Rheology of Poly(n-butyl methacrylate) and Its Composites with Calcium Carbonate

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ABSTRACT: Poly(n-butyl methacrylate) (PBMA) composites with calcium carbonate ($CaCO_3$) were prepared by *in situ* radical copolymerization of butyl methacrylate (BMA) and methacrylic acid (MA) with precipitated calcium carbonate. To compare the different rheological behaviors of the monomer mixtures with $CaCO_3$ and the composites, the steady and dynamic viscosities of $BMA/MA/CaCO_3$ and poly($BMA/MA/CaCO_3$) were measured by means of steady and oscillatory shear flows. The viscosity of the mixture $BMA/MA/CaCO_3$ was found to increase evidently with the increasing of $CaCO_3$%. The influence of MA% on viscosity of $BMA/MA/CaCO_3$ was slight. During the *in situ* polymerization, the viscosity of the reacting system was measured to be enhanced by a factor of about 10^4 from the monomer/$CaCO_3$ mixture to composites. The dependency of zero-shear viscosity on molar mass of PBMA was also investigated. The relation between the zero-shear viscosity and molar mass is $\eta_0 = 10^{-15} M_w^{3.5}$. The evolution of the viscosity with the temperature for both PBMA and its composites was obtained and time–temperature superposition was used to build master curves for the dynamic moduli. The flow activation energies were found to be 115.0, 148.6, and 178.7 kJ/mol for PBMA, composite $PBMA/CaCO_3$ (90/10), and $PBMA/MA/CaCO_3$ (89/1/10), respectively. The viscosity of the composites containing less than 10% $CaCO_3$ was lower than that of pure PBMA with the same molar mass. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1376–1383, 2003

Key words: rheology; butyl methacrylate polymer; calcium carbonate; composites; mechanical properties

INTRODUCTION

Calcium carbonate is widely used as a commodity plastic filler because of its low cost and its ability to modify mechanical properties such as modulus, hardness, and toughness. Thermal resistance, flame retardancy, and dimensional stability can also be improved.[1–4] The addition of calcium carbonate may also enhance the polymer processing behaviors by inducing, for example, low and controllable die swell.[5]

Calcium carbonate is considered as a chemically inert filler when blended with polyolefin, in which the filler/matrix interfaces are weak. In a polypropylene (PP)/calcium carbonate ($CaCO_3$) blend, microvoids around the particles are obtained, leading to porous materials.[6,7] Also, $LLDPE/CaCO_3$ or $PP/CaCO_3$ breathable film can be prepared, in which $CaCO_3$ particles create pathways for water or vapor transport through the polyolefin layers.[8,9]

On the other hand, to obtain correct mechanical properties, it is necessary to have high interfacial ad-

hesion. To improve the adhesion, treatment of the filler with coupling agents or reactive surface modifiers is generally employed.[10–16]

The use of poly(n-butyl methacrylate) (PBMA) as a structural material is often limited by its relatively poor mechanical properties. To modify these properties, composite materials can be prepared by adding fillers to PBMA. In this study, methacrylic acid (MA) was used as a modifier to improve the $CaCO_3$/PBMA interface: the carboxylic acid introduced from MA reacts with $CaCO_3$, leading to multiplets or clusters[17] and thus improved filler/matrix interfacial adhesion. A $PBMA/MA/CaCO_3$ composite preparation was examined here. The aim of this project was to prepare the composite in one step by reactive extrusion. As we previously showed, the polymerization of butyl methacrylate (BMA) can be performed by twin-screw extrusion.[18] During this synthesis the materials inside the extruder undergoes both chemical and physical changes from feeding to die exit. The rheological behavior of the system also changes during the reaction from monomer to polymer. It is important to understand this evolution for an optimization of the extrusion processes.

In this study, systematic research on the rheological behaviors for the monomers/filler mixture and PBMA as well as its composites was considered. In the first

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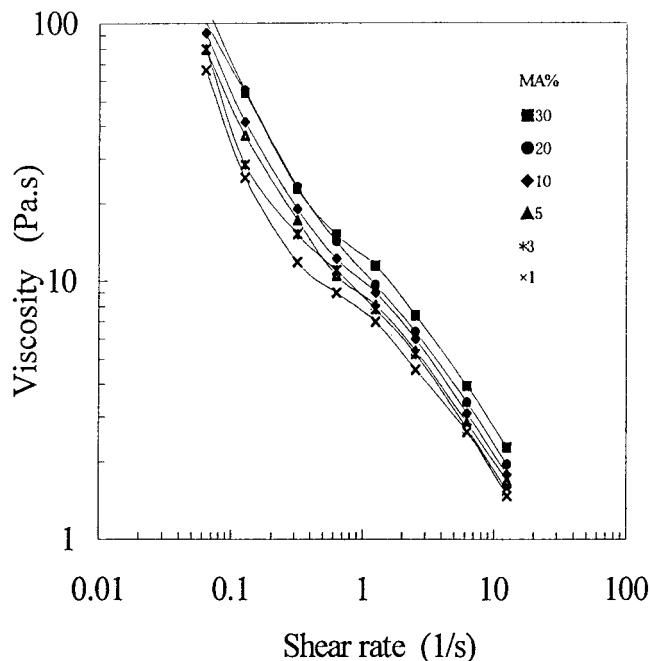
Figure 1 Viscosity versus shear rate for BMA/MA/CaCO$_3$ with 30% CaCO$_3$ and various MA%.

