

AB crosslinked polymer latexes via concentrated emulsion polymerization

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A series of polycaprolactone (PCL)/poly(methyl methacrylate) (PMMA) AB crosslinked polymers (ABCP) in the form of latexes were prepared via the concentrated emulsion polymerization method. PCL diols were first reacted with acryloyl chloride in toluene to form a solution of vinyl-terminated PCL. Dissolving the methyl methacrylate monomer and a suitable initiator in this solution, the solution was employed to prepare a concentrated emulsion in water. After completing the polymerization of the concentrated emulsion, latexes of ABCP were obtained, which, depending on their composition, can be either elastomers or tough plastic materials. The toughness of PMMA is greatly improved in both cases. The effects of the PCL chain-length, composition and self-crosslinking of PCL on the mechanical properties were investigated.

(Keywords: crosslinking; latex; emulsion polymerization)

INTRODUCTION

In order to improve the properties of polymers, two or more different polymer chains are often combined. There are several ways to combine two kinds of polymer molecules: bonding the end of polymer B to the backbone of polymer A results in a graft copolymer; different chains bonded end to end generate block copolymers. If polymer A is crosslinked by polymer B and not by itself, an AB crosslinked polymer (ABCP)^{1–4} is obtained. In both the ABCP and in the interpenetrating polymer network (IPN), two kinds of polymer chains are combined in a network structure. The difference between the two is that in an ABCP the two kinds of chains form one single network and in an IPN they form two separate networks. Like the IPN, the ABCP has received attention in the past 20 years⁴. However, because of the crosslinking, the processability of the material prepared by bulk polymerization is poor and consequently its commercial importance has been limited. If ABCP could be prepared as latexes, it could become employed in melt-processing and find wider applications.

In the present work, a novel system, polycaprolactone (PCL)/poly(methyl methacrylate) (PMMA), was prepared in the form of latexes via a recently developed method, the concentrated emulsion polymerization method^{5,6}. A concentrated emulsion differs from the conventional one in that the volume fraction ϕ of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of spheres of the same size) and may be as high as 0.99. The continuous phase has a low volume fraction and for large values of ϕ is in

the form of a network of thin liquid films that separate polyhedral drops. Because of its structure, the concentrated emulsion polymerization method possesses a number of advantages:

- (1) high yield per unit volume: since it is 'concentrated', the volume fraction is higher than 0.74; in contrast, for a conventional emulsion, it is lower than 0.57 (ref. 7)
- (2) easy to handle: since the volume fraction of the dispersed phase is very high, the cells from which the emulsion is formed are tightly compacted; this gives the emulsion the appearance and behaviour of a paste
- (3) the system is more stable and more uniform than a conventional emulsion.

In previous publications^{8,9}, rubber toughened polystyrene and polyvinylidene composites were successfully prepared via the concentrated emulsion polymerization method. For the preparation of ABCP latexes, the same method seems to be the proper one to follow.

The modification of PMMA, which is brittle, was tried for years. The attempts were mainly focused on using polyurethanes based on polyglycol ethers as modifiers^{10–13}. However, because of their hydrophilicity, those ethers cannot be employed in the presence of water (as the continuous medium) to prepare concentrated emulsions. In the present work, PCL, which has proven to be a good modifier of poly(vinyl chloride)^{14,15} was employed, and a series of ABCP latexes from vinyl-terminated PCL and methyl methacrylate (MMA) monomer were prepared. Since the crosslinking is limited to each latex, the material possesses flowability and can therefore be melt-processed. The relationships between their properties and various structural parameters, e.g. crosslinking density, the length of the soft segments (PCL) and the PCL/PMMA weight ratio, were investigated.

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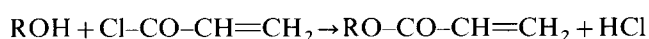
EXPERIMENTAL

Materials

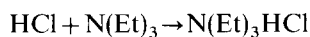
The chemicals employed are listed in Table 1. MMA was distilled before use. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. The other compounds were used as received. Water was deionized and distilled.

