The tensile behaviour and toughness of poly(vinylidene chloride)/poly(butyl methacrylate) composites prepared by the concentrated emulsion approach

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Procedures for the preparation of poly(vinylidene chloride)/poly(butyl methacrylate) (PVDC/PBMA) composites based on concentrated emulsions are described. In one of them, two partially polymerized paste-like concentrated emulsions in water of two different systems were blended and subjected to complete polymerization. One of the systems was butyl methacrylate monomer (BMA), while the other was either vinylidene chloride monomer (VDC) or a dilute solution of PBMA in VDC. In the other procedure, a partially polymerized concentrated emulsion of VDC in water was blended with BMA monomer, and the paste-like system obtained was further polymerized. The composites thus obtained contained PVDC, PBMA and also some copolymer. The glass transition temperatures and the melting points measured by differential scanning calorimetry allowed qualitative identification of the presence of the above compounds. VDC-*co*-BMA copolymers of various compositions were also prepared via the concentrated emulsion method for comparison purposes. The effects of the preparation procedure, of the molar ratio of the two monomers and of the concentration of surfactant in the continuous water phase on the tensile properties were investigated. The toughness of the composites is much better than that of the copolymers.

(Keywords: PVDC/PBMA composites; concentrated emulsions; mechanical properties)

INTRODUCTION

To improve the mechanical properties of polymeric materials, various modifications have been employed, such as copolymerization[1,2], blending[3,4], reinforcement[5], interpenetrating networks[6], etc. Composites of dissimilar polymers often exhibit a synergistic behaviour. A novel pathway to polymer blends was developed[7] in this group recently. It involved the partial polymerization of two concentrated emulsions of different monomers in water and their subsequent mixing, followed by complete polymerization. In concentrated emulsions[8,9], the volume fraction of the dispersed phase is larger than 0.74, which represents the most compact arrangement of spheres of the same radius, and can be as high as 0.99. At high volume fractions, the continuous phase is in the form of a network of thin liquid films that separate polyhedral cells of the dispersed phase. The concentrated emulsions have the appearance and behaviour of a paste. Two such emulsions were mixed after their partial polymerization, and the mixture was additionally polymerized to generate a composite containing two different homopolymers and some copolymer[7].

In this paper, additional work based on the concentrated emulsion approach is described with the emphasis on the tensile behaviour of poly(vinylidene chloride)/poly(butyl methacrylate) (PVDC/PBMA) composites. Copolymers of vinylidene chloride (VDC) and butyl methacrylate (BMA) are useful materials because they have high flexibility[10]. The tensile strength and toughness of these copolymers can be further improved by including proper amounts of VDC and BMA homopolymers. Since the melting point of PVDC is high (near 200°C), the melt mixing method is not appropriate to achieve this improvement[11]. The inclusion of homopolymers via the concentrated emulsion method appears to be a proper pathway to follow. Three preparation procedures were employed to obtain PVDC/PBMA composites with various molar ratios. Homopolymers of VDC and BMA as well as VDC-*co*-BMA copolymers of various molar ratios were also prepared via the concentrated emulsion method for comparison purposes.

EXPERIMENTAL

Materials

Vinylidene chloride (VDC, Aldrich, 99%) and butyl methacrylate (BMA, Aldrich, 99%) were distilled before use. Sodium dodecyl sulfate (SDS, Aldrich), ammonium persulfate (Aldrich), sodium metabisulfite (Aldrich), ferrous sulfate (Aldrich), dibutyltin maleate (Polysciences) and poly(butyl methacrylate) (PBMA, Aldrich) were used as received.

In the previous concentrated emulsion pathway[7], the initiator azobisisobutyronitrile (AIBN) was dissolved in

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a hydrophobic monomer (such as BMA) to initiate the polymerization. Such a method is not, however, suitable for VDC, which is a highly volatile liquid with a boiling point of 32°C. Consequently, temperatures higher than 60°C, which are necessary for AIBN to become sufficiently active, cannot be employed at atmospheric pressure. For this reason, in the present work, a redox system[12] dissolved in the water phase was used to catalyse the polymerization through the oil–water interface. The redox system consists of an oxidant (ammonium persulfate, 0.5 g for 100 g monomer), a reductant (sodium metabisulfite, 0.5 g for 100 g monomer) and an activator (ferrous sulfate, 0.01 g for 100 g monomer).

