Evaluation of Poly(4-Methyl-1-Pentene) as a Dielectric Capacitor Film for High-Temperature Energy Storage Applications

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ABSTRACT: Poly(4-methyl-1-pentene) (P4MP) was characterized to evaluate its viability as a high-temperature dielectric film for capacitors. Detailed investigation of thermal, mechanical, rheological, and dielectric properties was carried out to assess its high-temperature performance and processability. P4MP was melt-processable below 270 °C without degradation and application temperatures as high as 160–190 °C can be achieved. The dielectric constant and loss of melt-processed P4MP films was comparable to biaxially oriented polypropylene (BOPP) capacitor films, although the dielectric strength was lower. Enhancements in dielectric strength up to 250–300% were achieved via solution-processing P4MP films, which could be easily scaled up on a roll-to-roll platform to yield isotropic, free-standing films as thin as 3–5 μm. The influence of crystal structure, crystallinity, and surface morphology of these films on the dielectric properties was examined. The dielectric strength was further increased by 450% through biaxial stretching of solution-cast films, and a Weibull breakdown field of 514 V/μm was obtained. The dielectric constant was very stable as a function of frequency and temperature and the dielectric loss was restricted to <1–2%. Overall, these results suggest that BOP4MP is a promising candidate to obtain similar energy density as a BOPP capacitor film but at much higher operating temperatures. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. 2017, 00, 000–000

KEYWORDS: capacitor; dielectric; energy storage; morphology; poly(4-methyl-1-pentene); roll-to-roll (R2R)

INTRODUCTION With the world’s ever-growing energy demands, effective energy storage, utilization, and management have become one of the most important and challenging areas of the twenty-first century. Research in the area of energy storage devices such as batteries, fuel cells, supercapacitors, and dielectric capacitors has increased significantly in the last two decades.1–4 The requirements for new generation telecommunication devices, electric/hybrid vehicles, electromagnetic weaponry, and other power electronics applications for commercial, industrial, and military use are projected to drive the growth of the existing technologies for energy storage devices. Compared to batteries and fuel cells, dielectric capacitors provide a high power density but relatively low energy density. Increased power density and operating frequency of power electronics required development of high energy density capacitors. Therefore, recent research in the area of dielectric capacitors is intended to increase energy density while minimizing the energy loss.5–11 The maximum energy that can be stored in a dielectric medium is given by

\[ W = \int_0^{E_{\text{max}}} EdD = \frac{1}{2} \varepsilon_0 \varepsilon_r E_{\text{ds}}^2 \]  

if the dielectric constant is independent of field, as is usually the case. Here \( E \) is the externally applied electric field (input), \( D \) is the electric displacement field (output) within the medium, \( \varepsilon_0 \) is the permittivity of vacuum (8.85 × 10⁻¹² F/m), \( \varepsilon_r \) is the relative permittivity or dielectric constant of the medium, and \( E_{\text{ds}} \) is the dielectric strength or the breakdown field strength of the medium.

The present state-of-the-art polymer for high-voltage, high-energy-density capacitor is dominated by metallized biaxially oriented polypropylene (BOPP).10–12 BOPP provides a high breakdown field of 600–750 V/μm for ~10-μm-thick films,5,13 a very low dielectric loss (<0.01%), and good self-healing characteristics.11,12 BOPP is especially suitable for applications that require high voltage, short pulse length, and high repetition rates. BOPP, however, has two major limitations. First, it has a low dielectric constant (~2.2) that

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limits the stored energy density to 3–5 J/cm³ at breakdown.\textsuperscript{5,13} Second, the usage of BOPP capacitors is limited to temperatures below 105 °C because PP has a peak melting point of ~162 °C with a relatively low melting onset between 85–100 °C. The thermomechanical stability, and therefore, the dielectric strength decreases dramatically above 85 °C.\textsuperscript{14} In spite of these drawbacks, PP consumption for capacitor films has almost doubled in the last 5 years.

Although polymers such as poly(ethylene terephthalate) (PET) and poly(vinylidene fluoride) (PVDF) have shown promise, these polymers suffer from critical property defects that limit their use in industrial capacitors. While PET provides a higher dielectric constant than BOPP, and has a higher operating temperature of 125 °C compared to 105 °C for BOPP, it suffers from poor thermal stability and a high dielectric loss that increases with temperature and pressure.\textsuperscript{1,15} PVDF possesses one of the highest dielectric constants (~10) among polymers due to the polar –CF₂ groups, with a dielectric breakdown strength of 200 V mm⁻¹. However, PVDF suffers from high dielectric hysteresis losses that severely limit the maximum energy density that can be obtained from this polymer. In addition, PVDF exhibits an unstable dielectric constant which varies with voltage, temperature and frequency. Some of these problems have been mitigated with the use of PVDF based copolymers, such as poly(vinylidene fluoride-co-trifluoroethylene-co-chlorotrifluorooxyethylene), and energy density as high as 17 J/cm³ has been reported\textsuperscript{6–8,10} but the energy losses are still high. Use of such copolymers is therefore limited to low repetition rate (low-voltage, low-frequency) applications.