Preparation procedure

Preparation of vinyl-terminated PCL. A solution of PCL diol, (MW = 2000, 1250 or 530) in toluene (20 g per 100 ml) was placed in a single-necked flask equipped with a magnetic stirring bar. Triethylamine (TEA) (1 mol for each mole of OH groups of the dissolved PCL diol) was added to the solution. The flask was sealed with a rubber septum and the solution subjected to magnetic stirring. Acryloyl chloride (AC) (1 mol for each mole of OH groups) was introduced dropwise with a syringe through the rubber septum, at room temperature. The OH group reacts with AC to form a vinyl group:



The HCl molecules produced in the above reaction react with TEA:



and the formed quaternary ammonium salt remains suspended in the system as a white powder. Removing the white powder by filtering, a toluene solution of vinyl-terminated PCL (VTPCL) was obtained.

VTPCL_x (with $x = 530, 1250, 2000$) was prepared by this procedure, x denoting the average molecular weight of the PCL diol employed.

If the molar amounts of TEA and AC used are only half the molar amount of OH groups, semi-vinyl-terminated PCL (SVTPCL) can be obtained. In this case, AC must be diluted to 0.1 g ml^{-1} toluene before being introduced, and the addition of the AC solution must be as slow as one drop per 2 s in order to increase the uniformity of distribution of the remaining OH groups.

VTPCL3250 and 4000. Introducing the proper amount of tolylene 2,4-diisocyanate (TDI) into a solution of SVTPCL2000 in toluene, pairs of SVTPCL2000 become connected by one TDI molecule and VTPCL4000 is obtained. Of course, 4000 represents the average molecular weight of VTPCL. VTPCL 3250, was obtained

in the same way, starting from a toluene solution of SVTPCL2000 and 1250.

VTPCL6000 and 5250. These compounds were prepared in two steps. In the first step, a solution of SVTPCL2000 in toluene was allowed to react with TDI (NCO/OH = 2/1), for 4 h. Because of the excess of TDI, it is likely that the OH groups of SVTPCL will react with different TDI molecules. In the second step, PCL diol 2000, in a molar amount half that of SVTPCL2000, was introduced. Each molecule of PCL diol 2000 can react with two molecules of isocyanate-terminated SVTPCL2000 to generate VTPCL6000. The reaction lasted 24 h. When PCL diol 1250 replaced PCL diol 2000, VTPCL5250 was obtained.

It should be emphasized that the two steps are absolutely necessary, since if TDI and PCL diol had been introduced at the same time, polyurethane of ultra-high MW would have been formed and the solution would have had too high a viscosity to be usable in preparing concentrated emulsions. More importantly, the expected molecular weight could not have been obtained.

Uni-vinyl-terminated PCL2000. Reacting VTPCL2000 with propionyl chloride, the OH groups were replaced by ethyl groups and the uni-vinyl-terminated PCL2000 (UVTPCL2000) was obtained.

Concentrated emulsion polymerization. In the modified PCL polymer toluene solutions (0.2 g/ml toluene), MMA monomers in various proportions and a suitable initiator (AIBN, 0.008 g/g MMA) were introduced. The solution thus prepared was used as the dispersed phase of a concentrated emulsion. An aqueous solution of sodium dodecyl sulfate (SDS) (10 wt%) was first placed in a single-necked 100 ml flask provided with a mechanical stirrer. Then, the solution containing the modified PCL and MMA was added dropwise with vigorous stirring into the flask with a syringe, until the volume fraction of the SDS aqueous solution became 0.2. The whole addition process lasted about 15 min and took place at room temperature. The gel-like concentrated emulsion thus formed was additionally stirred for 15 min under a flow of nitrogen, and finally transferred to a tube of 30 ml capacity. The tube was sealed with a rubber septum and introduced into a water bath at 60°C to carry out the copolymerization of MMA and modified PCL, which lasted 48 h. The product thus obtained was washed with methyl alcohol in an extractor for 24 h and dried in a vacuum oven for another 24 h.