Preparation methods

Procedure 1. A small amount (4 ml) of a 10 wt% SDS aqueous solution was introduced into a 100 ml round-bottomed flask that contained a magnetic stirring bar. The redox system was dissolved in this aqueous solution. After the flask was tightly sealed with a rubber septum, 16 ml VDC monomer was added with a syringe through the rubber with vigorous magnetic stirring, over about 15 min, at room temperature. After stirring for another 15 min a concentrated VDC emulsion with the appearance of a paste was obtained. The concentrated emulsion of BMA was prepared separately, in the same way, using the same redox system, concentration of SDS and water/monomer volume ratio. Each of the two concentrated emulsions was partially polymerized at 45°C in its tightly sealed flask until a 5% conversion was achieved (2.5 h). Since the boiling point of VDC at atmospheric pressure is 32°C, a small part of VDC vaporizes, thus increasing the pressure inside the sealed flask. (When the concentrated emulsion of VDC was heated in the sealed flask at temperatures higher than 60°C, the concentrated emulsion separated into two phases.) Subsequently, the two concentrated emulsions were mixed with magnetic stirring in the presence of air. The mixture of pastes thus obtained was further heated at 45°C for 16 h to complete the polymerization. The composites obtained were washed with methanol for 24 h and dried under vacuum at room temperature for another 24 h.

Procedure 2. PBMA (Aldrich) was dissolved in VDC monomer to form a solution of 2 wt%. This solution was employed as the dispersed phase to obtain a concentrated emulsion in water, the other steps being the same as in procedure 1.

Procedure 3. The preparation and partial polymerization of a concentrated emulsion of VDC in water was the same as in procedure 1. A very small amount of water (a single drop) containing the redox system was injected at room temperature into the BMA monomer and the system thus obtained was introduced after shaking, dropwise, also at room temperature, into the partially polymerized VDC emulsion, with vigorous magnetic stirring. Because of the presence of water and surfactant in the emulsion, the system remained a concentrated emulsion, after the addition of the BMA monomer, which was subjected to additional polymerization for 16 h at 45°C. In this procedure, the partial polymerization time of the concentrated emulsion was 2.5 h. A shorter time makes the final concentrated emulsion unstable, while a longer time increases the viscosity of the system to such an extent that the mixing with BMA monomer becomes difficult.

Preparation of the copolymer. The copolymers have been prepared as in procedure 1, using a mixture of VDC and BMA as the dispersed phase.

Glass transition temperature and melting-point determination

These quantities have been measured by differential scanning calorimetry, with a Perkin–Elmer DSC instrument. Each sample was heated twice from −50 to 210°C, with a heating rate of 10°C min^{-1}. After the first heating, the sample was cooled quickly to a temperature below −50°C and then heated for the second time.

Tensile testing

The powder of a sample was mixed with a stabilizer (dibutyltin maleate, 5 g per 100 g powder), then thermopressed at a temperature of 150–180°C with a Laboratory Press (Fred S. Carver Inc.) to form a sheet, which was cut to the size required by the ASTM D-1708. The tensile testing was conducted with an Instron Universal Testing Instrument (model 1000) at room temperature. The elongation speed was 50 mm min^{-1}. For each case, five sample bars were prepared and tested. The arithmetic average of the five readings was taken as the experimental result.

Scanning electron microscopy (SEM)

A small amount of powder sample was pasted on an SEM holder, then coated with a thin film of carbon. The surface morphology was examined by scanning electron microscopy (SEM, Hitachi S-800).

