

Novel Poly(methyl methacrylate)-based Ionomers Used as Multifunctional Aids to Modify Poly(vinyl chloride)

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Abstract Poly(methyl methacrylate) (PMMA) based ionomers with different lanthanum (La(III)) contents (PMMA-XLa) synthesized by free radical solution polymerization were applied to poly(vinyl chloride) (PVC) resins as a kind of multifunctional aids, and their performances were evaluated by measuring the static stability time, initial discoloration, transparency, fusion behavior and tensile strength of the modified PVC. The ionomers with proper lanthanum (La(III)) contents show a better thermal stability efficiency in comparison with traditional stabilizer lanthanum stearate. Meantime, they can accelerate PVC plasticization more efficiently than PMMA. The rigid PVC products stabilized with the ionomers present good transparency and enhanced tensile strength.

Keywords: Rigid PVC; Ionomers; Thermal stability; Plasticization; Multifunction.

INTRODUCTION

Poly(vinyl chloride) (PVC) as one of the five general plastics has been widely used because of its desirable properties and low cost. However, PVC suffers from poor thermal stability and is easy to degrade during processing due to the presence of various defect sites such as allylic chlorine and tertiary hydrogen and chlorine atoms introduced in polymer chains during synthesis^[1, 2]. It has long been recognized that PVC eliminates hydrogen chloride (HCl) when exposed to high processing temperature, resulting in polyene sequences in the polymer chains accompanying with drastic coloration and loss of mechanical properties of the products^[3]. Therefore various types of thermal stabilizers have been used in PVC processing, among which nontoxic rare earth stabilizers attract more attentions because of their compatibility, transparency, and weather resistance^[4–8]. However, the traditional thermal stabilizers as small organic molecules are easy to migrate, which affects the transparency and long-term electrical insulation of the products^[9, 10]. On the other hand, PVC resins are usually difficult to plasticize due to the multi-particle microstructure and low heat transfer efficiency^[11]. Processing aids like acrylate polymers are most commonly used to promote the PVC plasticization during thermal processing, and poly(methyl methacrylate) (PMMA) can modify the inter-grain coefficient of friction and the packing density of PVC^[12, 13].

In order to overcome the shortcomings of small molecular thermal stabilizers and simplify the compositions of reinforced PVC resins, PMMA-based ionomers are designed for combining the advantages of processing aids (PMMA) and rare earth thermal stabilizers. In our previous investigations, it has been verified that an acrylate ionomer could be used as novel processing aids with great advantages for improving thermal stability and

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promoting plasticization of PVC resins^[14–16]. Here, PMMA-based ionomers with different lanthanum (La(III)) contents, (PMMA-*X*La), were synthesized by free radical polymerization, and their effects on the processing behavior and mechanical properties of PVC products were investigated.

EXPERIMENTAL

Materials

PVC (s-700) used was purchased from Qilu Petrochem. Co., Shandong, China. Zinc stearate (ZnSt₂), lanthanum stearate (LaSt₃) and hydrated lanthanum chloride (LaCl₃) were supplied by Aladdin Industrial Co., Shanghai, China. Glyceryl monostearate, epoxidized soybean oil, dioctylphthalate and paraffin were commercially available. Methyl methacrylate (MMA), acrylic acid (AA) and 2,2-azobisisobutyronitrile (AIBN) were obtained from Sinopharm Chem. Reagent Co. Ltd., Shanghai, China. MMA was used after being purified with 10 wt% sodium hydroxide (NaOH) solution and then distilled, and AA was used after being distilled. All of the other chemicals were used as received.

Synthesis of La-complex and PMMA-*X*La

Ethanol solution of AA (5 wt%) was neutralized with aqueous NaOH solution (4 mol/L) to pH = 6–7. The AA solution was dropped into the ethanol solution of LaCl₃ to reach a mole ratio of $n(\text{AA}):n(\text{LaCl}_3) = 3:1$. The precipitations were filtered and washed several times with ethanol and were dried in vacuum. The synthesis process of La-complex is shown in Fig. 1(a).