part, both steady and dynamic viscosities for the mixture BMA/MA/CaCO$_3$ in various ratios were measured. Then, the influence of molar mass of PBMA and of the measuring temperature on the dynamic viscosity of PBMA were analyzed and determined. Third, the rheological behavior and dynamic mechanical properties of composites PBMA/MA/CaCO$_3$ were investigated and compared to those of pure PBMA.

EXPERIMENTAL

Materials

Precipitated calcium carbonate (CCP SOCAL 31) was supplied by Solvay (Brussels, Belgium). Monomers methacrylic acid (MA), butyl methacrylate (BMA), and initiator 2,2'-azobis(2-methyl-propionitrile) (AIBN) were purchased from Acros (France). BMA was purified by distillation before use. All other reactants were used as received without further purification.

Polymerization

PBMA was prepared by the free-radical polymerization of BMA at 60°C using AIBN as initiator, with [AIBN]/[BMA] = 5 × 10^{-3}.

The composites were prepared by *in situ* radical polymerization of BMA/CaCO$_3$ and/or BMA/MA/CaCO$_3$ under the same conditions as for PBMA synthesis.

Monomer BMA or BMA/CaCO$_3$ or BMA/MA/CaCO$_3$ and initiator were stirred in a reactor at high speed (18,000 rpm) for 4 min using an Ultra Turrax mixing tool. The reactor was then placed in a bath at 60°C for 40–50 min. The reactive system became viscous and it was then poured into a mold (2 × 100 × 100 mm) and pressed under 200 bar at 60°C for 12 h, at 80°C for 10 h, and at 100°C for 2 h.

Molecular weight distribution analysis

A Waters size-exclusion chromatography (SEC) instrument (Waters Chromatography Division/Millipore, Medford, MA) equipped with differential refractometer R401 and UV absorbance detector model 440 was used to analyze the molar mass and distribution of the PBMA and its composites. The solvent was tetrahydrofuran (THF) at a 1.0 mL/min flow rate at room temperature. Styragel HR1, HR3, and HR4 columns were used. Number- and mass-average molecular weight (M_n and M_w) were calculated using a calibration with polystyrene standards.

Melt rheology

A Couette Brookfield rotational viscometer (Brookfield Instruments) was used to measure the viscosity of the monomer mixture of BMA/MA/CaCO$_3$ at room temperature. Oscillatory shear flow was used to obtain both dynamic viscosity and modulus of the polymers and composites in the molten or liquid state above the glass transition of the components. Measurements were carried out in a Rheometric Scientific
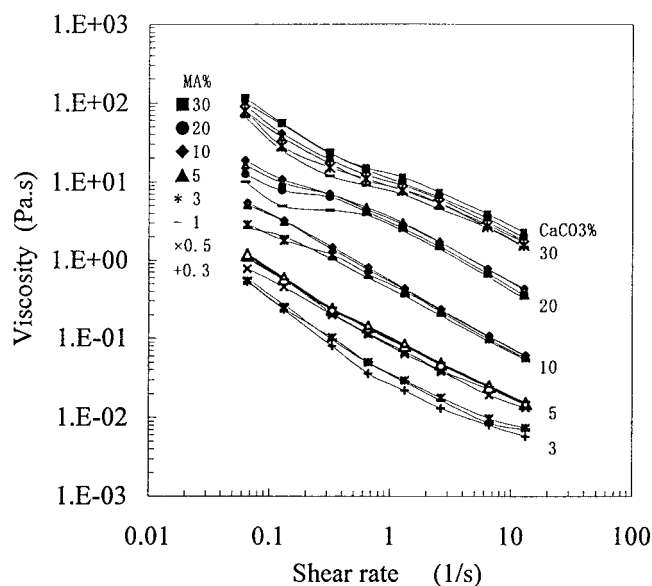

