Improving the Processability of Biodegradable Polymer by Stearate Additive

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ABSTRACT: Maleated poly(propylene carbonate)/calcium stearate (MAPPC/CaSt$_2$) composite was prepared through melt-extruding poly(propylene carbonate) (PPC) with maleic anhydride and CaSt$_2$. The processability, thermal stability, interaction between two components as well as the morphology of the composites were systematically characterized. The flow instability of biodegradable PPC was greatly alleviated due to the incorporation of stearate additive in polymer matrix. It was found that the MAPPC and MAPPC/CaSt$_2$ composites were more thermostable than pristine PPC under melt-processing conditions. The melt fluidity of the composites was noticeably superior to that of MAPPC, arising from the lubricating effect of CaSt$_2$ on the polymer/barrel wall interface as well as from the improvement of resistance to thermal degradation of the composite. The coordination interaction between MAPPC and calcium ion also contributes to the enhanced thermal stability and high melt stability of composites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 692–700, 2011

Key words: polycarbonates; additives; processing; stick-slip transition

INTRODUCTION

The utilization of CO$_2$ as a feedstock for the production of organic products has been attracting considerable attention of chemistry workers all over the world,[1–3] because the substantial progress in this field will help to exhaust this waste gas released in the atmosphere and to diminish the greenhouse effect. In the late 1960s, Inoue et al.[4,5] developed a new method to prepare aliphatic polycarbonate via the copolymerization of CO$_2$ and propylene oxide. This pioneering work has led to international efforts in obtaining more efficient catalysts for synthesizing this biodegradable material.[6–8] Poly(propylene carbonate) (PPC), a low cost aliphatic polycarbonate with the character of complete degradability under natural environment, has been considered as a promising candidate for industrial applications in fabricating one-off plastic products, biomedical materials, and toughening agent, etc.[9–12] Unfortunately, this amorphous copolymer is prone to degrade when subjected to statically

thermal treatment even at 180°C,[13,14] which arises from a chain unzipping decomposition reaction. Although some modification methods including end-capping and polymer blending have been adopted to improve the performances of PPC,[15–18] the high melt viscosity of this polymer at relatively low temperatures has caused many difficulties during processing with common thermoplastic techniques.[19]

Calcium stearate (CaSt$_2$), as a typical nontoxic metal soap, has been widely used as thermal stabilizer, lubricant, and acid absorbing agent in plastics industry.[20] As a processing additive, CaSt$_2$ is also characterized with the ability to reduce surface tension, which makes it suitable for application as a surfactant in cosmetics and pharmaceuticals.[21] Because of its typical amphiphilic feature, another application of such a surfactant is to modify the condensed structure of polymers. Over the past decades, numerous studies have demonstrated that self-assembled ordered structure of polymers can be constructed through specific non-covalent interactions, such as hydrogen bonding, ionic interactions, or coordination complexation between polymer chains and the polar heads of amphiphiles. These studies have suggested that such structure is beneficial for improving the thermal stability, processability of polymer materials.[22–24] Both supramolecular structures and physicochemical properties of polymer-amphiphile complexes can be adjusted by the nature of macromolecules and surfactants, such as flexibility, charge density, polar groups, and alkyl chains.[25–28]

In a recent work, we prepared PPC-CaSt$_2$ complexes with different compositions using simple solution blending method.[29] The mesomorphous structure containing long alkyl tails of the amphiphilic stearate was observed in the complexes, which was constructed through metal ion coordination interaction between PPC and CaSt$_2$. The study suggested that this coordination complexation plays a key role in stabilizing the self-organized structure of the complexes at elevated temperatures, which leads to the improvement of thermal stability of the polycarbonate matrix.

In this study, CaSt$_2$ was selected as a modifier to suppress the unsteady flow encountered in the melt extrusion process of PPC resin. The unique lubricating and stabilizing effects of metal dicarboxylates on this copolymer were corroborated, resulting in the alleviation of abnormal rheological behaviors of PPC melt. The change of absorption state of the macromolecular chains on the die wall caused by the addition of CaSt$_2$ is primarily responsible for the significant improvement of melt processability of this aliphatic polycarbonate.

EXPERIMENTAL

Materials

PPC was produced by Mengxi High-tech Materials Company. The weight-average molecular weight and polydispersity determined by gel permeation chromatography were 6.1×10^5 and 2.09, respectively. The carbonate unit content of the copolymer, estimated from ^{1}H-NMR spectrum using the method described in previous literatures,[30,31] was 98.0 mol %. Analytical grade maleic anhydride (MA) was obtained from Shantou Xilong Chemical Plant. Calcium stearate (CaSt$_2$) was purchased in pure form from Alfa Aesar Co. and used as received.