Preparation of semi-simultaneous interpenetrating network (semi-IPN). The semi-IPN was prepared by simultaneous bulk polymerization. The reactants (PCL diol 2000, trimethylolpropane with TDI (TMDI), MMA and initiator, free of solvent) were mixed in a tube which was introduced into a Cole Parmer ultrasonic mixer at 60°C for 3 h. After 3 h the viscosity of the system became so high that further mixing was no longer possible. Consequently, the tube was transferred into a water bath of 60°C, where it was kept for 48 h.

Tensile testing

The powders of the products of the concentrated emulsion polymerization, or the bulk material for the

Table 1 Chemicals used (purchased from Aldrich)

Chemical	Description	Code
Diols	Poly(caprolactone) diol MW = 530 1250 2000	PCL530
		PCL1250
		PCL2000
Isocyanate	Tolyene 2,4-diisocyanate, 80% remainder 2,6 isomers	TDI
	Trimethylolpropane, carbamate with tolylene diisocyanate, 70 wt%	TMDI
Triethylamine	99%	TEA
Acryloyl chloride	96%	AC
Propionyl chloride	97%	—
Monomer	Methyl methacrylate, 99%	MMA
Initiator	Azobisisobutyronitrile	AIBN
Surfactant	Sodium dodecyl sulfate salt, 70%	SDS
Solvents	Toluene, 99%	—

products of bulk polymerization, were hot-pressed in a Laboratory Press (Fred S. Carver Inc.) at 180°C for 3–5 min, and then cooled to room temperature. The sheets thus obtained were cut to the size required by ASTM D.638-58T. The tensile testing was conducted at room temperature with an Instron Universal Testing Instrument (model 1000). The elongation speed of the instrument was 20 mm min⁻¹.

Molecular weight (MW) and molecular weight distribution (MWD)

These properties were determined by gel permeation chromatography (g.p.c.; Waters 150C). The determination was carried out at 30°C with tetrahydrofuran as the mobile phase.

Thermal transition temperatures

The thermal transitions of the samples were measured by differential scanning calorimetry (d.s.c.) with a Perkin-Elmer DSC instrument. Each sample was heated from -70 to 210°C, with a heating rate of 10°C min⁻¹.

Scanning electron microscopy

The particle morphology was examined by scanning electron microscopy (SEM; Hitachi S-800).

RESULTS AND DISCUSSION

The MW and MWD of the VTPCL

The MW and MWD of VTPCL are listed in Table 2. Since the range of MWs of the VTPCLs is low (500–6000) and their Mark-Houwink constants are not available, the polystyrene standards could not be used for calibration. However, the PCL diols provided by the supplier have been prepared via anionic ring-opening polymerization and have, for this reason, a narrow MWD ($M_w/M_n = 1.4$ – 1.6); consequently they have been used as standards. One can see from Table 2 that the number average MW values of the prepared VTPCLs do not deviate appreciably from the designed values, being only somewhat smaller. VTPCL530 constitutes an exception, because the MW (530) is smaller than the lower limit of g.p.c. sensitivity (about 800). One may also note the wider distributions of VTPCL3250 and VTPCL5250. Since they were prepared by connecting species of different MWs, broader distributions are expected.

D.s.c. measurements

The PCL homopolymer has a crystalline structure, and using d.s.c. we determined its melting point to be near

40°C. The PMMA homopolymer is amorphous, with a glass transition temperature (T_g) of about 115°C (ref. 16). However, the d.s.c. diagrams of the ABCP samples exhibited neither of these thermal transitions; instead they showed a diffuse thermal transition region between about 50 and 75°C. In the PCL/PMMA ABCP, different segments are bonded to each other. One may consider that the chains in the network constitute a kind of copolymer with very long sequences. Consequently, the PCL segments can no longer crystallize and the T_g of PMMA is lowered by its combination with the PCL segments. The different long sequences move together and as a result a common thermal transition region is generated. The presence of a single thermal transition also constitutes the proof that an AB network was indeed formed. The absence of a T_g near 115°C indicates that very little (if any) PMMA homopolymer was formed.