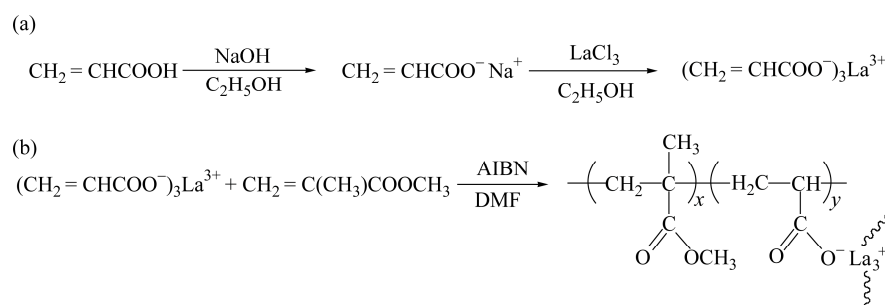


Fig. 1 Synthesis of La-complex and PMMA-*X*La ionomers

The ionomers were prepared by free radical polymerization, as depicted in Fig. 1(b), using *N,N*-dimethylformamide (DMF) as solvent and AIBN as initiator in a four-neck flask equipped with a thermometer, a mechanical stirrer, an allihn type condenser and a nitrogen inlet. After MMA and La-complex were dissolved in DMF, the initiator was added and polymerization was performed at 75 °C for 7 h. The ionomers were obtained after being precipitated in ethanol and were filtered and washed several times with ethanol. The products were dried under vacuum at 80 °C for 48 h. The ionomers were named as PMMA-*X*La with *X* denoting mass fractions of La(III) that was determined by inductively coupled plasma atomic emission spectrometry, *e.g.* PMMA-4.2La representing the ionomer containing 4.2 wt% of La(III).

Preparation of PVC Blends

The modified PVC containing 0.5 phr ZnSt₂, 4.0 phr dioctylphthalate, 0.3 phr paraffin, 2.0 phr glyceryl monostearate, 3.0 phr epoxidized soybean oil and 3.0 phr ionomer were melt blended in a Brabender torque rheometer (Germany) for 6 min at a rotor speed of 65 r/min at 180 °C. For comparison, the ionomer was replaced by LaSt₃ or a LaSt₃/PMMA mixture. The LaSt₃/PMMA mixture had the contents of La(III) and PMMA same as the ionomer PMMA-4.2La. The processed mixtures were hot-molded into tested samples at 180 °C and 15 MPa for 6 min.

Measurements

Characterization of La-complex and ionomers

Fourier transform infrared (FTIR) spectra were recorded using a spectrometer (VECTOR 22, Bruker, Germany) with a 4 cm^{-1} resolution and 64 scans at room temperature. The samples were prepared by mixing the ionomers with dried potassium bromide powders and compressing into discs. X-ray photoelectron spectroscopy (XPS) was measured using a VG ESCALAB MARK II (VG Company, UK) spectrometer with Mg K α source (1253.6 eV).

Evaluation of the stabilizing efficiency of PVC resin compounds

Congo red test was used to measure the static stability time (t_s) of modified PVC at 180 °C in air according to ASTM D4202, for t_s reflects the HCl release. The samples were prepared by crushing the modified PVC into powders. Thermogravimetric analysis (TGA) measurements were performed using a thermogravimetric analyzer (SDT Q600, TA, USA) from 40 °C to 600 °C at a heating rate of 10 K/min under nitrogen atmosphere.

Transparency and discoloration of rigid PVC

Transmittance spectra of PVC discs of 1 mm in thickness and 25 mm in diameter were measured using a UV-Visible spectrometer (CARY 100 bio, USA) over a wavelength range 200–800 nm at room temperature. The discs were aged in an oven at 180 °C, and the extents of discoloration were tested every 5 min by using a precise color reader (HP-200, Chin. Spec., China).