Preparation of maleated poly(propylene carbonate)/calcium stearate/CaSt$_2$ composites

Before melt blending, PPC was dried under vacuum at 60°C for 48 h. MA and CaSt$_2$ powders were dried under vacuum at room temperature and 90°C, respectively, for 24 h. The premixing procedure was as follows. MA and PPC were first mixed homogeneously in the weight proportion of 1.0/99.0, then the stearate was dispersed uniformly into the above premixture in the weight ratios of 0.1/99.9, 0.5/99.5, 1.0/99.0, 2.0/98.0, and 5.0/95.0, respectively. The maleated PPC/CaSt$_2$ composites were prepared by using a twin screw extruder (Mess-Technic GmbH, Germany) with a rotating speed of 50 rpm. The processing temperatures from the hopper to die zones were set at 130°C, 145°C, 145°C, and 135°C.
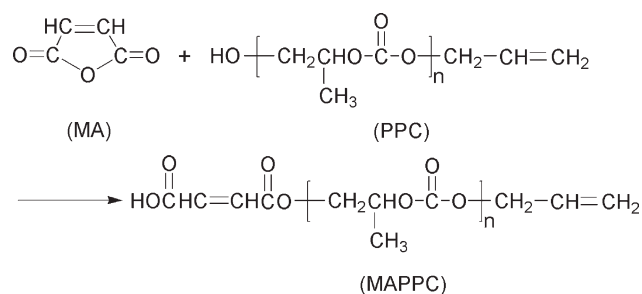
Scheme 1 Melt end-capping PPC with MA.

For comparison, PPC end capped with MA (MA/PPC = 1.0/99.0 wt %) was also fabricated at the same temperature and screw speed. The extrudates were pelletized for thermal stability and rheological measurements.

Characterization

The average molecular weight and polydispersity of maleated poly(propylene carbonate)/calcium stearate (MAPPC) and MAPPC/CaSt$_2$ composites were measured on a Waters 1515 gel permeation chromatography system at 35°C using chloroform as the solvent and monodisperse polystyrene as the standard. Grafting degree of MAPPC and MAPPC/CaSt$_2$ composites (G) was defined as weight percent of grafted MA in PPC and determined according to the titration method suggested by Zhang et al.[32] Differential scanning calorimetry (DSC) experiments were performed on a Mettler DSC 882e calorimeter to determine the glass transition temperature (T_g) of PPC, MAPPC and MAPPC/CaSt$_2$ composites. The samples were heated from 20 to 140°C at a rate of 20°C/min under nitrogen atmosphere. The midpoints of the transitions in the traces recorded in the heating scan were taken as the values of T_g. Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer Pyris 1 TGA thermal analyzer to evaluate the thermal stability of CaSt$_2$, pristine PPC, MAPPC, and MAPPC/CaSt$_2$ composites. The samples were heated from 20 to 800°C at a rate of 20°C/min under nitrogen atmosphere. Fourier transform infrared spectroscopy (FT-IR) was used to investigate the interactions between CaSt$_2$ and MAPPC. For FT-IR measurement, the acetone solutions of samples were cast into films on KBr crystal. All the films were sufficiently thin to be within the absorbance range where the Beer-Lambert law was obeyed. All the FT-IR spectra were recorded on a Bruker EQUINOX 55 FT-IR at room temperature, which were collected at a resolution of 2 cm^{-1} with 64 scans being signal-averaged. To get a direct glimpse into the processability, the photographs of melt-extrusion behaviors of pure PPC, MAPPC and MAPPC/CaSt$_2$ composites near the die exit were taken by a Canon digital

	$\overline{M}_w$	$\overline{M}_n$	Polydispersity	G (wt%)	T_g (°C)
MAPPC	101 200	59 300	1.71	0.12%	32.6
MAPPC-0.1% CaSt$_2$	126 700	79 700	1.58	0.10%	33.5
MAPPC-0.5% CaSt$_2$	129 000	79 900	1.61	0.15%	33.9
MAPPC-1% CaSt$_2$	141 100	91 300	1.54	0.12%	34.2
MAPPC-2% CaSt$_2$	147 200	90 900	1.62	0.13%	34.4
MAPPC-5% CaSt$_2$	170 600	120 000	1.42	0.11%	34.1

$\overline{M}_w$ and $\overline{M}_n$ are defined as weight-average and number-average molecular weight, respectively.

camera. Steady-state rheological measurements of MAPPC and the composites were carried out with a capillary rheometer (Advanced Capillary Rheometer RH7, Bohlin Instruments) under three temperature conditions (150°C, 160°C, and 170°C). The length-to-diameter (L/D) ratio of the capillary was fixed at 32. For each individual test at a different temperature, the sample was preheated to reach the specific temperature before the measurements. The apparent melt viscosity was obtained from the software attached to the rheometer. The Bagley correction for the apparent shear stress was negligible because the L/D ratio of the capillary was >30.

RESULTS AND DISCUSSION

Thermal properties of MAPPC/CaSt$_2$ composites

MA was selected as a end-capping agent during melt extrusion (Scheme 1) to restrain the chain unzipping degradation initiated from the terminal hydroxyl groups of PPC.[13,14] Although the relatively percentage content of grafted MA in PPC (G) (Table I) is small due to few reactive end groups of this high molecular weight material, the thermal properties of MAPPC and MAPPC/CaSt$_2$ composites were obviously enhanced compared with uncapped PPC.

It is known to all that the glass transition temperature is crucial for the utilization of thermoplastic materials. With increasing the contents of stearate additive in the MAPPC matrix, the glass transition temperature of MAPPC/CaSt$_2$ composites is slightly elevated (Fig. 1 and Table I). Therefore, the stearate will not act as a plasticizer and the basic performance of the polycarbonate composites will be retained compared with MAPPC.