Stress-strain curves

Two sets of stress-strain curves are presented in Figures 1 and 2. The samples of Figure 1 have the same PCL/PMMA weight ratio but different MWs of PCL, and those of Figure 2 were prepared with the same PCL (PCL1250) but with various PCL/PMMA weight ratios. In Figure 1 one can see that the curve for PCL1250 has a pronounced yield point and that for PCL2000 has a smeared yield point. The curves for the PCLs with higher MWs have no yield point. The yield point is characteristic of a plastic material with moderate physical crosslinking. In the present systems, PCL has only non-polar, soft, relatively short segments and the physical crosslinking can be generated only by the polar segments of PMMA. By introducing the PCL segments among the PMMA

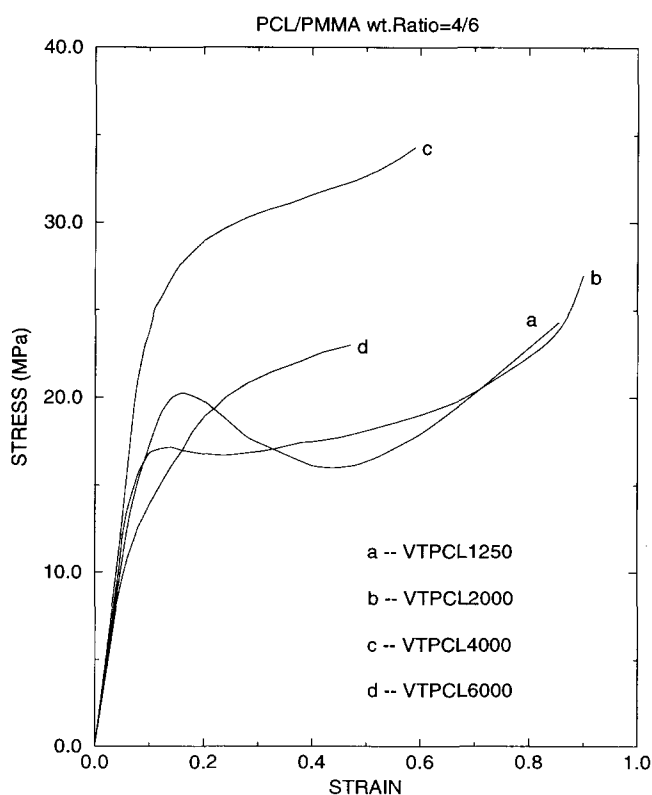


Figure 1 Stress-strain curves of ABCP (PCL/PMMA weight ratio = 4/6): (a) VTPCL1250; (b) VTPCL2000; (c) VTPCL4000; (d) VTPCL6000

Table 2 MW and MED of VTPCL_x

x	Designed MW	Determined MW		M_w/M_n
		Number average MW	Weight average MW	
530	580	610	1160	1.9
1250	1300	1220	2070	1.7
2000	2050	2000	3200	1.6
3250	3470	2900	7250	2.5
4000	4220	4090	6140	1.5
5250	5470	4850	14 060	2.9
6000	6390	5970	11 940	2.0