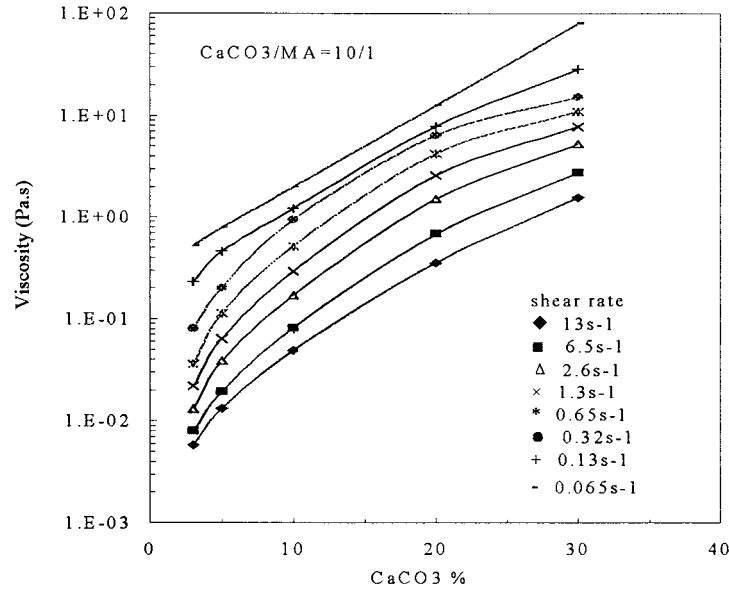**Figure 2** Viscosity versus shear rate for BMA/MA/CaCO$_3$ containing various CaCO$_3$% and MA%.

Figure 3 Viscosity under different shear rates for various $CaCO_3$% for BMA/MA/$CaCO_3$ with $CaCO_3$/MA (10/1).

ARES system (Rheometrics, Poole, UK) equipped with a plate–plate geometry (diameter 25 mm, gap 2 mm) during frequency sweeps at 0.1 to 100 rad/s at various constant temperatures ranging from 130 to 210°C within the linear viscoelastic domain.

Mechanical spectrometry in the solid state

Oscillatory measurements were also performed during temperature sweeps from 25 to 150°C at 1 rad/s using torsion experiments on rectangular bars (length 50 mm, width 4 mm, thickness 2 mm) in the same

ARES system. The strain amplitude was 0.5% with automatic adjustment throughout the test.

RESULTS AND DISCUSSION

Rheology of BMA with filler

Dependency of viscosity on shear rate

The BMA and $CaCO_3$ mixture was prepared using an Ultra Turrax mixing tool. After a few hours, an important $CaCO_3$ sedimentation was clearly observed.
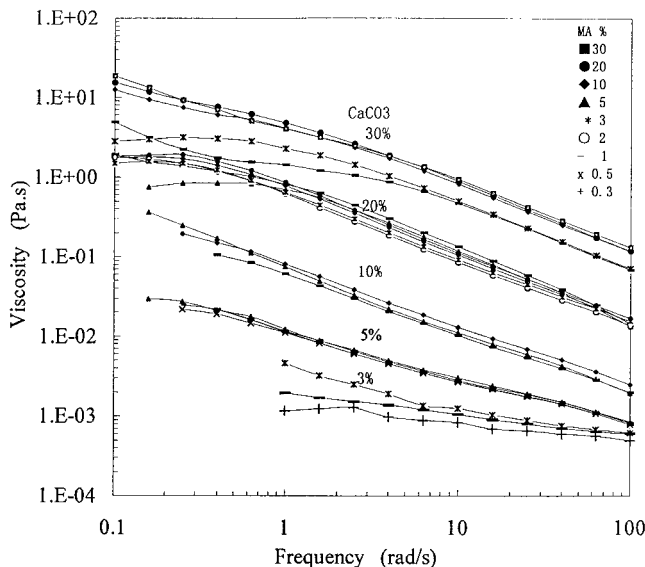

Figure 4 Dynamic viscosity of mixture BMA/MA/$CaCO_3$ at various $CaCO_3$ contents, measured at 25°C.
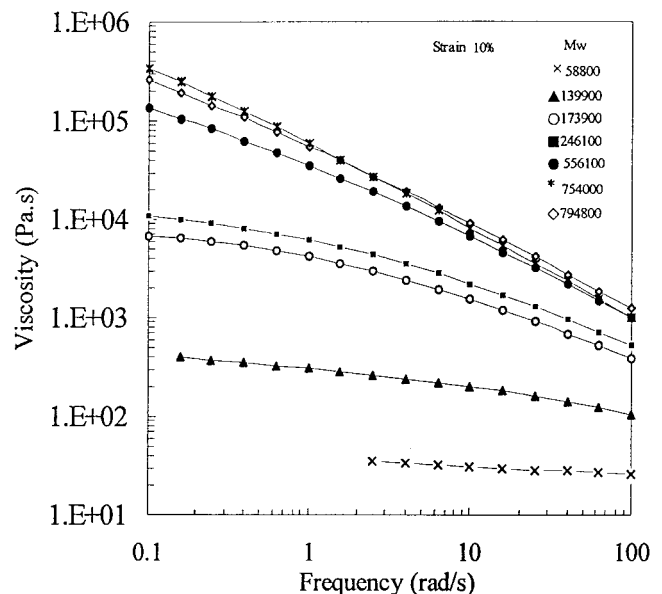