The TGA curves of CaSt$_2$, PPC, MAPPC, and MAPPC/CaSt$_2$ were presented in Figure 2. It is evident that the degradation of MAPPC and MAPPC/CaSt$_2$ composites occurred at much higher temperatures when comparing to pure PPC. The TGA data (Table II) showed that the $T_{5\%}$ of maleated PPC is raised to ~ 256°C, a temperature which is much higher than that for the pure PPC (179.0°C), demon-

strating that end capping has a pronounced effect on the improvement of thermal stability of PPC. The improved thermal stability can be attributed to the chain unzipping process originating from a "back-biting" reaction of free terminal hydroxyl groups,[13,14] which is consistent with the report that end capping PPC with some chemical agents including MA leads to the inhibition of initial chain unzipping because nucleophilic terminal hydroxyl groups are replaced with less reactive groups.[15] In contrast, the $T_{5\%}$ values of all the MAPPC/CaSt$_2$ composites are ~ 5–15°C higher than that of MAPPC (Table II), indicating that the addition of calcium stearate further enhanced the heat resistance performance of MAPPC. It is also noticeable that there is little difference between the T_{max} values of MAPPC and MAPPC/CaSt$_2$ composites (Table II), confirming that neither end capping nor processing aid has serious influence on the random chain scission occurring at relatively higher temperatures.[13,14] Considering that there is no oxidative reaction during thermal degradation of PPC in air,[15] this work strongly suggests that MAPPC and MAPPC/CaSt$_2$ composites are more thermostable than pure
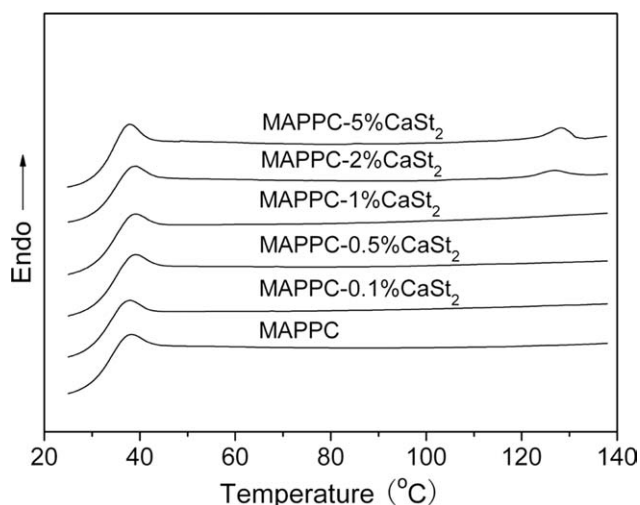

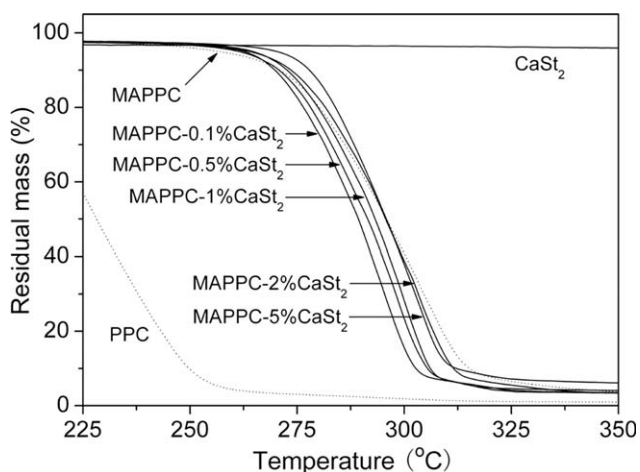**Figure 1** DSC traces of MAPPC and MAPPC/CaSt$_2$ composites.

Figure 2 Thermal stability comparison of PPC, MAPPC, $CaSt_2$, and MAPPC/$CaSt_2$ composites.

PPC when subjected to melt extrusion, as supported by the data presented in Table II.

Study on specific intermolecular interactions in the composites

It is well known that the polymer-filler interactions significantly affect the rheological properties and mechanical performances of the filled polymer systems.[33] Because FT-IR spectroscopy is highly sensitive to intermolecular interactions, this technique was employed to detect the interactions existing in the MAPPC/$CaSt_2$ composites (Fig. 3). The splitting absorption peaks observed at 1578 and 1543 cm^{-1} are assigned to the resonances of ionic and chelating carboxylate groups of $CaSt_2$.[34–37] The strongest band at 1747 cm^{-1} [Fig. 3(a)] is reasonably attributed to the stretching vibrations of carbonyl groups (C=O) of MAPPC.[32] In the previous work, we have reported the noticeable displacement of FT-IR absorption peaks caused by the hydrogen bonding

TABLE II
Thermal Degradation Data of PPC, MAPPC, $CaSt_2$, and MAPPC/$CaSt_2$ Composites

	$T_{5\%}$ (°C)[a]	T_{max} (°C)[b]
$CaSt_2$	399.3	450.6
PPC	179.0	205.1
MAPPC	256.9	276.6
MAPPC-0.1% $CaSt_2$	261.5	274.9
MAPPC-0.5% $CaSt_2$	262.7	276.7
MAPPC-1% $CaSt_2$	264.8	280.0
MAPPC-2% $CaSt_2$	270.3	279.8
MAPPC-5% $CaSt_2$	269.8	280.2