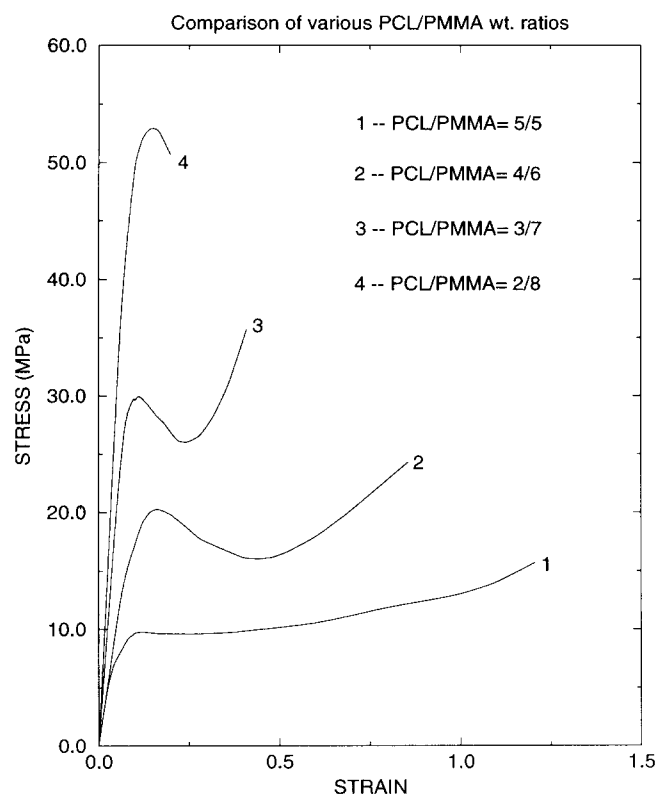


Figure 2 Stress-strain curves of ABCP made from VTPCL1250. PCL/PMMA weight ratio: 1, 5/5; 2, 4/6; 3, 3/7; 4, 2/8

chains, the inter-PMMA chain distance is increased and the density of physical crosslinks is reduced. One can conclude that, for a weight ratio PCL/PMMA = 4/6, if the MW of PCL is higher than about 2000, the physical crosslinking entirely disappears and the material behaves like a rubber. From Figure 2 one can see that the amount of PCL introduced affects the physical crosslinking. When the PCL/PMMA weight ratio is 5/5, too many PCL molecules keep the PMMA chains separated from each other, and the stress-strain curve exhibits only a smeared yield point. When the PCL/PMMA weight ratio is 2/8 or lower, there is strong physical crosslinking and the samples break before the yield point is reached. For the intermediary ratios of 4/6 or 3/7, clear yield points can be observed.

From these stress-strain curves one can conclude that, depending on composition, the PCL/PMMA ABCPs can be either tough plastic materials or elastomers.

Effect of PCL free ends

By free ends we understand the ends of PCL chains which are not bonded to the PMMA chains. The samples listed in Table 3 were prepared via the copolymerization of MMA with various proportions of bi-vinyl-terminated PCL (VTPCL) and uni-vinyl-terminated PCL (UVPCL). Sample no. 1 constitutes a full ABCP with no free ends, and sample no. 5 has each of the PCL chains with one end free. (It should be noted that the full ABCP is only an ideal limit that involves a conversion of 100%.) Table 3 shows that the presence of free ends plays a negative role regarding, in particular, the elongation at break. Sample no. 2 has the optimum tensile strength. Sample no. 5, the graft copolymer, has the lowest tensile strength

and is the most brittle. From the effect of the free ends one can conclude that without chemical crosslinking the PCL and PMMA will grossly phase separate and the mechanical properties of the composite will be poor.

Effect of PCL/PMMA weight ratio

One can see from Table 4 that as the PCL/PMMA weight ratio increases, the tensile strength decreases and the elongation at break increases. The inclusion of a larger number of PCL chains among the PMMA molecules changes the system in two ways: (i) the stiff segments of PMMA are separated by a larger number of flexible segments of PCL and thus more free volume is generated; (ii) the crosslinking density is increased. At moderate crosslinking densities, the chemical bonding increases the tensile strength; it also increases the elongation, because the physical crosslinking among the PMMA segments is diluted by the soft segments of PCL. The increases in the free volume and crosslinking density

Table 3 Effect of free ends on tensile properties of PCL/PMMA ABCP^a

Sample no.	VTPCL2000/ UVPCL2000 weight ratio	Tensile strength (MPa)		Elongation (%)	
		Average value	Std error	Average value	Std error
1	0/1	27.0	1.5	90.7	4.1
2	0.25/0.75	31.5	0.9	72.1	5.2
3	0.5/0.5	28.3	1.1	48.7	3.3
4	0.75/0.25	21.8	2.4	22.2	3.0
5	1/0	18.3	2.2	12.1	1.7