Figure 5 Variation of the dynamic viscosity with the weight-average molar mass of PBMA at 160°C.

TABLE I
Molar Mass Distribution of Poly(butyl methacrylate) from SEC Analysis

M_w (g/mol)	58,800	139,900	173,900	246,100	556,100	754,000	794,800
M_n (g/mol)	31,900	64,800	81,800	105,600	322,400	529,600	500,300
Polydispersity	1.84	2.16	2.13	2.33	1.72	1.41	1.59

An equivalent experiment made with the addition of a small quantity of MA led to more homogeneous and more viscous mixtures. In addition, no sedimentation was observed even after several hours. In this last experiment, MA and CaCO$_3$ reacted to form an ionic compound and then stabilized the carbonate composition in the MA/BMA monomer mixture.

Figure 1 shows the dependency of the viscosity on shear rate for a mixture BMA/MA/CaCO$_3$ with 30% CaCO$_3$ and various amounts of MA. The viscosity decreases with the increasing of shear rate and displays non-Newtonian behavior. A yield behavior is also noted at low shear rates, which can be expected in the case of anisometric small particles at high concentration even in Newtonian liquids. In such conditions, colloidal behavior is often noticed for the suspensions of fillers in liquid because of large filler–filler interactions.

In addition, increasing the MA content also increases the viscosity of the mixture. Indeed, MA/CaCO$_3$ interaction increases the effective volume of the filler, which in turn increases the viscosity.

Evolution of the viscosity with the filler content

The variation of the viscosity with the shear rate for the mixtures with various amounts of CaCO$_3$ and MA is shown on Figure 2. The system displays non-Newtonian flow. Comparison of the contribution of CaCO$_3$ and MA shows that the viscosity of the mixture BMA/MA/CaCO$_3$ increases evidently with the amount of CaCO$_3$. It is enhanced by a factor 10^3 when the CaCO$_3$ content increases from 3 to 30%. When the content of CaCO$_3$ is higher than 10%, a yield stress is observed at low shear rates because of the shape and size of the particles. This yield generally reflects strong filler–filler or filler–matrix interactions.

The effect of MA on viscosity is generally small at high shear rate. In this range the mixture behavior is mainly that of the liquid matrix. On the other hand, a marked influence is noted in the low shear rate range, which is a proof of the interaction of MA toward the filler (Fig. 3). As soon as the filler content exceeds 10%, the effect of the addition of MA becomes significant. In fact, in these particular systems, CaCO$_3$ not only acts as rigid filler but also reacts with MA to form an ionic compound, which contributed to viscosity in two ways: an increase of the effective volume of particle because of the building of clusters and a specific in-

teraction between liquid and fillers. Nevertheless, at small amounts of MA, the covering of the particles remains incomplete and only further addition of MA may lead to a significant increase of the viscosity. Generally, it is found that a large amount of MA can induce a saturation of the viscosity level, which means a complete covering of the particle.

Dynamic viscosity

The dynamic viscosity of the BMA/MA/CaCO$_3$ mixture was measured by means of oscillatory shear flow and the flow curves are shown in Figure 4. It should be noted that the viscosity for BMA/CaCO$_3$ cannot be measured because of the settle sedimentation of the immiscible system without MA. At low carbonate content, the viscosity is very low, inducing some uncertainty on the torque signal. The curves in Figure 4 show the same tendency as the flow curves shown in Figure 2. The viscosity increases significantly with the increasing of the carbonate content, and increases slightly with the addition of MA.