[a] $T_{5\%}$ is defined as the temperature at 5% weight loss.
[b] T_{max} is defined as the temperature at the maximum weight-loss velocity.

or the coordination interaction between the carbonate groups of pure PPC and the polar groups of the calcium cations.[28,29] However, as for the MAPPC/$CaSt_2$ composites, only a minor shift to lower wavenumbers (one is from 1578 to 1575 cm^{-1}, the other from 1543 to 1538 cm^{-1}) was observed for the two doublet bands related to the carboxylate group [Fig. 3(b)]. Thus it can be concluded that there is no strong specific interaction between calcium stearate and the polycarbonate matrix, which accounts for the slight influence of $CaSt_2$ on the improvement of thermal stability of MAPPC.

The melt-extrusion behavior of MAPPC/$CaSt_2$ composites

The photographs of melt-extrusion behaviors of pure PPC, MAPPC and MAPPC/$CaSt_2$ composites near the die exit are displayed in Figure 4. A complete chaotic extrudate distortion was observed for uncapped PPC [Fig. 4(a)], which can be described as gross melt fracture that is often related to the severe flow instability at the entrance of a converging die.[37]
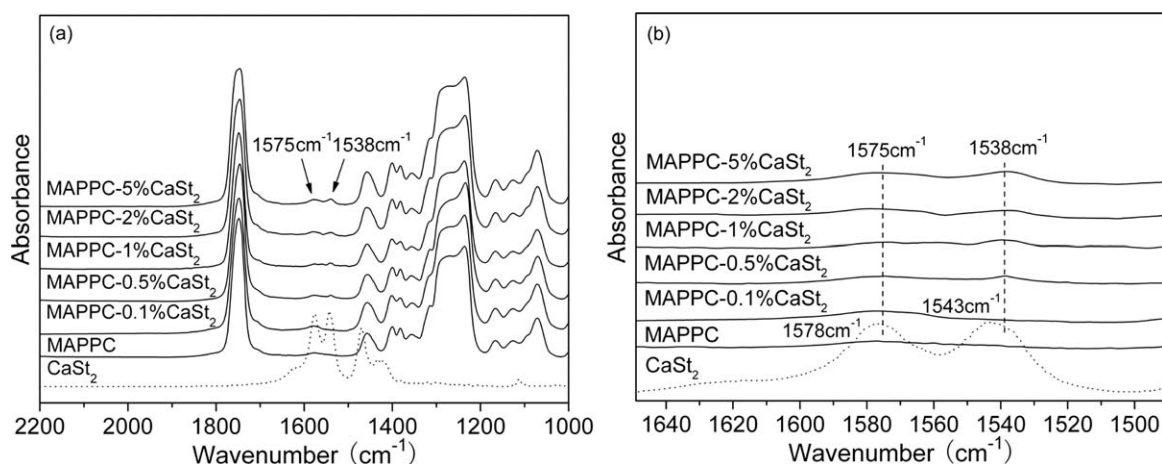

Figure 3 FT-IR spectra of MAPPC, $CaSt_2$, and MAPPC/$CaSt_2$ composites: (a) in the range of 2200–1000 cm^{-1}, (b) in the range of 1650–1490 cm^{-1}.

In general, the primary unsteady flow behavior for linear polymer melt at low shear rates is surface melt fracture, which is also known as the phenomenon of "sharkskin." However, some researchers have found that the unzipping degradation of PPC occurring at relatively low processing temperatures,[16,19] which is responsible for the abnormal melt fracture behavior of this linear polycarbonate. Although the severe melt fracture and extrudate distortion were eliminated due to the depression of end-initiated thermal degradation, a periodic small-scale distortion on the surface could be visible for MAPPC extrudate [Fig. 4(b)], indicating that end-capped PPC still suffers from sharkskin instability. In contrast, glossy and smooth appearances were observed for the extruded MAPPC/CaSt$_2$ composite with only a slight tendency of die swell [Fig. 4(c)]. Because CaSt$_2$ has been widely used as the die lubricant in polyolefin extrusion process to eliminate or postpone the melt fracture phenomenon,[37] this stearate additive may have a similar effect on the processability of aliphatic polycarbonate.

To further investigate the role of CaSt$_2$ in the extrusion process of PPC, the capillary rheological tests were performed to compare the flow behaviors of MAPPC and MAPPC/CaSt$_2$ composites. To rule out the possibility of depolymerization that takes place in the degradation temperature range, the testing temperatures were set <180°C. As shown in Figure 5, both MAPPC and the composites exhibited a typical non-Newtonian shear thinning behavior with the increase of shear rates. However, the value of critical shear rate at which the shear thinning starts for MAPPC is larger compared with the composites. Thorat et al.[38] have proposed that the shear thinning for aliphatic polycarbonate originates from the breakdown of secondary intermolecular bonds existing in polar polymer chains at high shear rates. These physical interactions are weakened by the shielding effect of CaSt$_2$ which pushes the molecules apart, thus the PPC chains can slide past each other more easily and lead to the occurrence of shear thinning at lower shear rates.