Apart from PET and PVDF, alternate polymer chemistries are also being explored to find a suitable match to the capacitor industry requirements such as those of high-energy high-temperature dielectrics (>200 °C).\textsuperscript{3,14–19} Poly(ether imide) (PEI), poly(phenylene sulfide) (PPS),\textsuperscript{14} polyacylamides,\textsuperscript{16} poly(ethylene naphthalate) (PEN),\textsuperscript{17} poly(carbonate) (PC), poly(tetrafluoroethylene) (PTFE), and poly(sulfone)\textsuperscript{18} are few of the polymers that have been studied. However, compared to BOPP, most of these polymers suffer from limitations as described above for PET or PVDF, or provide comparable energy densities but with poorer mechanical and thermal properties so that BOPP is still considered to be a superior dielectric.

One of the polymers that seems interesting as a high-temperature dielectric is poly(4-methyl-1-pentene) (P4MP). P4MP is a high temperature semicrystalline polyolefin that has not yet been evaluated properly as a high-temperature polymer dielectric for capacitor applications. It has been cited as a capacitor film in several patents,\textsuperscript{20,21} but it does not appear from those patents that the dielectric properties of P4MP film have been evaluated or any capacitor has actually been built with P4MP. In addition to high temperature, P4MP provides the benefit of being one of the lowest density (0.83 g/cm³) polyolefins available commercially and is therefore useful for critical applications such as aerospace and military where weight reduction is attractive.

In this work, the thermal, mechanical, and rheological properties of two commercial grades of P4MP were investigated to evaluate its processability for melt extrusion and further biaxial stretching. Thin films were prepared through melt processing and solution processing and their dielectric properties were compared. The real-time dynamics during drying of solution-processed P4MP films were studied in a customized instrumented platform which yielded insights into the surface morphology formation in these films and provided optimum conditions for scaling thin film manufacturing on a R2R platform. Finally, the effect of crystal structure, percent crystallinity, surface morphology and biaxial stretching on the dielectric properties of P4MP was evaluated.

**EXPERIMENTAL**

**Materials**

Two grades of P4MP were provided by Mitsui Chemicals Ltd.—TPXTM MX0020 and TPXTM DX845 (hereafter referred to as MX and DX, respectively). The two grades varied in their comonomer content, which was ~8 mol % for MX and <5 mol % for DX. However, the comonomer chemistry was proprietary and was not provided. Typical comonomers used with 4-methyl-1-pentene during polymerization include pentene, hexene, octene, decene, and octadecene.\textsuperscript{22} The polymers were provided in pellet form and were used as-is. Cyclohexane (≥99.8%, C100307) and toluene (≥99.5%, 179418) were purchased from Sigma-Aldrich Co., and cyclopentane was purchased from Fisher Scientific Co. (99% pure, AC111480025). All solvents were used as-is.

**Characterization**

The viscosity-average molecular weight ($M_v$) was calculated from the intrinsic viscosity measurements performed with a Cannon-Ubbelohde viscometer using decahydrornaphthalene (Decalin) solution at 135 °C with a standard of pure P4MP. $M_v$ was estimated by the Mark–Houwink equation using the constants for P4MP, $[\eta] = K \times M_v^x$, where $K = 1.94 \times 10^{-5}$ (L/g) and $x = 0.81$.\textsuperscript{22}

Thermal characterization was performed using a TA Instruments Q-200 differential scanning calorimeter (DSC), a TA Instruments Q-50 thermogravimetric analysis (TGA), and TA Instruments Q-800 dynamic mechanical analysis (DMA).

DSC was used to measure the glass transition temperature ($T_g$), the crystallization temperature ($T_c$), the melting point ($T_m$), and the heat of fusion ($\Delta H_f$) of the polymers. Before the measurements, temperature calibration was performed using an Indium standard ($T_m = 156.6$ °C). All heating and cooling scans were made from −20 °C to 260 °C at a rate of 10 °C/min. $T_g$ was defined as the inflection point in the change of the heat capacity associated with the glass transition. The melting point ($T_m$) and the crystallization point ($T_c$) were defined as the peak of the melting endotherm and the cooling exotherm, respectively. Mass fraction crystallinity of the polymer ($\phi_m$) was calculated from the ratio of $\Delta H_f/\Delta H_{f,P4MP}$ where $\Delta H_f$ was the area under the DSC melting endotherm and $\Delta H_{f,P4MP}$ is the enthalpy of fusion for a 100%
crystalline P4MP, which is reported to be 5.20 kJ/mol (or 61.85 J/g).23