Rheology of PBMA

Influence of molecular weight on the viscosity of PBMA

To distinguish the different flow behaviors of pure PBMA and its composites, it is necessary to determine the rheological behavior of PBMA. It is well known that the viscosity relies greatly on the molecular weight of polymeric materials. The dependency of the
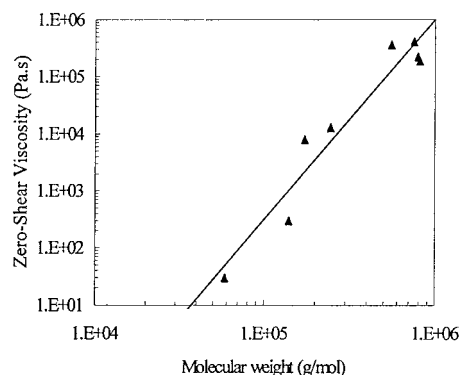

Figure 6 Zero shear viscosity η_0 versus weight-average molar mass of PBMA at 160°C.
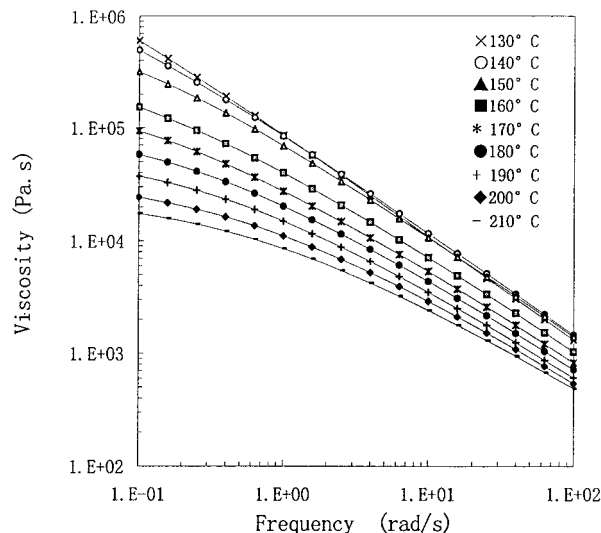
Figure 7 Viscosity of PBMA (M_w = 794,800 g/mol) versus frequency at various temperatures.

Figure 8 Master curve for PBMA (M_w = 794,800 g/mol) at 160°C.

dynamic viscosity on molecular weight of PBMA at 160°C is shown in Figure 5.

The SEC analysis of the samples shows that the polymers under investigation have a relatively narrow molecular weight distribution (Table I). Thus, it is reasonable to look for a relation between the zero-shear viscosity and the weight-average molecular weight. Values of the zero shear viscosity η_0 from Figure 5 are plotted versus weight-average molecular weight in Figure 6. The relation of zero-shear viscosity (in Pa·s) to molecular weight (in g/mol) was established to be $\eta_0 = 10^{-15} M_w^{3.5}$ at 160°C, in good agreement with those expected exponents.

Dependency of viscosity on temperature

Figure 7 shows the variation of the viscosity with frequency at different temperatures for PBMA. By the use of time–temperature superposition, the moduli versus shear rate at various temperatures are converted to a single master curve at 160°C, as shown in Figure 8. The activation energy of flow, calculated from an Arrhenius plot on the shifting factors, was 115 kJ/mol.

Rheology of PBMA composites

Viscosity of PBMA/CaCO₃ composites

The PBMA composites with $CaCO_3$ were prepared by radical polymerization of BMA/$CaCO_3$ dispersion. The molar mass of the matrix PBMA was found to be different for the composites containing variable amounts of calcium carbonate. To make the comparison of the effect of filler on the viscosity of composites
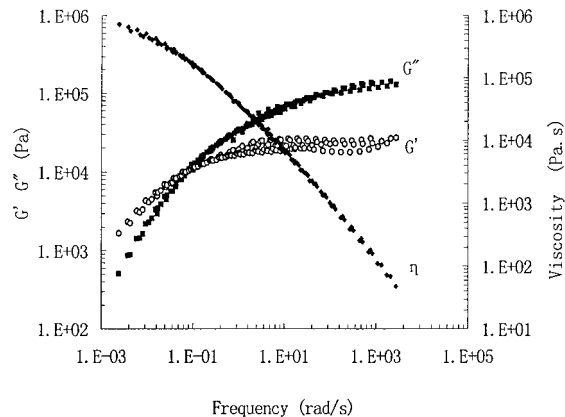
reliable, the viscosity curves were shifted both horizontally and vertically, to take into account the change of molar mass. For this purpose the scaling law obtained on pure PBMA was used. Using this superposition method, the curves with different molar mass were shifted to the same PBMA molar mass, as shown in Figure 9.