It has been widely accepted that temperature sensitivity of melts is one of the most important flow characteristics in determining the processability of polymers.[39] Thus, the apparent viscosity of MAPPC and MAPPC/CaSt$_2$ melts is plotted against the processing temperatures to show the inherent relationship more clearly (Fig. 6). It is evident that the decreasing amplitude of apparent viscosity of MAPPC/CaSt$_2$ melt with temperature rising is much smaller than those of MAPPC.

In addition, the temperature dependence of the apparent viscosity for MAPPC and MAPPC/CaSt$_2$ melts under the premise of no thermal decomposition can be described by the Arrhenius equation[39]:
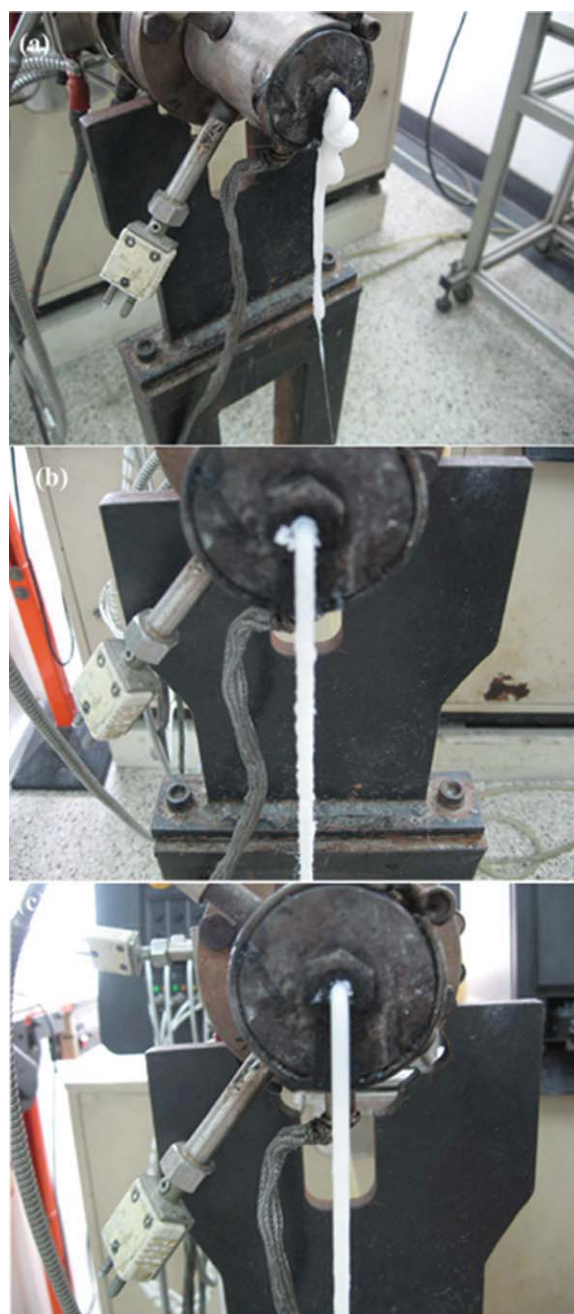
Figure 4 Photographs of the extrudates near the die exit region of the extruder taken during the melt-extrusion process for (a) PPC, (b) MAPPC, and (c) MAPPC-5% CaSt$_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\eta = A \times \exp(E_a/RT) \qquad (1)$$

