57
PVC-3(SG-3)	72	1300	101	50
PVC-5(SG-5)	67	1000	82.5	41
PVC-8(SG-8)	59	800	61	30.5

[a] The physical properties were offered by Qilu Petrochemical Corp.

[b] SG-suspension poly(vinyl chloride) resins of general purpose.

PVC, Poly (vinyl chloride); SG, suspended general.

2.2 Preparation of PVC/ABS blends

Two samples of PVC/ABS blends were melt mixed by using a blending two-roll mill for 5 min either at 165°C or at 180°C. The obtained samples were then submitted to a sheet compression molding press for 5 min under 15 MPa separately at 185°C and 200°C. The sheet thickness was set to 5 mm for the Izod impact tests.

2.3 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) for the PVC/ABS blends was performed on a DMA apparatus (Diamond-DMA, PerkinElmer, USA). The tests were carried out under the tensile mode, at 1 Hz frequency and a heating rate of 3°C/min with a temperature range from 25°C to 160°C. All of the samples had the following dimension $30\times10\times1$ mm^3.

2.4 Mechanical properties

Notched Izod impact tests of the PVC/ABS blends were performed with the ASTM D-256 standard at 23°C on a

XJU-22 apparatus (Hebei machinery factory, China). Specimens (63.5×12.7×5 mm^3) were cut from the compression molded sheet. The standard impact specimens were kept at 23°C for 24 h before testing.

2.5 Measurement of the molecular weight

The intrinsic viscosities of the different molecular weighted PVC were measured with an Ubbelohde viscometer at 30°C. Tetrahydrofuran was chosen as the solvent. The K and α values were taken from the Polymer Handbook and set to 0.00015 and 0.77, respectively. The viscosity average molecular weight was calculated by using the Mark-Houwink equation.

2.6 Morphology

The transmission electron microscopy (TEM) samples from the impact specimens were cut using a microtome to examine the PB dispersion in matrix. The specimens were cut at -100°C under nitrogen atmosphere and had a thickness of 45 nm. The samples were studied by exposing the ultrathin sections to a vapor of 1% O_sO_4 solution for 2.5 h before observation. Microscopy (JEOL 1210, JEOL, Japan) was operated at 100 kV to observe the dispersion morphology of blends. The percent of ABS contained in the PVC/ABS blends was set to 21 wt% for the TEM experiment.

3 Results and discussion

3.1 Effect of the PVC molecular weight

It is well known that the miscibility between PVC and ABS played an important role in determining the properties of PVC/ABS blends. Many reports previously stressed that the preparation method of blending could affect the miscibility between PVC and ABS. Kim et al. [15] and Gan et al. [16] proposed that the phase separation temperature between PVC and ABS was 160°C. Based on these results, we carried out the melt milling experiments at 165°C. The miscibility of the PVC/ABS blends can be determined from the viscoelastic data obtained by DMA. Figure 1 shows DMA curves of PVC/ABS blends with different molecular weights of PVC. In the PVC/ABS blends, the tan δ peak occurred at 93°C, corresponding to the glass transition temperature (T_g) of the PVC phase, while the tan δ peak occurred at 110°C, corresponding to the T_g of the copoly (styrene-co-acrylonitrile) (SAN) phase. The T_g of different contents are summarized in the Table 2 where the T_g of pure PVC resins and of the pure SAN copolymer are indicated. The position of the tan δ peaks did not move when the curves were compared which proves that the molecular weight of the PVC has little influence on the miscibility of the PVC/SAN blends. The tan δ peak of PVC and SAN are partly overlapped, meaning that the PVC and SAN were partly miscible with each other. This observation corresponded to the T_g of PVC resins and the value of the SAN which moved closer to each other in contrast to the case of pure PVC and SAN. In this work, PVC and SAN resins were partly miscible, and the miscibility is not dependent on the molecular weight of PVC. Therefore, we can ensure that the PB particles uniformly dispersed in different molecular weight PVC matrix.