RESULTS AND DISCUSSION

Thermal properties of the samples

Table 1 lists the transition temperatures and the melting points (T_m) of the samples, determined with the d.s.c. instrument. It shows that each composite has a T_g, another thermal transition denoted T_t, as well as a sharp T_m. In contrast, the copolymers have a T_g and a diffuse T_m. The T_g values of the composites and copolymers are located in the narrow range of 20–36°C. The T_g of the BMA homopolymer was reported to be 13–35°C[13–16] and that of VDC/BMA copolymer type 1 (with short VDC sequences) to be 16–20°C[12]. Consequently, the T_g of the composite may represent the glass transitions of both the BMA homopolymer and the VDC/BMA

Table 1 The transition temperatures of the composites and copolymers (°C)

		Heating 1			Heating 2
Preparation	Mole ratio VDC/BMA	T_g	T_t	T_m	T_g
Procedure 1	1/0.1875	35.7	83.0	203	27.1
	1/0.25	27.0	81.0	192	18.7
Procedure 2	1/0.1875	27.9	82.1	198	20.9
	1/0.25	23.0	76.9	192	23.2
Procedure 3	1/0.1875	21.9	80.2	190	18.7
	1/0.25	31.6	89.0	203	20.0
Copolymn.	1/0.1875	22.4	–	191 (diffuse)	18.8
	1/0.25	27.2	–	198 (diffuse)	26.7

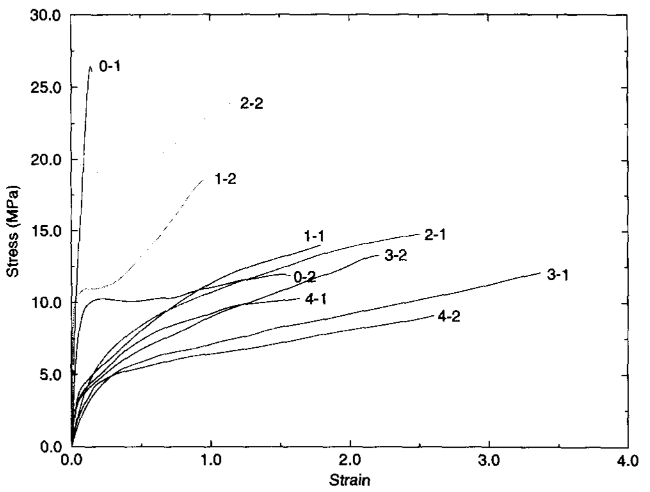


Figure 1 Stress–strain curves of the samples: 0-1, VDC homopolymer; 0-2, BMA homopolymer; 1-1, procedure 1 (1/0.25); 1-2, procedure 1 (1/0.5); 2-1, procedure 2 (1/0.25); 2-2, procedure 2 (1/0.5); 3-1, procedure 3 (1/0.25); 3-2, procedure 3 (1/0.5); 4-1, copolymer (1/0.25); 4-2, copolymer (1/0.5). The ratios in parentheses represent the VDC/BMA molar ratios

copolymer type 1. One may note that during the first heating the composites exhibit another thermal transition T_t in the vicinity of 80°C, which is no longer present during the second heating. Since this transition temperature is higher than the T_g values of both PBMA (13–35°C) and PVDC (−17 to −20°C[17,18]) and there are no hydrogen bonds between the BMA and VDC monomers, it probably has its origin in the crystallization of the long sequences of VDC units of the copolymer molecules (this VDC/BMA copolymer with long VDC sequences will be denoted as copolymer type 2). Our composites were prepared by mixing a partially polymerized concentrated emulsion of VDC either with a partially polymerized concentrated emulsion of BMA or with the BMA monomer. During this first stage, VDC oligomeric domains are probably generated, which contribute to long VDC sequences in the VDC/BMA copolymers formed in the second stage. Since the long sequences crystallize, the motion of the BMA segments between two successive VDC crystals is rather restrained. As a result, a high transition temperature is generated. However, the time between the first and second heating is too short for the VDC sequences to crystallize again. Consequently, the chains of type 2 copolymer remain in an amorphous state during the second heating and the temperature T_t is no longer present. The T_g of the composite becomes lower during the second heating because the mobility of the system is facilitated by the presence of the more flexible chains of type 2 copolymer. One may also note that the copolymer samples do not exhibit a T_t. This is because no VDC oligomeric domains are present and the copolymerization parameters of VDC/BMA are 0.22 and 2.41[12]. Consequently no long sequences of VDC are generated and hence no T_t should exist. The thermal transitions indicate that at least three types of species are present in the composites, namely the VDC homopolymer and the VDC/BMA copolymers of type 1 and 2. VDC homopolymer has a T_g of −17 to −20°C, which was not detected in the present experiments by d.s.c. because of its crystalline structure. However, its presence was identified by the sharp melting point $T_m = 190$–200°C. Furthermore, since the T_g of the BMA homopolymer is near that of the type 1 copolymer, its presence in the composites can only be inferred from the preparation procedure.