The thermal stability of the polymers was checked by TGA using a heating rate of 20 °C/min and a nitrogen atmosphere. Isothermal hold-up measurements were also carried out from 180–280 °C under nitrogen atmosphere. The temperature was increased in increments of 20 °C, and isothermal conditions were maintained for at least 10 hours to check long-duration thermal stability. DMA was used to measure the temperature and frequency-dependent dynamic, \( E'(T_f) \), and loss, \( E''(T_f) \), moduli and to identify the secondary-transition temperature associated with the slip-page of crystal planes, \( (T_c)_r \).24 \( T_c \) was defined as the temperature of the peak in the loss modulus, \( E'(T_f) \), associated with that transition. The DMA measurements were performed in tension using a multiple-frequency strain mode and frequencies of \( f = 1, 100 \) Hz from −150 °C to 230 °C, a heating rate of 2 °C/min and a strain of 1%.

In addition to the thermal properties, rheological properties of a polymer such as elasticity and viscosity and their temperature-dependence are also critical for thin film manufacturing. Hence rheological characterization was performed to check the melt processability of P4MP and to find the correct temperature range for the same. Linear viscoelastic (LVE) properties were measured with a TA Instruments ARES G2 rheometer using small amplitude oscillatory shear (SAOS) measurements from 230 to 300 °C at frequencies (\( \omega \)) = 0.1–100 rad/s and strain amplitudes of 5–10% on a 25 mm parallel-plate fixture. Strain-sweeps were performed at 250 °C and 100 rad/s to determine the LVE limit, and master-curves were constructed using time-temperature superposition (TTS) with a reference temperature, \( T_r = 250 ^\circ \text{C} \). Steady shear experiments were carried out from 230 to 280 °C with the ARES G2 rheometer using a 25 mm cone-and-plate fixture with a cone angle of 0.04 rad. Viscosity at higher shear rates from \( 10^2 \) to \( 10^4 \) s\(^{-1} \) was measured using a Bohlin (Malvern) RH7 capillary rheometer from 250 to 270 °C. A capillary die with \( L/D = 32:1 \) was chosen so that the Bagley correction was negligible and could be ignored.25 The Rabinowitch–Mooney correction was applied to the apparent shear rate to calculate the true shear rate and the true viscosity.

The crystal structure in P4MP thin films (10–20 \( \mu \text{m} \)) was characterized with wide-angle X-ray diffraction (WAXD) using a Bruker AXS D8 Goniometer with a CuK\( _\alpha \) radiation (\( \lambda = 0.1542 \text{nm} \)). The surface morphology of those films was characterized using a JEOL-7401 (Japan Electron Optics Laboratory) scanning electron microscope (SEM).

The dielectric constant and dielectric loss were measured isothermally using time-domain dielectric spectroscopy (TDDS). Approximately 10–20-\( \mu \text{m} \)-thin film with 2 cm\(^2\) exposed area was used, and measurements were conducted at 10 V from a frequency of \( 10^{-3}–10^4 \) Hz at room temperature (RT), 50, 100, and 150 °C. The dielectric breakdown measurements were performed at room temperature under the ramp DC high voltage with a constant ramping rate of 300 V/s. The high voltage was generated by HV power supply (Stanford Model PS375) which was controlled by a ramp signal generator. The P4MP films were sandwiched between two metallized BOPP films which were used as electrodes with the metallization side in contact with the P4MP film surface. An active area of 2 cm\(^2\) was used and it was controlled through a 100 \( \mu \text{m} \) polyimide mask to protect against discharge between the two electrodes. The dielectric strength was characterized using the two-parameter Weibull cumulative distribution function (CDF).26

\[
F(x) = 1 - \exp \left( -\left(\frac{x}{\eta}\right)^{\beta} \right)
\]

(2)

where \( \eta \) is the Weibull characteristic breakdown field defined as the breakdown field at 63.2% probability of breakdown (\( x = \eta, F(x) = 0.632 \)), and \( \beta \) is the Weibull slope parameter which is a measure of dispersion in the data. The \( F(x) \) value for each \( x \) (breakdown strength in the current case) was assigned based on its position (\( i \)) among the \( N \) ordered \( x \)-values, and was calculated using the Benard’s (empirical) approximation,

\[
F_i = \frac{i - 0.3}{N + 0.4}
\]

(3)

Sample Preparation

**Melt Processing Thin Films**

Melt processing of P4MP films was carried out by compression molding the polymer pellets at 260 °C under vacuum using the TMP vacuum compression press. The mold was placed between preheated platens and allowed to thermally equilibrate for 10 min. followed by compression at 20,000 psi for 5 min. The sample was then cooled back to room temperature at 40 °C/min. Approximately 50-\( \mu \text{m} \)-thin films were obtained using this procedure. The films were prepared either without a substrate (i.e., the polymer film was in contact with stainless-steel surface of the mold on both sides) or using a 100-\( \mu \text{m} \)-thick polyimide (Kapton®) substrate.