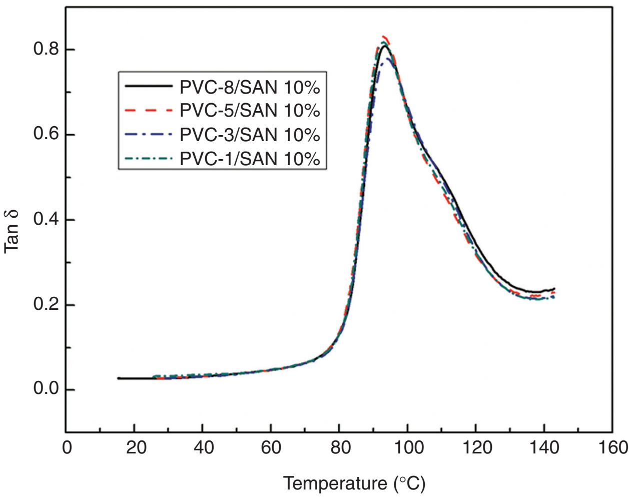

Figure 1: The tan δ curves of the poly (vinyl chloride) (PVC) blends with different molecular weight of PVC.

Figure 2 shows the Izod impact strength plotted against the PB rubber content for the different PVC/ABS blends prepared at milling temperatures of 165°C and

Table 2: T_g of poly (vinyl chloride) (PVC)/styrene-acrylonitrile (SAN)[a] (90/10) blends and PVC resins.

Sample	PVC/ABS blends		PVC resin
	$T_{g\,PVC}$(°C)	$T_{g\,SAN}$(°C)	T_g (°C)
PVC-1	93.2	110.2	92.1
PVC-3	93.2	111.3	91.6
PVC-5	94.1	110.6	91.7
PVC-8	93.6	111.0	90.6

[a] T_g of SAN copolymer was 118.9°C.

ABS, acrylonitrile-butadiene-styrene; PVC, poly (vinyl chloride).

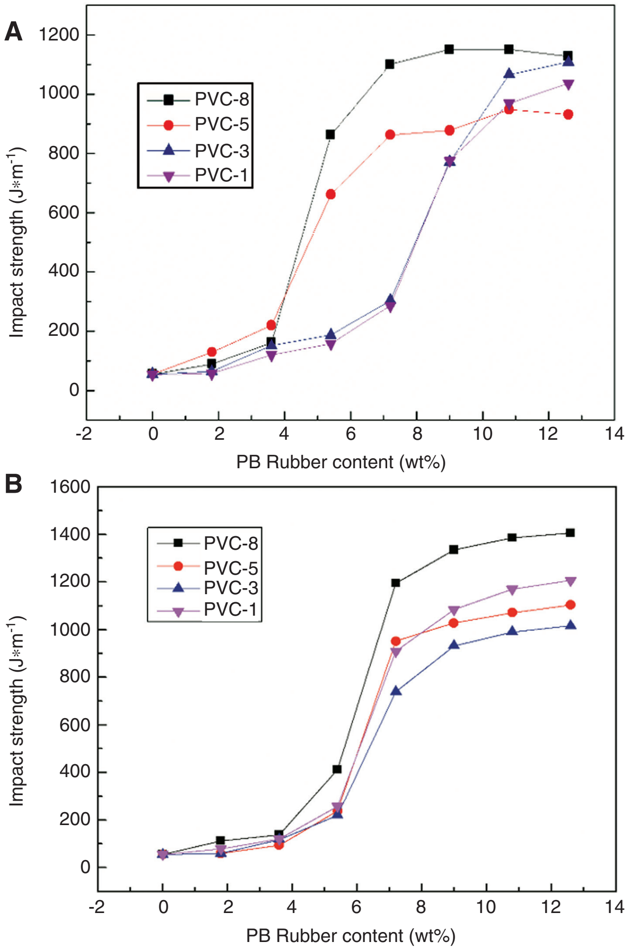

Figure 2: The influence of polybutadiene (PB) rubber content on the impact strength of poly (vinyl chloride) (PVC)/acrylonitrile-butadiene-styrene (ABS) blends prepared by different milling temperature: (A) 165°C, (B) 180°C.

180°C. The impact strength of blends increased together with the PB rubber content as expected from previous studies [14, 17, 18]. At low PB rubber contents, all of the notched impact strength of brittle blends occurred in the range of 50–200 J/m, independent of the type of PVC resin used. At high PB rubber contents, all of the notched impact strength of ductile blends occurred between 900 J/m and 1200 J/m. It is clearly observed in Figure 2A that when the molecular weight of PVC was increased, the brittle-ductile transition (BDT) of PVC/ABS blends occurred at higher PB rubber content. The BDT of PVC-5 and PVC-8 occurred with a PB of 3.6 wt%, while for PVC-1 and PVC-3, a higher PB content of 5.4 wt% was required.