It is noted that the viscosity of composites decreases when the $CaCO_3$ content is less than 10% and increases when it exceeds 20%, compared with pure PBMA. This phenomenon was rather unexpected, given that addition of filler generally leads to an enhancement of the viscosity of polymer melts. This effect can be attributed to the existence of a hydrophilic boundary layer on the surface of the $CaCO_3$ particles that prevents the adhesion of polymer to the
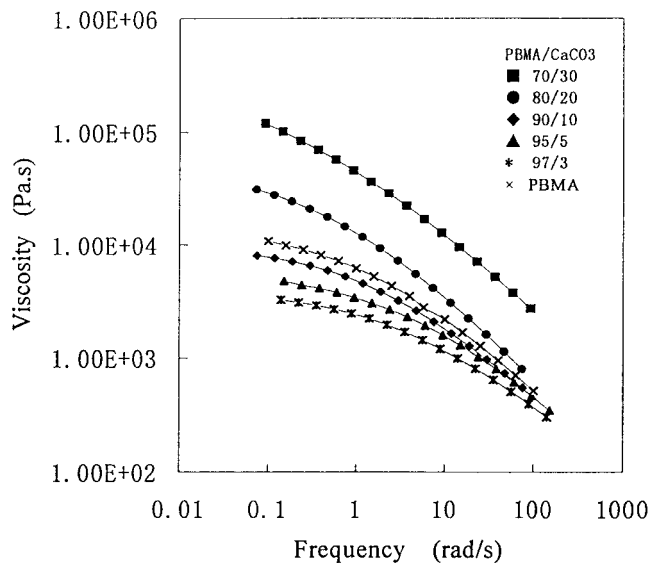

Figure 9 Comparison of the viscosity of composites PBMA/$CaCO_3$ with PBMA at 160°C for the same molar mass, M_w = 246,000 g/mol.
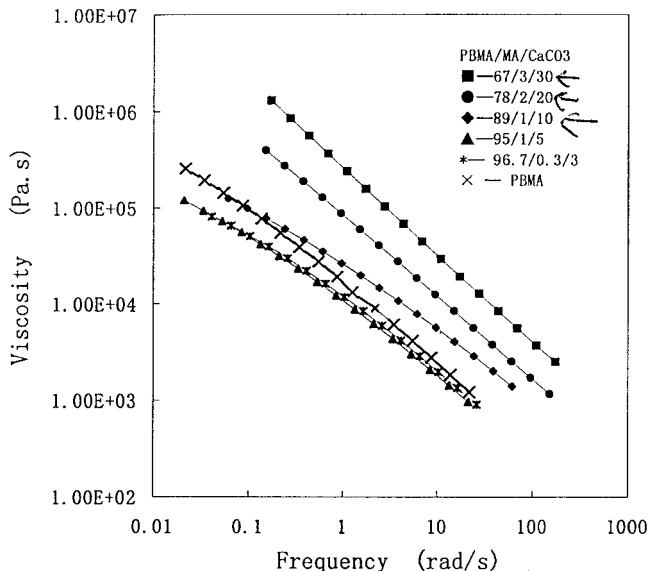
Figure 10 Comparison of viscosity of composites PBMA/MA/CaCO$_3$ with PBMA at 160°C for the same molar mass, M_w = 360,000 g/mol.

Figure 11 Pseudomaster curves of viscosity and modulus at 160°C for composites PBMA/CaCO$_3$ 90/10 and PBMA/MA/CaCO$_3$ 89/1/10, M_w = 267,000 g/mol.

carbonate and may generate an effect similar to voiding. As soon as the quantity of CaCO$_3$ is large enough, the rheological behavior of the matrix is dominated by particle–particle interaction and the viscosity increases because of additional friction. In this case, the viscosity of the system depends not only on the PBMA matrix but also on the CaCO$_3$. This evolution shows that the PBMA/CaCO$_3$ interactions are either very low or nonexistent.

Viscosity of PBMA/MA/CaCO$_3$ composites

Figure 10 presents the dynamic viscosity evolution of PBMA/MA/CaCO$_3$ composites at 160°C shifted to take into account the molar mass difference of PBMA/MA using a procedure equivalent to that in Figure 9. It can be clearly seen that, in this case, the viscosity of the composite exceeds that of pure PBMA even for filler content as low as 10%. Comparison of the composites having the same CaCO$_3$ content but containing MA and without MA showed that the addition of relatively low MA quantities can enhance the viscosity.