where η, A, E_a, R are the apparent viscosity of melt (Pa s), the pre-exponential factor, the viscous flow activation energy (kJ/mol) and the universal gas constant (8.314 J/mol K), respectively. The E_a values of MAPPC and MAPPC/CaSt$_2$ composites at various shear rates, determined from the slope of ln η versus $1/T$ with linear regression, are listed in Table III.
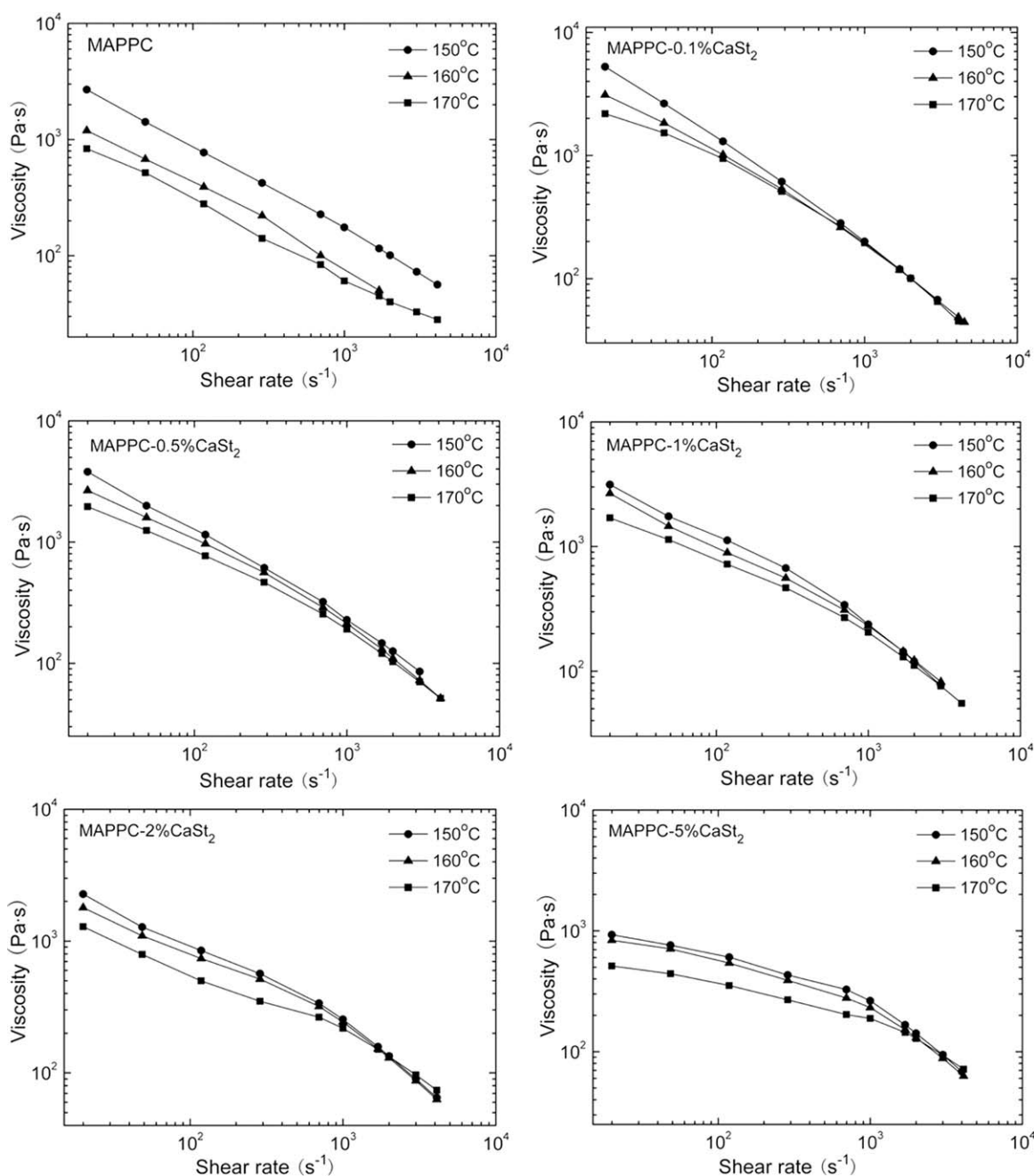
Figure 5 Plots of melt viscosity versus shear rates for MAPPC and MAPPC/CaSt$_2$ composites at different temperatures.

The results indicated that the flow activation energies of the composites tended to decline rapidly with the increasing content of the stearate. Thus, it is reasonable to conclude that MAPPC/CaSt$_2$ is less sensitive to temperature variation than MAPPC, which accounts for the rapid drop of viscosity for maleated PPC with the elevation of temperatures and results in a broader processing window for extruding this thermoplastic material.

The effect of CaSt$_2$ contents on the rheological behaviors of MAPPC/CaSt$_2$ composites at the selected processing temperatures is presented in Figure 7. It can be seen that the melt viscosity values of the com-