Stress–strain curves

Since the emphasis in this paper is on the mechanical properties of the composites, the best characterization of the materials can be made by comparing their tensile behaviour to those of the homopolymers and copolymers that they contain. For this reason, stress–strain curves have been determined not only for the composites, but also for the latter polymers. In *Figure 1*, the stress–strain curves of typical samples of homopolymers, copolymers and composites are presented. PVDC is a highly crystalline polymer, with a high tensile strength, which is rather brittle. PBMA is somewhat more flexible. Its stress–strain curve is typical of plastic behaviour, since it exhibits a yield point. From the stress–strain curves of the composites and copolymers, one can see that the samples prepared by procedures 1 and 2 have a plastic behaviour, while the samples prepared by procedure 3 and by copolymerization have a rubber-like behaviour. This suggests that copolymerization plays a role in procedure 3 and is less important in procedures 1 and 2.

Tensile strength and elongation of the copolymers

From *Table 2*, in which the tensile data of copolymers at the break point are listed, one can see that the tensile strength and elongation change in opposite directions as the molar ratio of BMA changes. Because of their symmetric structure, the PVDC chains can easily crystallize[11]. The introduction of BMA units, however, generates some disorder and the free volume becomes larger. As a result, the larger the amount of BMA monomer introduced, the poorer is the ability of the polymer chains to crystallize, and the more flexible they become. Consequently, the greater the amount of BMA monomer, the higher is the elongation and, because the interactions are weakened, the smaller is the tensile strength. This is also shown in *Figure 2*.

Tensile strength and elongation of the composites

In *Tables 3–5* the data for the samples prepared by procedures 1, 2 and 3 are listed, and they are plotted in *Figure 2*. One may notice that the changes in tensile strength and the break point elongation occur in different directions, the tensile strength passing through a minimum and the elongation through a maximum as the molar ratio of VDC/BMA monomer increases. This can be explained as follows: The VDC homopolymer has a crystalline structure and hence a high tensile strength and a low elongation. At low contents of BMA, copolymers form and the degree of crystallinity decreases. As a result, the tensile strength of the composite decreases

Table 2 The tensile properties of the copolymers at the break point

Mole ratio VDC/BMA	Tensile strength (MPa)		Elongation (%)	
	Ave. value	Std. error	Ave. value	Std. error
1/0.125	11.9	1.40	93	19.3
1/0.1875	11.3	0.70	103	12.8
1/0.25	10.3	0.98	164	26.3
1/0.3125	9.8	0.54	173	16.5
1/0.5	9.1	1.30	260	18.8