A comparison of the viscosity evolution of PBMA/CaCO$_3$ and PBMA/MA/CaCO$_3$ composites when increasing CaCO$_3$ content (Figs. 9,10) clearly shows the MA/CaCO$_3$ interaction effect on viscosity. For PBMA/MA/CaCO$_3$ composites, only a slight decrease of viscosity was observed with the addition of up to 5% CaCO$_3$. For 10% and higher CaCO$_3$ quantities, the viscosity of composites was higher than that of pure PBMA. These experiments show that the com-
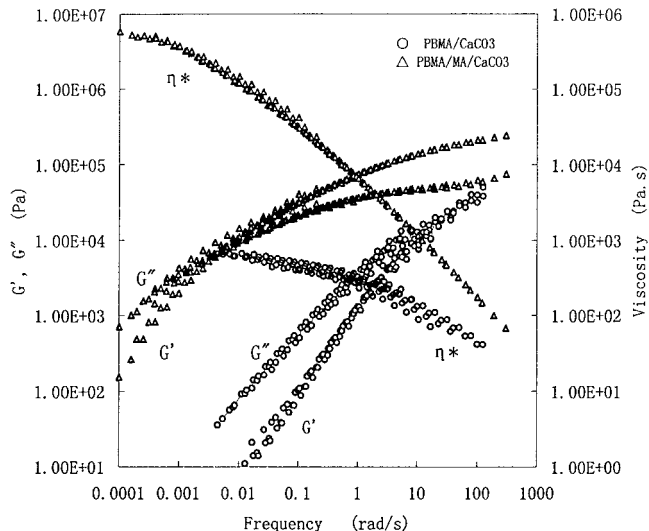
patibility of calcium carbonate and a composite matrix is improved by the addition of MA.

Master curve of composites

In general, the principle of time–temperature superposition is used for pure and homogeneous polymer systems and not for composites with inorganic fillers because of possible structural evolution. Attempts to superimpose the viscosity and modulus to frequency data for composites PBMA/CaCO$_3$ and PBMA/MA/
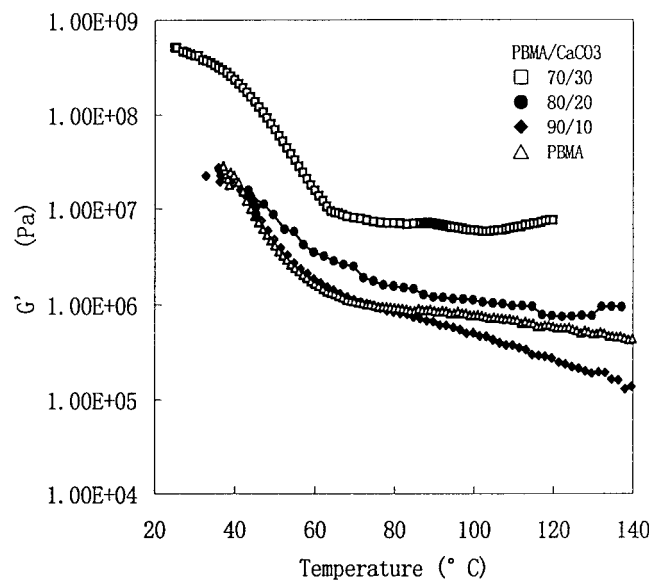

Figure 12 Temperature dependency of the storage modulus of PBMA and composites PBMA/CaCO$_3$ (strain 0.5%, frequency 1 rad/s).
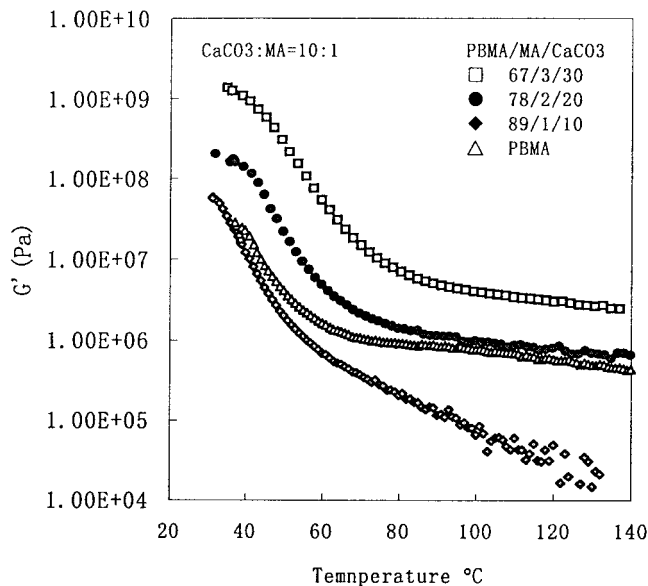
Figure 13 Temperature dependency of the storage modulus of PBMA and composites PBMA/MA/CaCO$_3$ (strain 0.5%, frequency 1 rad/s).

Figure 15 Spectrum of tan δ for PBMA and composites PBMA/MA/CaCO$_3$.

CaCO$_3$ lead to pseudomaster curves, as shown in Figure 11.