posites at the CaSt$_2$ content level <5 wt % were clearly higher than that of MAPPC. The variation of flow viscosity of polymer melt is closely related to the construction and removal of the entanglements of molecular chains. The flow resistance usually ascends quickly with the increase of entanglement density. As for the polymer/filler systems, the addition of filler particles facilitates the formation of a more tightly entangled network structure in comparison with the unfilled polymers.[39] Therefore, the relatively few CaSt$_2$ particles dispersed in the PPC matrix may lead to the increase of melt viscosity of the composites. But as the CaSt$_2$ content in the MAPPC/CaSt$_2$ composite exceeds
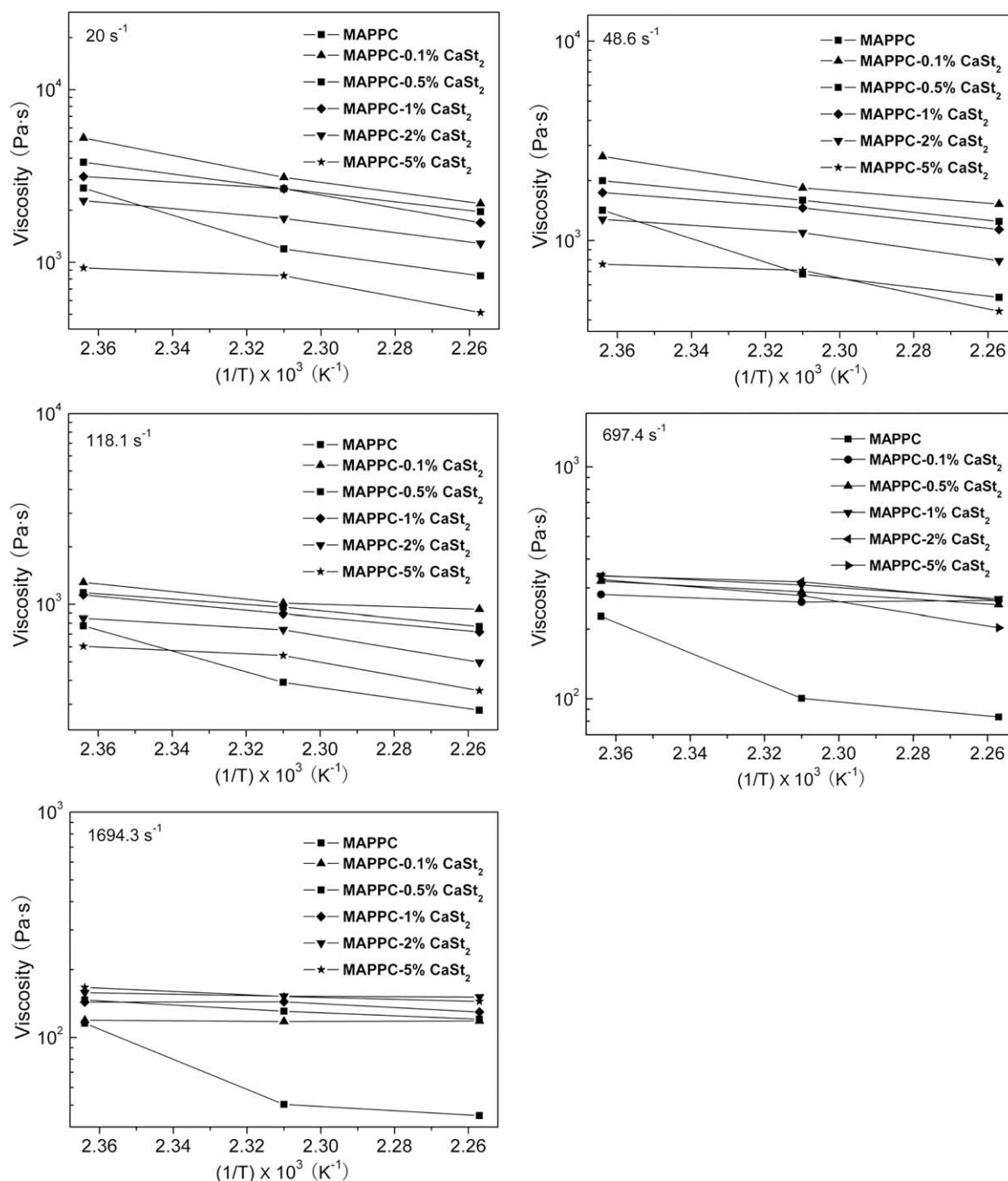
Figure 6 Effect of extrusion temperatures on the melt viscosity for MAPPC and MAPPC/CaSt$_2$ composites at shear rates.

5 wt %, some of the stearate molecules in the composite melt may migrate to the PPC/capillary wall interface and effectively reduce the flow friction of the melt system by its lubricating effect.

Although rheological measurements are widely applied to provide essential information on the flow behaviors of polymer melt, it is unfortunate that the sharkskin-type melt fracture of linear polymers can not be confirmed by the appearance of discontinuity portion in the flow curves as other unsteady flow behaviors such as pressure oscillation.[37]

TABLE III
The Viscous Flow Activation Energies (E_a, kJ/mol) for MAPPC and MAPPC/CaSt$_2$ Composites at Different Shear Rates

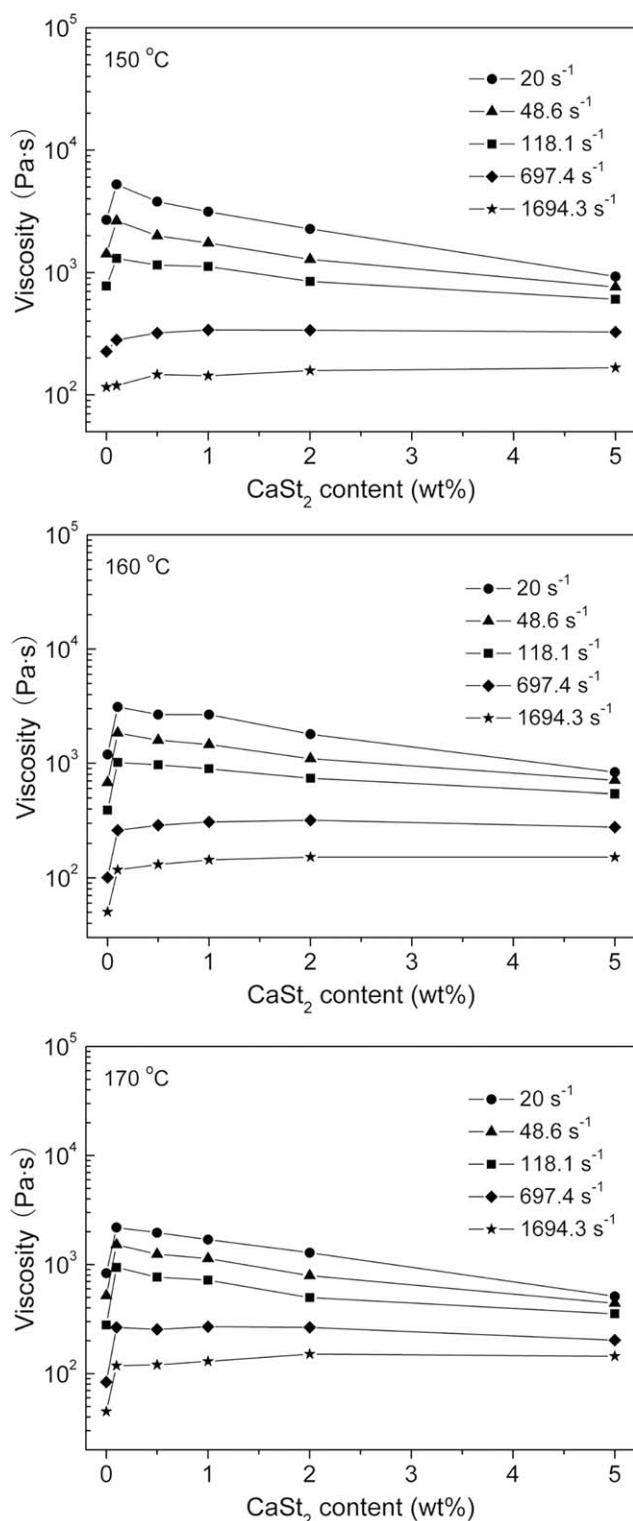|	Shear rate (s^{-1})				
	20	48.6	118.1	697.4	1694.3
MAPPC	12.44	10.71	10.84	10.65	10.12
MAPPC-0.1% CaSt$_2$	9.27	5.85	3.45	1.47	1.24
MAPPC-0.5% CaSt$_2$	6.97	4.96	4.26	2.46	2.08
MAPPC-1% CaSt$_2$	6.42	4.48	4.66	2.45	1.61
MAPPC-2% CaSt$_2$	6.05	5.22	4.83	2.52	1.47
MAPPC-5% CaSt$_2$	6.23	5.66	5.62	3.02	1.53