Characterization of the plasticizing effect and tensile strength

Fusion behavior of modified PVC was measured by using a Brabender torque rheometer. The parameters of fusion (fusion time, minimum torque and fusion torque) were recorded according to the method mentioned everywhere^[11, 17]. Tensile tests were performed using a universal machine (CMT4202, SANS Test Machine Co. Ltd., Shenzhen, China) according to GB16421-1996 with a crosshead velocity of 30 mm/min at room temperature. At least five specimens were tested for each set of samples.

RESULTS AND DISCUSSION

FTIR spectra of La-complex $\text{La}(\text{AA})_3$, ionomer PMMA-4.2La and PMMA are shown in Fig. 2. The spectrum of La-complex exhibits two peaks at 1641 cm^{-1} and 1440 cm^{-1} belonging to C=C double bond and asymmetrical stretch of methylene, respectively. The peaks at 1544 cm^{-1} and 1365 cm^{-1} are assigned to the asymmetrical and symmetrical stretching vibrations of $-\text{COO}-$, respectively. A wavenumber difference 179 cm^{-1} indicates a bidentate chelating coordination of $-\text{COO}-$ to $\text{La}(\text{III})$ ^[18, 19]. Compared to the spectrum of PMMA, the ionomer shows bidentate chelating peaks of $-\text{COO}-$ at 1559 cm^{-1} and 1384 cm^{-1} , indicating that $\text{La}(\text{III})$ has been

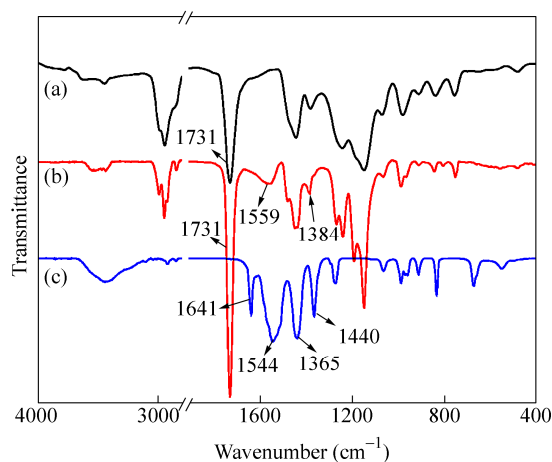


Fig. 2 FTIR spectra of PMMA (a), ionomer PMMA-4.2La (b) and La-complex (c)

incorporated into the ionomer chains. In addition, both PMMA and the ionomer show a characteristic peak at 1731 cm^{-1} belonging to $\text{C}=\text{O}$. These characteristic peaks demonstrate that the La-complex is copolymerized with MMA to generate the ionomer PMMA-XLa.

XPS spectrum is applied to compare the chemical changes of the ionomers, as shown in Fig. 3. PMMA exhibited carbon and oxygen, characteristic of its molecular structure. Besides carbon and oxygen, the ionomer PMMA-4.2La exhibits characteristic peaks in the regions of 90–120 and 830–860 $\text{eV}^{[20]}$, evidencing the presence of lanthanum element in the ionomer.