The comparison of two composites shows that the modulus of PBMA/MA/CaCO$_3$ is higher than that of PBMA/CaCO$_3$, and the master curve of the former is smoother than that of the latter. This can be also attributed to the presence of MA, which improves the stability of the dispersion and prevents the evolution
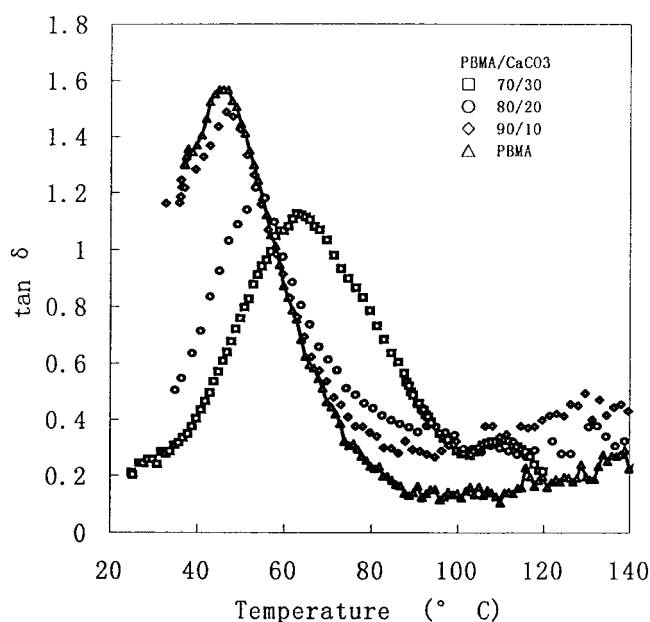

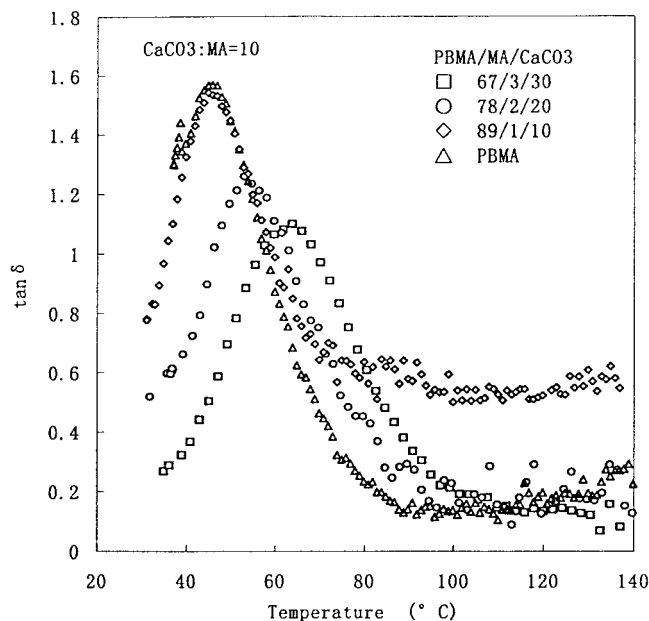**Figure 14** Spectrum of tan δ for PBMA and composites PBMA/CaCO$_3$.

of the structure. In this case, the time–temperature superposition principle holds.

From the data of viscosity versus frequency at different temperatures, the activation energy of viscous flow is found to be 148.6 and 178.7 J/mol for PBMA/CaCO$_3$ 90/10 and PBMA/BM/CaCO$_3$ 89/1/10, respectively. The relative magnitude of the values indicates that the mobility of the chain is severely hindered for the composite 89/1/10, which could also be seen as an increase in the glass-transition temperature. This is also a proof of the adhesion of the filler to the matrix.

In addition, the activation energies of composites are significantly higher than that of pure PBMA.

Dynamic mechanical properties of composites

Usually the fillers are used to improve the mechanical properties of polymeric materials, especially with regard to the modulus. The dependency of the modulus on temperature for composites with various proportions of CaCO$_3$ was measured by mechanical spectroscopy in rectangular torsion. Figures 12 and 13 show the curves of the storage modulus for pure PBMA and its composites both without and with MA. It is worth noticing that the modulus of the composite with 10% of CaCO$_3$ is less than that of PBMA, as was observed with melting viscosity. This is also a consequence of the lack of adhesion and probable voiding at the interface between CaCO$_3$ and the matrix. When the CaCO$_3$ content is increased, the contribution of hard particles to the modulus becomes dominant in the

system but addition of MA increases the modulus of the system, especially in the transition and glassy zones.

Furthermore, the maximum of tan δ is shifted toward higher temperatures upon addition of large amounts of CaCO₃, as shown in Figures 14 and 15.

CONCLUSIONS

In this study the rheological properties of PBMA and its composites were investigated by considering the influence of the amounts of CaCO₃ and MA, molar mass, and temperature. The effect of methacrylic acid was detected through the reactive system sedimentation and its rheological behavior, as well as on the rheological behavior of molten PBMA/MA/CaCO₃ composites. A relatively low quantity of MA leads to an improvement of the polymer matrix and CaCO₃ interface.

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