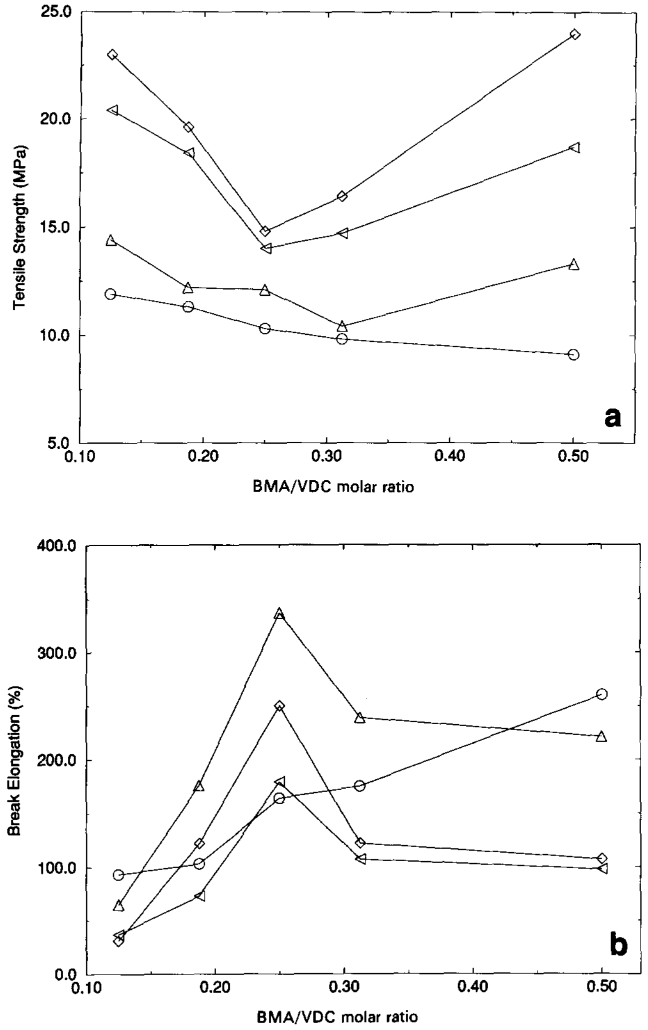


Figure 2 (a) Tensile strength and (b) elongation of the samples: (◁) procedure 1, (◇) procedure 2, (△) procedure 3, (○) copolymer

and the elongation increases. At moderate contents of BMA, the VDC/BMA copolymer molecules acquire a large number of VDC segments, which are long enough to generate crystallized domains that are interlinked via BMA, or VDC/BMA type 1 segments. The formation of the interlinked domains is reponsible for the increase of the tensile strength and the decrease of the elongation with increasing amount of BMA. At large amounts of BMA (outside the range employed in the present paper), the number of crystalline domains decreases. As a result, the tensile strength again decreases and the elongation increases with increasing amount of BMA.

Effect of predissolved PBMA

Comparing the results of procedures 1 and 2 (*Tables 3* and *4*) one can observe that the predissolution of a small amount of PBMA into the VDC monomer may have favourable effects for both the tensile strength and elongation. The presence of the PBMA molecules in the PVDC latexes may increase the compatibility between the latter and the PBMA latexes, thus increasing the tensile strength. In addition, the viscosity of the dispersed phase is increased. The stability of a concentrated emulsion is of kinetic origin and is due to: (i) the adsorption of surfactant molecules on the interface between the media and the repulsion thus generated between the charged interfaces, and (ii) the viscosities of the two media. The increased viscosity of the dispersed phase increases the stability and also diminishes the bi-radical termination, resulting in a broader molecular-weight distribution. The broader molecular-weight distribution is responsible for the higher elongation.

Effect of SDS concentration in aqueous phase

The samples listed in *Table 6* were prepared using procedure 1 but with different concentrations of surfactant in the aqueous phase. Although a larger amount of surfactant may make the emulsion more stable and the composite more uniform as concerns the sizes of the polymer particles, it is more difficult to remove the surfactant by washing from the system. The presence of these small molecules in the polymer matrix lowers both the tensile strength and elongation. However, if the surfactant concentration is lower than 10 wt%, the concentrated emulsion becomes rather unstable. A concentration near 10 wt% seems to be necessary.

Evaluation of toughness

The toughness can be evaluated on the basis of the area under the stress–strain curve, which represents the energy needed to break the sample. The stress–strain curves were graphically integrated and the results are listed in *Table 7*. For the homopolymers PVDC and PBMA the work has the values 5.8 and 11.2 kJ m^{-3}, respectively. One can see that the concentrated emulsion pathway ensures not only suitable tensile strengths and elongations, but also suitable toughness. The comparison with the copolymers indicates that the composites are