^a PCL/PMMA weight ratio = 4/6

Table 4 Tensile properties of PCL/PMMA ABCP

VTPCL	Sample no.	PCL/ PMMA weight ratio	Tensile strength (MPa)		Elongation (%)	
			Average value	Std error	Average value	Std error
1250	1-1	5/5	15.7	1.2	120.6	4.4
	1-2	4/6	24.3	1.7	85.4	5.0
	1-3	3/7	35.7	2.3	40.9	3.2
	1-4	2/8	50.7	2.7	23.2	2.2
2000	2-1	5/5	18.5	0.9	130.5	7.7
	2-2	4/6	27.0	1.5	90.7	4.1
	2-3	3/7	37.2	2.8	43.3	2.7
	2-4	2/8	54.6	2.0	30.8	2.5
3250	3-1	5/5	21.6	1.5	67.7	4.2
	3-2	4/6	32.8	1.9	33.1	3.0
	3-3	3/7	42.1	2.5	17.0	1.1
	3-4	2/8	49.7	3.6	11.3	1.2
4000	4-1	5/5	25.9	1.2	110.8	6.3
	4-2	4/6	34.3	0.4	59.9	2.1
	4-3	3/7	41.1	2.6	30.6	2.3
	4-4	2/8	49.7	2.3	19.3	1.7
5250	5-1	5/5	22.2	1.4	51.1	4.3
	5-2	4/6	32.1	1.2	27.8	2.0
	5-3	3/7	38.6	2.1	15.6	1.1
	5-4	2/8	46.7	3.2	10.2	0.8
6000	6-1	5/5	17.2	0.8	77.6	5.4
	6-2	4/6	23.0	1.1	47.9	3.2
	6-3	3/7	32.5	1.6	29.4	1.3
	6-4	2/8	38.8	1.8	15.5	1.4

(at moderate crosslinking) increase the elongation at break, but have opposite effects on the tensile strength. The net effect depends on which of the effects dominates. The data of *Table 4* suggest that the effect of the free volume is dominant. At high crosslinking (such circumstances appear to be outside the range considered in *Table 4*), the tensile strength is expected to increase and the elongation at break to decrease with increasing crosslinking.

Effect of the MW of the PCL chains

Table 4 shows that, for the range of MWs of VTPCL employed, both the tensile strength and the elongation at break pass through a maximum as the MW of PCL changes. The maximum elongation at break is exhibited by PCL2000. For any given PCL/PMMA weight ratio, the increase in the MW of PCL decreases the crosslinking density. At large crosslinking densities, the free volume in the system is expected to grow as the density decreases. At low crosslinking densities, the free volume is expected to decrease as the density decreases, since the PMMA and VTPCL molecules can arrange in a more compact manner. This explains the occurrence of the maximum in the elongation at break. The samples based on VTPCL530 have a high crosslinking density, since the PCL chains are short; as a result, the material lacks flowability and could not be tested.

The effect on the tensile strength is somewhat more complex. At a given MW of VTPCL, the tensile strength increases as the ratio of PCL/PMMA decreases from 5/5 to 2/8 because the dominance of PMMA increases the strength. At a given ratio PCL/PMMA and low MW PCL, the tensile strength is expected to decrease as the MW of the VTPCL increases, because the number of crosslinks decreases; it attains a minimum (the minimum was not observed in our experiments because it is probably located below MW = 1250) and increases again, because the fewer PCL molecules allow for stronger interactions between the PMMA chains. At moderately high MW of VTPCL, the tensile strength is expected to decrease again with increasing MW because of the fewer crosslinks and increasing free volume among the PMMA chains.

Not only the MW, but also the MWD of PCL plays an important role in the elongation at break. *Table 4* shows that the elongation at break of the samples based on PCL3250 or PCL5250 is unusually low. From *Table 2* one can note that the polydispersity coefficients (M_w/M_n) of PCL3250 and PCL5250 are 2.5 and 3.0, respectively, which are much larger than those of the other PCLs (1.5–2.0). The broader distribution of the molecular weights results in non-uniformities in the network which may be the reason for the low elongation at break.