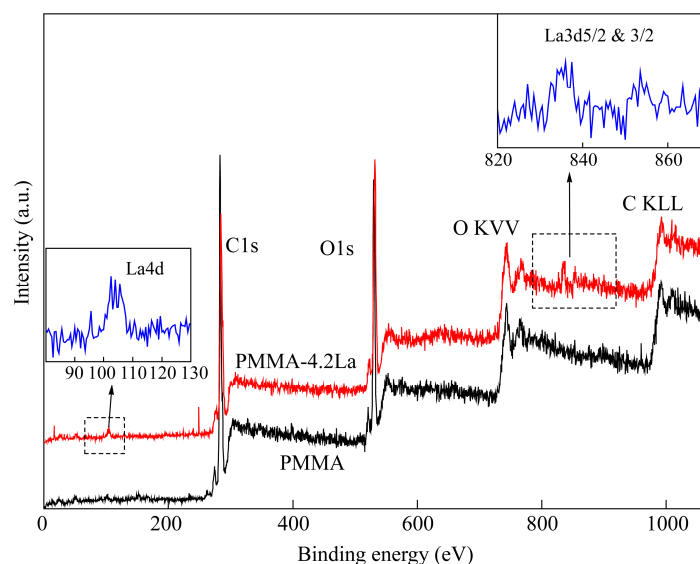


Fig. 3 XPS spectra of PMMA and PMMA-4.2La

Figure 4(a) represents the influence of investigated stabilizers on t_s of modified PVC. The histogram shows that LaSt_3 exhibits greater stabilizing efficiency (54 min) than the other stabilizers because of its higher La(III) content. As increasing La(III) content in the ionomers, t_s tends to increase first and decrease later and exhibits a maximum of $t_s = 48\text{ min}$ at 4.2 wt% La(III). The $\text{LaSt}_3/\text{PMMA}$ mixture with the La(III) and PMMA contents same as PMMA-4.2La, however, exhibit a slightly inferior stabilizing efficiency ($t_s = 46\text{ min}$).

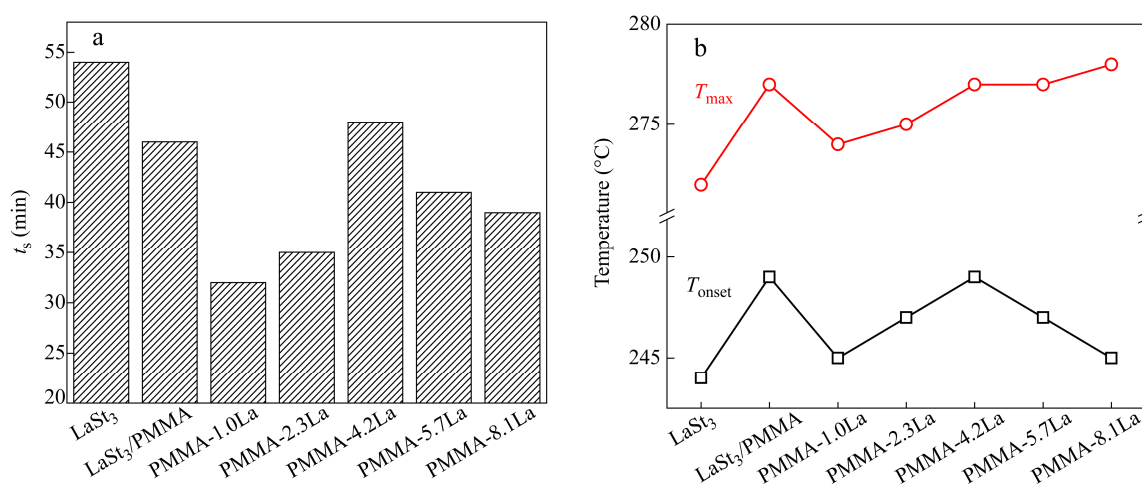


Fig. 4 Static stability time t_s (a) and thermal decomposition temperatures at 5 wt% weight loss T_{onset} and at the maximum degradation rate T_{max} (b) for modified PVC

TGA was implemented for estimating effect of the ionomers on thermal degradation of modified PVC, and the results are shown in Fig. 4(b). The modified PVC containing LaSt₃ exhibits the lowest temperatures at 5 wt% weight loss and at the maximum degradation rate, T_{onset} and T_{max} . The combination of LaSt₃ and PMMA significantly improves T_{onset} and T_{max} in comparison with LaSt₃ because PMMA could stabilize PVC by producing free radicals to restrain the unzipping PVC chains^[21]. The ionomers can efficiently improve T_{onset} and T_{max} compared to LaSt₃ and the results are comparable to those of the LaSt₃/PMMA mixture when the ionomer contains 4.2 wt% La(III). It is shown that the ionomer with an optimized La(III) content could retard the PVC degradation.