Table 3 The tensile properties of the composites by procedure 1

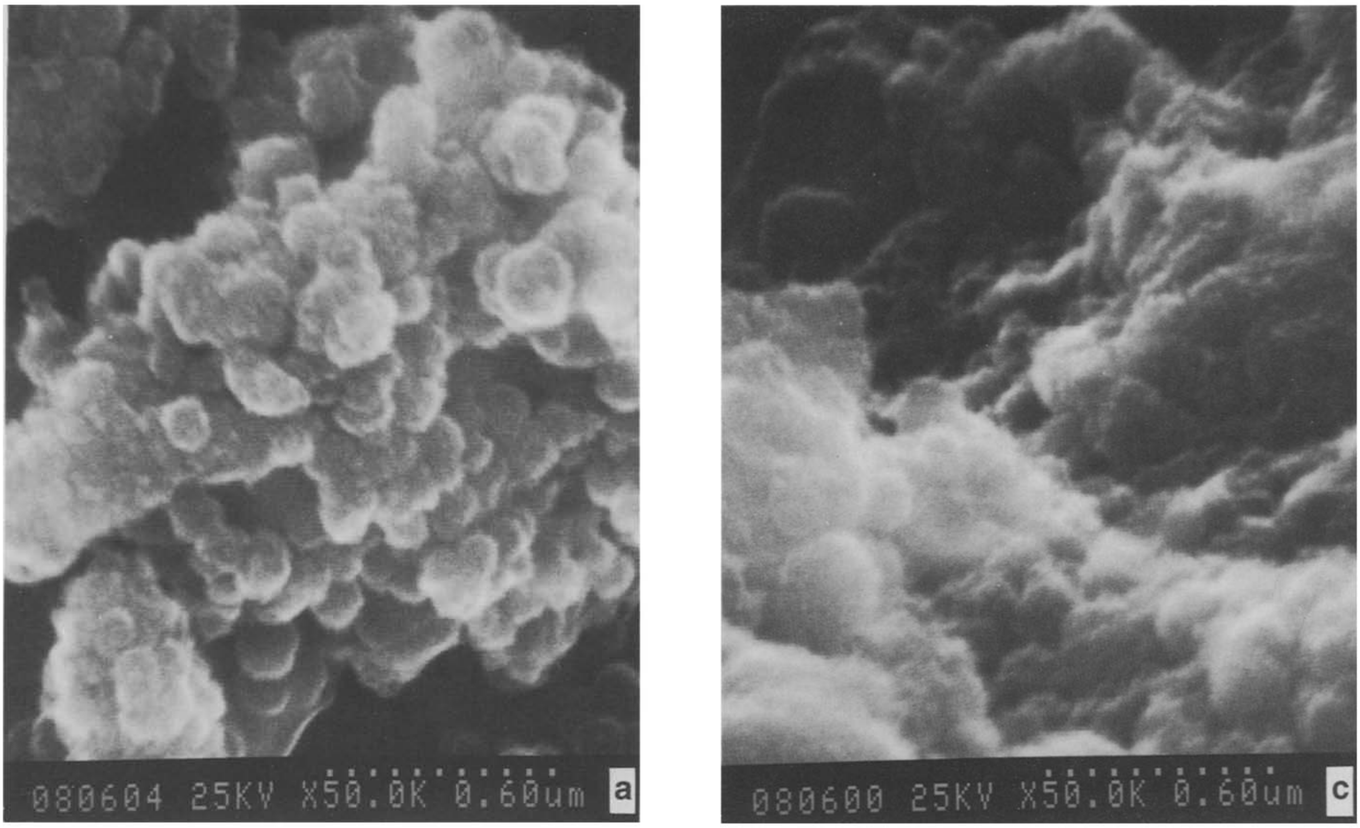
Mole ratio VDC/BMA	Tensile strength (MPa)		Elongation (%)	
	Ave. value	Std. error	Ave. value	Std. error
1/0.125	20.4	1.1	37	2.8
1/0.1875	18.4	2.8	73	5.0
1/0.25	14.0	2.3	179	12.7
1/0.3125	14.7	2.4	107	20.5
1/0.5	18.7	0.4	98	18.0

Table 4 The tensile properties of the composites by procedure 2

Mole ratio VDC/BMA	Tensile strength (MPa)		Elongation (%)	
	Ave. value	Std. error	Ave. value	Std. error
1/0.125	23.0	0.9	31	3.3
1/0.1875	19.6	1.5	122	10.2
1/0.25	14.8	1.4	250	18.5
1/0.3125	16.4	0.4	122	5.4
1/0.5	24.0	3.3	117	18.0

Table 5 The tensile properties of the composites by procedure 3

Mole ratio VDC/BMA	Tensile strength (MPa)		Elongation (%)	
	Ave. value	Std. error	Ave. value	Std. error
1/0.125	14.4	1.2	65	9.1
1/0.1875	12.2	0.7	176	24.0
1/0.25	12.1	1.4	337	19.0
1/0.3125	10.4	1.0	239	26.7
1/0.5	13.3	1.3	221	19.5