Effect of the self-crosslinking of PCL

The effect of self-crosslinking of PCL is presented in *Table 5*. Samples nos 1–4 (*Table 5*) were prepared as follows. Different percentages of OH groups present in the PCL diol 2000 were vinylized first, the remaining OH groups being crosslinked with TMDI, which is a trifunctional crosslinker. The crosslinked VTPCL was copolymerized with MMA monomers in a concentrated emulsion. Sample no. 5 constitutes an extreme case, representing a semi-IPN (linear PMMA penetrating a network of PCL) prepared by simultaneous

bulk polymerization, in which the combination of PCL and PMMA is achieved through semi-interpenetration. Sample no. 1 is the same as the sample no. 2-2 of *Table 4*. It is supposed to be a full ABCP with all chain ends bound to PMMA chains. Samples nos 2, 3, 4 and 5 represent systems with decreasing percentage of OH groups vinylized, hence with increasing PCL self-crosslinking. The increase in the self-crosslinking increases the interpenetration of PMMA in the PCL network. One may note that sample no. 1 has the highest elongation. As the percentage of the vinyl groups decreases, the tensile strength remains essentially the same, but the elongation at break decreases rapidly. This indicates that the crosslinking via the vinyl groups plays a more important role in the elongation than the interpenetration. For compatible systems there are no major differences between crosslinking of PMMA with PCL and interpenetration. However, for incompatible systems, the chemical crosslinking between PMMA and PCL plays a greater role than interpenetration. It was reported that for the poly(propylene glycol)/PMMA composites, the compatibility of the IPN is poorer than that of the corresponding ABCP^{14,15}. One can also see from *Table 5* that the tensile properties of samples nos 3, 4 and 5 are comparable. This means that, when the density of chemical crosslinking between PMMA and PCL is lower than some critical level, its effect is no longer important.

Particle morphology

The particle morphologies of the PCL/PMMA ABCP latexes are presented in the scanning electron micrographs of *Figure 3* for two PCL/PMMA weight ratios. The samples of *Figures 3a* and *3c* are based on VTPLC2000 and those of *Figures 3b* and *3d* on VTPCL4000. *Figures 3c* and *3d* show that the size of the latexes is in the range 0.5–2 μm . Because of the soft, flexible PCL, the latexes are bound to each other. The greater the amount of PCL, the stronger the latex binding. The particles prepared with VTPLC4000 are somewhat coarser than those prepared with VTPCL2000.

A comment on flowability

As already noted in the Introduction, the use of the concentrated emulsion method instead of bulk polymerization provides latexes which have flowability and can therefore be used in melt-processing. A sufficiently high molecular weight of the PCL constitutes another important factor that affects the flowability of the final material. Since sufficiently long PCL chains are flexible, they can be easily deformed during processing. This flexibility also

Table 5 Effect of self-crosslinking on tensile properties of PCL/PMMA ABCP^a

Sample no.	Percentage of the OH groups vinylized (%)	Tensile strength (MPa)		Elongation (%)	
		Average value	Std error	Average value	Std error
1	100	27.0	1.5	90.7	4.1
2	50	32.5	2.0	55.7	3.3
3	33	29.8	2.4	44.0	2.8
4	25	28.4	1.7	42.9	3.6
5	0	29.3	1.9	45.2	3.2