Figure 5(a) shows UV-Vis transmittance spectra of the modified PVC discs. For the discs containing LaSt₃ or LaSt₃/PMMA mixture, transmittance below 400 nm is nearly zero and the value between 400 nm and 800 nm is smaller than 30%. The low transmittance is related to the production of a plenty of polyene sequences during processing and to the fogging of the LaSt₃ compound with a poor compatibility to PVC. On the other hand, the ionomers have a good compatibility with PVC, which restrains the migration capability and improve transparency of the PVC discs in the visible light region. The modified PVC shows the highest transparency in the visible region when the ionomer contains 2.3 wt% La(III).

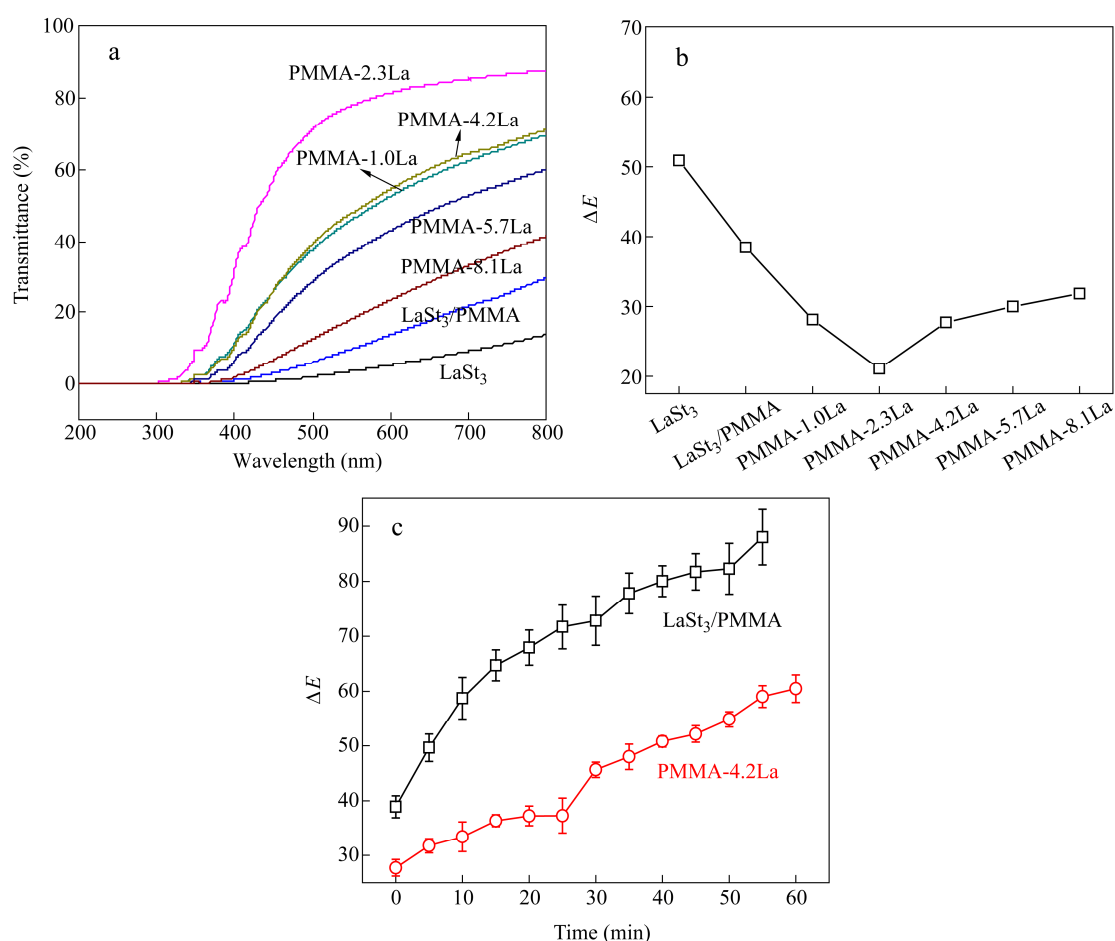


Fig. 5 UV-vis transmittance spectra (a), initial discolorations (b), and time dependence of discoloration (c) at 180 °C for the modified PVC samples