Martin et al. [19] claimed that an increased molecular weight led to the increase of the impact strength. However, the BDT of PVC/ABS blends occurred at lower PB rubber contents for lower molecular weights PVC in this work. We assume that low molecular weight PVC grains had already broken into primary particles at low processing temperatures. At the milling temperature of 165°C, the secondary particles might break into primary particles as flow units for PVC-5 and PVC-8, but the temperature was too low for the PVC-1 and PVC-3 matrices to break into primary particles. The PVC primary particles as flow units of PVC-8 and PVC-5 might have partially melted, and freed some PVC molecules, which can entangle at the flow unit boundary. This entanglement network might have performed high impact resistance. The secondary particles might have incompletely broken into primary particles in the PVC-3/ABS and PVC-1/ABS blends, in which case the entanglement point was less. The decrease in the entanglement density might have led to a poor impact resistance. This phenomenon could have possibly led to the BDT to occur at different PB rubber contents for different molecular weights of the PVC/ABS blends, as shown in Figure 2A. At a milling temperature of 165°C, the high molecular weight PVC resins cannot reach a well plasticized degree, thus the BDT occurred at higher PB rubber contents. It is well known that the impact strength and plasticizing degree are strongly dependent on the processing temperature [20]. In order to prove the deduction above, the BDT of the PVC/ABS blends at the milling temperature of 180°C was determined as shown in Figure 2B.

At the milling temperature of 180°C, the BDT of PVC-1 and PVC-3 blends occurred at a PB rubber content of 4.8 wt%. In the case of 165°C, the BDT of the PVC-1 and PVC-3 blends occurred at 7.2 wt% PB rubber content. For PVC-5 and PVC-8 blends, the BDT also occurred at 4.8 wt% PB rubber content. This phenomenon may be caused by the degradation of PVC molecular chains. Although the molecular chains entanglement existed around the primary particles of PVC-5 and PVC-8, the degraded molecules destroyed the formation of the entangled network. This ultimately led to the trend presented in Figure 2B. The viscosity average molecular weights of PVC resins at different temperatures were calculated using the Mark-Houwink equation, and the results are listed in Table 3.

Table 3: The viscosity average molecular weight of poly (vinyl chloride) (PVC) resins.

Type	M_η (g/mol) (resins)	M_η (g/mol) (165°C)	M_η (g/mol) (180°C)
PVC-1(SG-1)	78,623	78,623	68,649
PVC-3(SG-3)	69,643	69,564	68,271
PVC-5(SG-5)	69,046	69,046	61,979
PVC-8(SG-8)	65,758	65,010	59,226

PVC, poly (vinyl chloride); SG, suspended general.

Table 3 summarizes the viscosity average molecular weights of PVC resin and PVC matrices milled at 165°C and 180°C. The viscosity average molecular weights of PVC matrix milled at 165°C were 78,623, 69,564, 69,046 and 65,010 for different samples. The viscosity average molecular weight did not change compared to the PVC resins. When the milling temperature increased to 180°C, the viscosity average molecular weight of PVC-5 and PVC-8 matrices decreased severely (namely 61,979, 59,226), indicating a degradation of the PVC molecular chains. The improvement of the processing temperature promoted the plasticization of high molecular weight PVC, and enabled the further decrease of the rubber content of the BDT of PVC-1 and PVC-3.

3.2 Effect of the plasticizer DOP

It is well known that the matrix plasticizing behavior could also be improved by adding some plasticizer. With the addition of the plasticizer DOP in PVC/ABS blends, the effect of PVC plasticization behavior on the toughness of PVC/ABS blends at an operation temperature of 165°C is shown in Figure 3. The BDT of higher molecular weight PVC (PVC-1, PVC-3) occurred at the lower PB rubber content (3.6% PB rubber percent), while the BDT of PVC-8 and PVC-5 did not change. The function of DOP was to insert its molecular chains into the polymer during the milling procedure, which weakens the interaction between the chains [13]. The molecules of PVC resins moved freely and entangled at the flow unit boundary, and then formed an entanglement network. With the addition of DOP, the residue of unplasticized secondary particles in higher molecular weight PVC blends (PVC-1, PVC-3) were all broken into primary particles and the entanglement occurred at 165°C.