^a PCL/PMMA weight ratio = 4/6

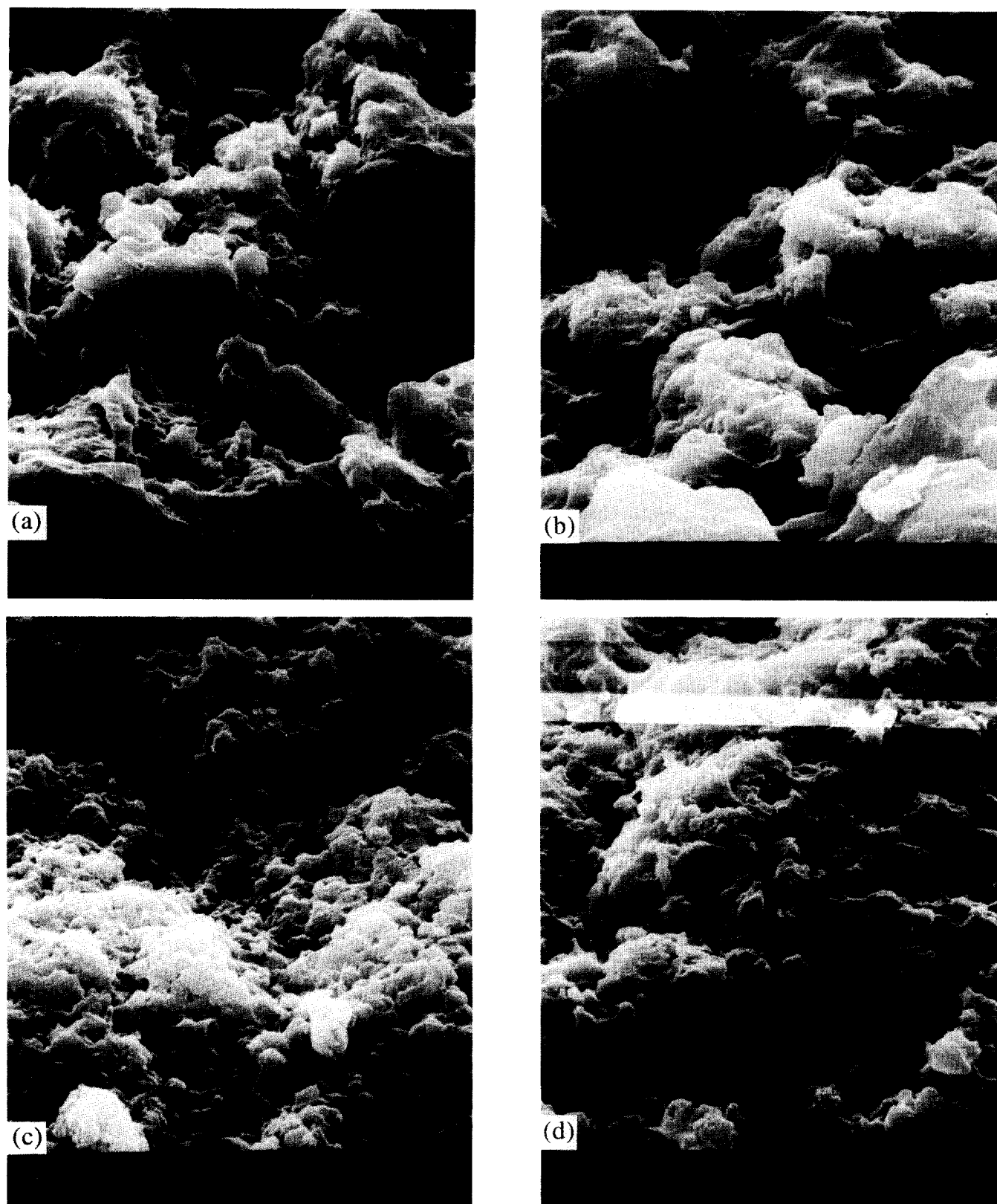


Figure 3 Particle morphology of PCL/PMMA ABCP. PCL/PMMA weight ratio: (a), (b), 5/5; (c), (d), 3/7

affects the toughness of the material. Short PCL chains will result in low flowability and toughness. The samples based on VTPCL530 constitute an example. Since the PCL chains are in this case short, the material had no flowability during the thermopressing and a sheet could not be generated.

CONCLUSION

ABCP latexes of PCL/PMMA were prepared via the concentrated emulsion polymerization method. Depending on the composition, they are either tough plastics or elastomers. The chemical bonding between PMMA and

PCL plays an important role in the mechanical properties of the composites. As the relative proportion of PCL in PMMA increases, the elongation at the break point increases, but the tensile strength decreases. The best tensile properties are associated with an optimum average MW of the PCL chains.

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