The initial discolorations of the modified PVC discs are shown in Fig. 5(b), where ΔE representing chromatic aberration is defined as the value of color change of sample with respect to a standard white plate. The

ΔE is about 51 for PVC stabilized with LaSt_3 . Usage of LaSt_3 /PMMA mixture or ionomers could reduce ΔE and the smallest ΔE is obtained when PMMA-2.3La is cooperated in the compound. During PVC compounding, LaSt_3 could form complex with ZnSt_2 in the formula to inhibit the polymer esterification depending on the free ZnSt_2 ^[22]. It seems that the ionomers have a low reaction activity with ZnSt_2 so that they have a little effect on the stabilization function of ZnSt_2 to restrain the discoloration of PVC at the beginning of processing^[14]. Figure 5(c) shows the time dependence of ΔE for the modified PVC containing LaSt_3 /PMMA mixture and PMMA-4.2La with the same La(III) content. At the same aging time at 180 °C, the ionomer could lower the PVC discolorations strongly in comparison with the LaSt_3 /PMMA mixture, indicating that the ionomers can benefit the long-term stabilization of PVC.

The processing rheology of modified PVC resin is characterized by a torque rheometer. Figure 6 illustrates fusion times and fusion and minimum torques of modified PVC processed at 180 °C at 65 r/min for 6 min. The sample stabilized with LaSt_3 exhibits the highest fusion time (95 s) and the smallest torques among the investigated stabilizers. This metal salt of fatty acid, as a lubricant, together with paraffin wax incorporated in the compound could form an interface encompassing the PVC particles, which inhibits an efficient transmission of shear stress, thus generating low fusion torques and retarding the fusion of PVC^[23]. Adding PMMA as a processing acid could reduce fusion time and improve torques because PMMA could modify both the inter-grain coefficient of friction and the packing density of PVC^[13]. In comparison with LaSt_3 in the presence or the absence of PMMA, the ionomers could sufficiently reduce the fusion time and improve the torques. At an equal amount of PMMA incorporated in the formula, the fusion time of PMMA-4.2La (30 s) is much smaller than that (72 s) of LaSt_3 /PMMA mixture. The ionomers could provide a strong ion-dipole interaction with PVC chains, which accelerates the PVC fusion during processing^[24].

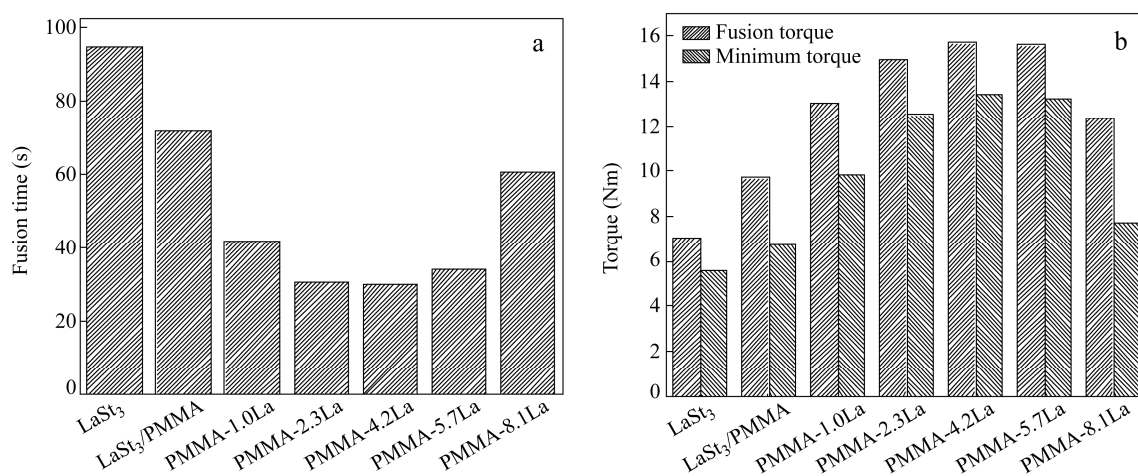


Fig. 6 Fusion time (a) and fusion and minimum torques (b) of modified PVC processed at 180 °C and 65 r/min