The schematic illustration of plasticized conditions for different molecular weight PVC is presented in Figure 4. Adding a plasticizer in the melting system appeared to be the optimum method to modify the impact resistance property in contrast to the operation temperature. The phase morphology was observed by TEM. Figure 5 presents the morphology of the PVC-8/ABS and PVC-1/ABS blends milled at 165°C with an ABS content of 21 wt%. It is obvious that the black part can be attributed to the PB rubber particles and that the residue came from the PVC matrix.

PB rubber particles dispersed uniformly in PVC-8/ABS blends. During the processing, the PVC-8 grains were generally broken into 1 μm primary particles which appeared to be the major flow unit [21]. As mentioned, the secondary particles size was about 20–250 μm, while the size of the primary particles was about 0.1–2 μm [22]. At the milling temperature of 165°C, the unstained area surrounded by the PB rubber particles of PVC-8 matched with the size of primary particles, meaning that the PVC-8 resin can be mostly plasticized. In contrast, in the PVC-1/ABS blends milled at 165°C, the PB rubber particles were slightly aggregated. Unstained areas surrounded by the PB rubber particles and circled in black in Figure 5B had larger dimensions than the size of primary particles (about 0.1–2 μm), which meant that a large number of secondary particles of PVC-1 did not plasticize totally. During the part

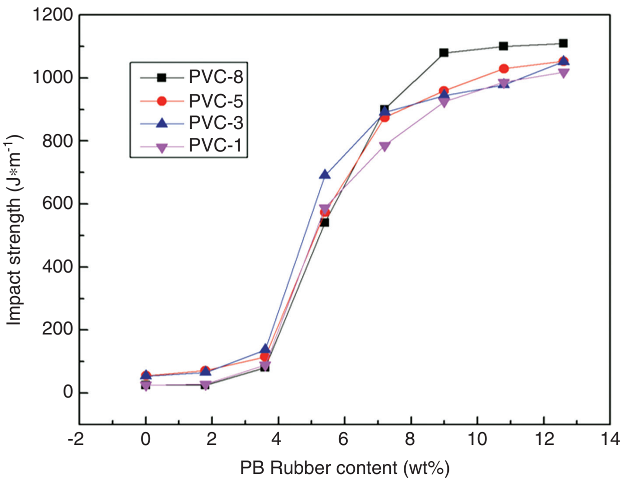

Figure 3: The influence of polybutadiene (PB) rubber content on the impact strength of poly (vinyl chloride) (PVC)/acrylonitrile-butadiene-styrene (ABS)/dioctyl phthalate (DOP) blends under the milling temperature of 165°C; DOP was added without changing PB rubber content.

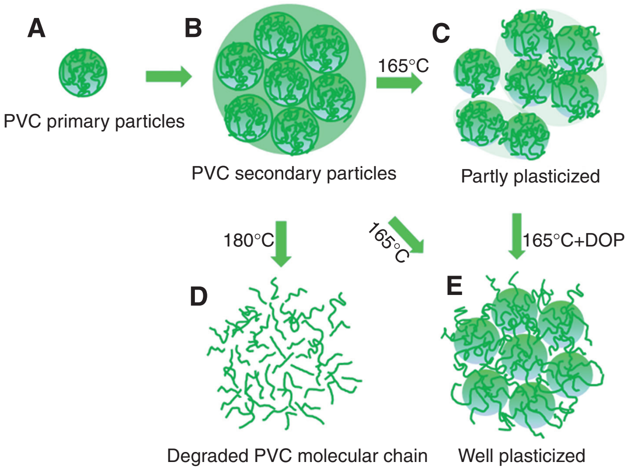

Figure 4: The schematic illustration of plasticized conditions of different molecular weight poly (vinyl chloride) (PVC).