Figure 7 Effect of CaSt$_2$ contents on the melt viscosity for MAPPC and MAPPC/CaSt$_2$ composites at determined temperatures.

Possible mechanism for the processing improvement of PPC

To further elucidate the contribution of CaSt$_2$ to the processability improvement of MAPPC composites, the relationship between the macromolecular chain

relaxation characteristics and the melt extrusion stability of MAPPC was proposed (Fig. 8). The origin of unsteady flow of linear polymer melts has been discussed in details in the relevant literatures.[40,41] All the abnormal flow behaviors are closely related to the drastic change of the absorption state for the tightly entangled polymer chains at the solid surface. In respect of the polar linear polymers like maleated PPC, a portion of molecular chains is usually absorbed on the die wall with high surface energy in the extrusion process.[41] Because the "tethered" melt layer is still completely entangled with the inner layer of free polymer chains, no unusual flow will be expected to occur under low shear rates. When the rotating speed of the extruder exceeds a critical value, some of the absorbed chains undergo a coil-stretch transition and are separated from the free macromolecular chains. However, this local entanglement-disentanglement transition is unstable due to the unsteady hydrodynamic boundary condition at the die region.[40] The fluctuated chain relaxation process result in a periodic oscillation of the entangled state for the absorbed chains and a sudden release of elastic energy stored in the polymer melt, which is reflected as the sharkskin-like extrudate surface of MAPPC. As the CaSt$_2$ content is adequately high in the composites, a lubricant layer is feasible to form at the interface of polymer/wall, originating from the migration of partial surfactant molecules from melt. As a result, the tethered macromolecular layer is eliminated and the integral slippage of all the polymer chains is attained, which lead to the transition from unstable turbulent flow to laminar shear flow at the die wall and the smooth appearance of this extruded polycarbonate material.
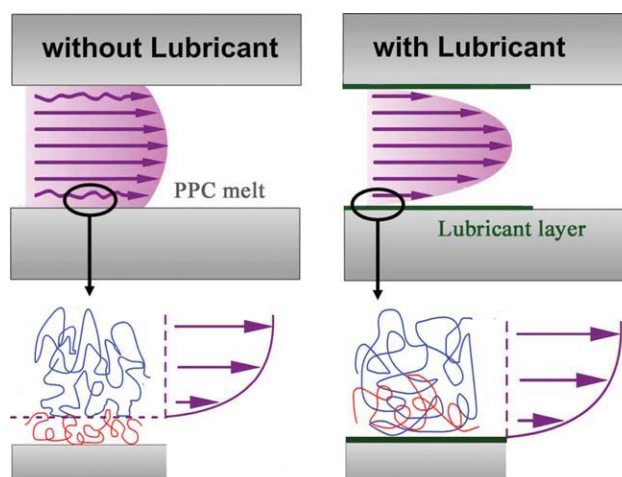

Figure 8 Schematic illustration of the role of CaSt$_2$ lubricant layers in suppressing unsteady flow behaviors of MAPPC by altering the strong absorption state of melt on the die wall. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The MAPPC/CaSt$_2$ composites have been prepared through a melt-extrusion process. This stearate is found to be an effective processing aid in enhancing the rheological properties and stability of the polycarbonate melt. The lubricant layer formed by this additive sufficiently eliminates the drastic change of the absorption state of the molecular chains at the polymer/die wall interface, which provides a simple solution to the problems for processing of PPC using conventional thermoplastics technique.

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