Figure 7 shows tensile strengths of reinforced PVC sheets. To achieve good mechanical properties, grain boundaries must be eliminated and the PVC microparticles must be altered and compacted together^[25]. LaSt_3 as a lubricant to PVC can weaken interactions of inter-grains of PVC, resulting in a low tensile strength of 52 MPa. PMMA and ionomers could promote PVC fusion and thus improve tensile strength. The ionomers combine the advantages of thermal stabilizer (La) and processing aid (PMMA), which could restrict the PVC degradation during processing and thus yield a higher tensile strength. The processed PVC sheet exhibits the highest strength when the ionomers have 2.3 wt%–4.2 wt% La(III).

As aforementioned, the ionomers with 2.3 wt%–4.2 wt% La(III) combining the virtues of PMMA and LaSt_3 could be used as a multifunctional aids to modify PVC resins. The beneficial effects of ionomers are ascribed to the stabilization function of the lanthanum carboxylate units like traditional thermal stabilizer LaSt_3 and the

PMMA segments promoting PVC plasticization during thermal processing. Compared to LaSt_3 , the macromolecular character of ionomer restrains its migration capability and reaction activity with ZnSt_2 , which makes it retard the PVC initial discoloration and improve PVC transparency in the visible light region. Besides, the PMMA segments being compatible to PVC could facilitate lanthanum carboxylates to maximize their stabilization function efficiency, leading to further reduced decoloration rate. Meantime, ionomers provide a strong ion-dipole interaction with PVC chains for accelerating the PVC fusion and improving tensile strength. However, the functional performance of the ionomers is limited at higher La(III) contents, which could be ascribed to the formation of a crosslinked structure due to the aggregation of La(III) ions and the reduced compatibility between PVC and the crosslinked ionomers.

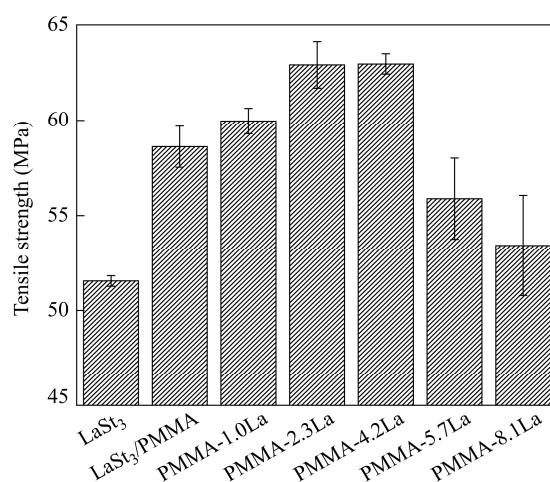


Fig. 7 Tensile strengths of modified PVC stabilized with the tested stabilizers

In short, PMMA-based ionomer processing aids are expected to overcome the shortcomings (migration) of small molecular thermal stabilizers, simplify the compositions of modified PVC and optimize the product performance. The results should be helpful for understanding the behaviors of other combinations of lanthanum-based thermal stabilizers like La-complex and its mixture with MMA or PMMA. It should be pointed that the low content of the ionomers added in the PVC would not significantly influence the morphology, glass transition, tensile modulus and impact strength of PVC resin. A combination of the ionomers with impact modifiers^[26, 27] and nanoparticles^[28] is expected as an advantaged strategy for developing high-performance PVC materials.

CONCLUSIONS

The ionomers synthesized by free radical polymerization behave as a kind of multifunctional processing aids for the modified PVC. In comparison with LaSt_3 , the ionomers with a proper La(III) content could improve the thermal stability of PVC more efficiently and accelerate PVC plasticization during processing, which is favorable for producing rigid PVC products with better initial discoloration, high transparency and high tensile strength.

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