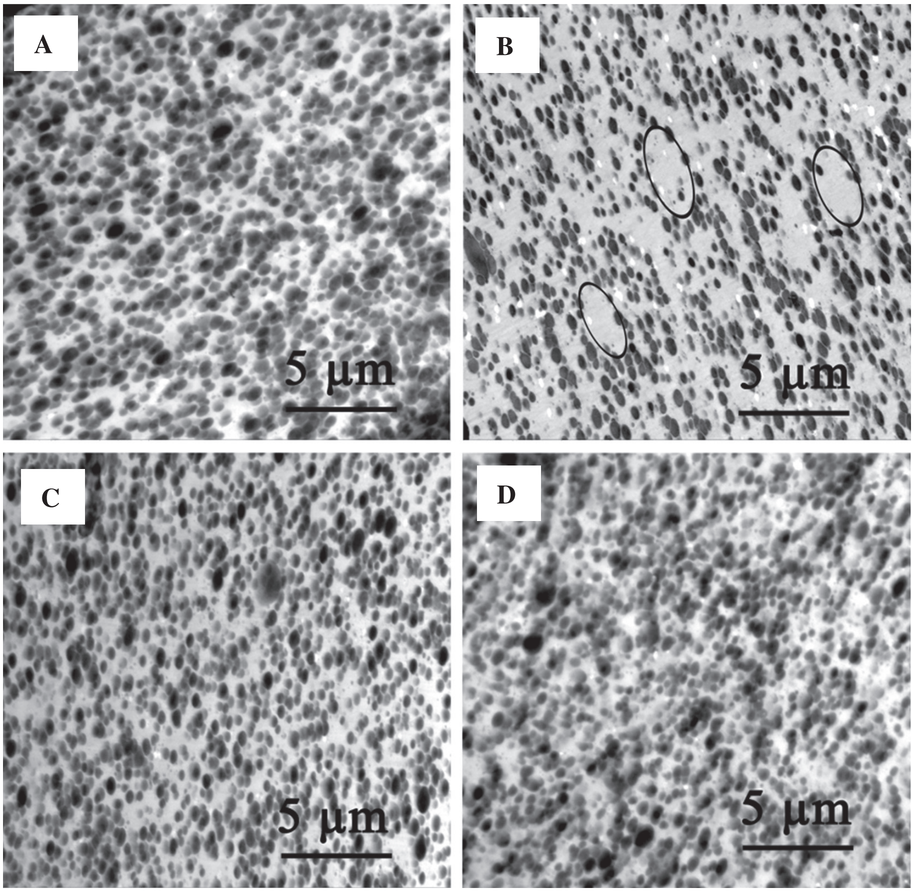

Figure 5: The morphology of polybutadiene (PB) rubber particles dispersed in poly (vinyl chloride) (PVC) resin. (A) PVC-8/acrylonitrile-butadiene-styrene (ABS) milled at 165°C; (B) PVC-1/ABS milled at 165°C; (C) PVC-1/ABS milled at 180°C; (D) PVC-1/ABS with 10% DOP milled at 165°C.

conversion of secondary particles of PVC-1 into primary particles, the residue secondary particles of PVC-1 hindered the PB rubber to disperse uniformly. The unplasticized PVC-1 matrix cannot resist the impact exerted on the samples because no PB rubber particles could stand the impact of the strength in the unplasticized zone. Subsequently, the impact efficiency of PVC-1 blends was worse in contrast to the PVC-8 blends when the milling temperature was 165°C.

To illustrate the influence of plasticization of PVC on the morphology of blends, the strategies of increasing the milling temperature and adding DOP were both adopted. The TEM morphology of PVC-1/ABS blends milled at 180°C and the PVC-1/ABS/DOP blends milled at 165°C are shown in Figure 5. We can observe that PB rubber particles are both uniformly dispersed in these two blends. The primary particles of the PVC-1 matrix can be totally plasticized. As the increase milling temperature and the content of DOP, the unplasticized PVC areas circled by ellipses as shown in Figure 5B gradually disappeared as shown in Figure 5C and D. These results show that the unstained area matched with the size of the primary particles at a milling temperature of 180°C and by adding DOP into the blends. Both measurements promote the PB rubber particles to disperse uniformly. From the morphology analysis, the plasticization of PVC has a great influence on the morphology of the PVC/ABS blends.

4 Conclusions

DMA, impact mechanical property and morphology of PVC/ABS blends were investigated systematically at different conditions. DMA showed that PVC and SAN were partially miscible ensuring the PB uniform dispersion in the matrix. The molecular weight of PVC has almost no influence on the miscibility of the PVC/SAN blends. Low molecular weight PVC has better impact mechanical property because it requires less PB rubber to achieve the BDT than in the case of higher molecular weight PVC.

Because of the non-complete plasticization of the high molecular weight PVC, the BDT of blends occurred at higher PB rubber contents. However, the BDT occurred at lower PB rubber contents for high molecular weight PVC by plasticizing. Observation of the morphology helps us to understand that plasticizing would promote secondary particles to break into primary particles. In addition, improving the milling temperature and adding a plasticizer into the blends were both valid for plasticizing the PVC matrix.

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