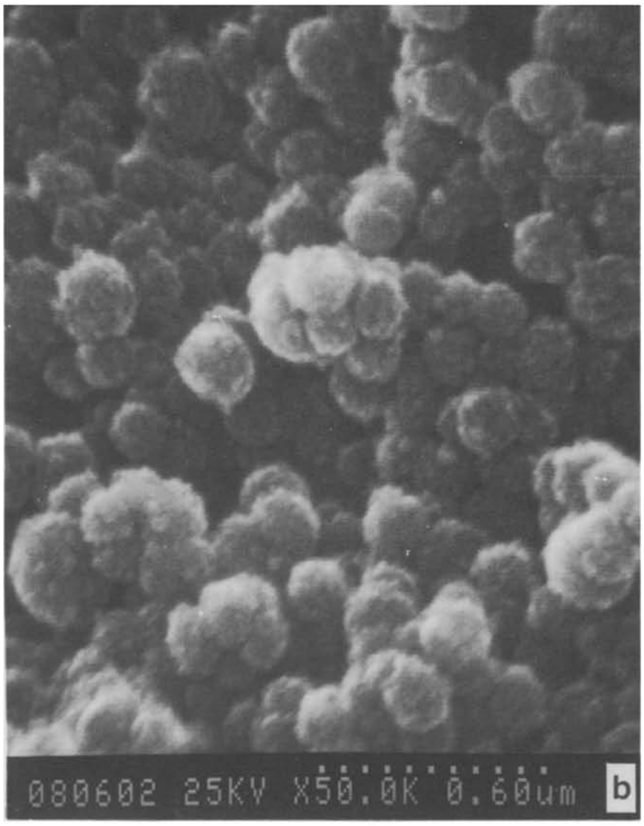


Figure 3 Surface morphology of the samples: (a) procedure 1, (b) procedure 2, (c) procedure 3

much tougher. It is well known that a stiff component and a flexible one must coexist at microscopic level to ensure a good toughness for a composite. The VDC/BMA copolymer has mostly flexible chains (since its T_m is diffuse, it contains some VDC homopolymer); consequently its toughness is poor. The composites prepared by the concentrated emulsion pathway contain both homopolymers and a copolymer, one of the homopolymers (PVDC) being stiff. As a result, a higher toughness is achieved.

Morphology of the particles

Figure 3 represents the SEM micrographs of typical samples prepared by the three different procedures. The sizes of the particles in the samples are comparable, about 0.12–0.25 μm. The particles obtained by procedure 2 are much more uniform in size than those obtained by the other two procedures. This brings some support for the explanation suggested above for the method involving predissolved PBMA. One may notice that in micrograph (c) the morphology is quite different. The edges of the particles are rather vague and the particles are surrounded by fibre-like structures. This is a reflection of some of the details involved in procedure 3. When the BMA monomer is added to the partially polymerized VDC emulsion, a fraction of the BMA monomer forms latexes and another fraction reacts with the VDC monomers or oligomers to form a copolymer, which surrounds the latex particles. The tensile strength, elongation and toughness data indicate that such a morphology has a favourable effect on the mechanical properties.

CONCLUSION

Composites containing VDC and BMA homopolymers as well as their copolymer can be prepared via the mixing of two partially polymerized concentrated emulsions, followed by complete polymerization. Since the different

Table 6 Comparison among various SDS concentrations in the continuous phase

	10 wt%		15 wt%		20 wt%	
Mole ratio VDC/BMA	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
1/1875	18.4	73	17.8	27	10.1	23
1/0.25	14.0	179	19.1	24	17.1	18

Table 7 Work needed to break the samples (kJ m^{-3})

Mole ratio VDC/BMA	Procedure 1	Procedure 2	Procedure 3	Copolymer
1/0.25	12.7	18.5	19.0	10.7
1/0.5	18.0	18.0	19.5	15.5

components are mixed in the form of very small partially polymerized latex particles, excellent dispersity and therefore improved mechanical properties can be achieved. Predissolving PBMA in VDC monomer increases the viscosity of the hydrophobic phase of the concentrated emulsion, resulting in better mechanical properties. In the procedure in which the BMA monomer is introduced into the partially polymerized VDC emulsion, composites with a special morphology, in which polymer particles are surrounded by fibre-like structures, are obtained. They have higher toughness than those prepared by the other procedures.

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