**Solution Processing and Real-Time Dynamics**

Apart from melt processing, P4MP thin films can also be processed from a solution under appropriate conditions. While most of the common polyolefins such as polypropylene or polyethylene are not solution-processed commercially, P4MP offers a unique opportunity due to its relatively high solubility in common nonpolar solvents at temperatures as low as 35–40 °C. Thin films (10–20 \( \mu \text{m} \)) of P4MP were prepared with a combination of different nonpolar solvents and casting temperatures. The real-time drying dynamics of these films were studied using a custom-built solvent casting platform whose schematic is shown in Figure 1. The instrumentation and working details are provided elsewhere.27

With this setup, film thickness, weight, surface temperature, birefringence (in-plane and out-of-plane), and % transmission through the film were measured while the film was drying. These measurements provided information about the real-time development of local chain orientation, suitable
conditions for solvent-casting (e.g., casting temperature or the initial polymer concentration in solution), and the time required to reach a steady-state behavior. This information was then used to replicate favorable conditions for preparing larger films on a roll-to-roll platform as described below.

**Roll-to-Roll (R2R) Fabrication**

Large-scale R2R fabrication of P4MP films was successfully accomplished by blade-coating polymer solution under favorable conditions obtained from the batch processing studies described above. A nominal thickness of 10–20 μm was used, although films as thin as 3–5 μm could also be obtained. Films were cast on a PET (Mylar®) substrate with a carrier speed of 50 cm/min using a 1200 wide doctor blade. The films were dried overnight under atmospheric pressure, detached from the substrate, and collected on a separate roll. TGA measurements were performed to confirm the absence of solvent in these films. The films were then used for dielectric measurements and further processing by biaxial stretching.

**RESULTS AND DISCUSSION**

**Thermal Properties**

The physical and thermal properties of the MX and DX grades are summarized in Table 1, and their DSC endotherms are shown in Figure 2. MX had a lower crystallization temperature (T_c), melting point (T_m), and crystallinity (ϕ_m) compared to DX. MX had a T_g of 21.1 °C, T_c of 204 °C, and T_m of 225 °C, while DX had a T_g of 204 °C, T_c of 190 °C, and T_m of 207 °C. MX had a lower ϕ_m of 36%, while DX had a ϕ_m of 56%.

**Biaxial Stretching of Solution Cast Films**

Biaxial stretching of P4MP thin films was performed using a modified Iwamoto biaxial stretcher. The instrumentation and working details are provided elsewhere. Samples with dimensions 14 × 14 cm were cut from the cast P4MP films. The biaxial stretching was performed at 50 °C with a constant stretch rate of 15 mm/min to different stretch ratios. The sample was held between the pneumatic clamps with sandpaper sandwiched between the film and clamp to avoid slip and tear, heated up to the stretching temperature, thermally equilibrated for at least 10 min, equibiaxially stretched and cooled back slowly to room temperature.

**TABLE 1 Physical and Thermal Properties of the Two Commercial Grades of P4MP**

<table>
<thead>
<tr>
<th>Grade</th>
<th>Comonomer (mol %)</th>
<th>M_a (kDa)</th>
<th>ρ (g/cm³)</th>
<th>T_0,deg (°C)</th>
<th>T_g (°C)</th>
<th>T_c (°C)</th>
<th>T_m,onset (°C)</th>
<th>T_m (°C)</th>
<th>ϕ_m (%)</th>
<th>T_b (°C)</th>
<th>T_a* (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX</td>
<td>~8</td>
<td>155</td>
<td>0.834</td>
<td>341</td>
<td>21.1</td>
<td>204</td>
<td>160</td>
<td>225</td>
<td>36</td>
<td>−139</td>
<td>200</td>
</tr>
<tr>
<td>DX</td>
<td>&lt;5</td>
<td>125</td>
<td>0.833</td>
<td>361</td>
<td>27.6</td>
<td>207</td>
<td>190</td>
<td>234</td>
<td>56</td>
<td>−141</td>
<td>217</td>
</tr>
</tbody>
</table>

_a Calculated from [η] = K × M_a^z, where K = 1.94 × 10^{-5} and z = 0.81.\(^{21}\) [η] was measured in decalin at 135 °C.

_b From TGA at 2 °C/min.

c From DSC, heat and cool at 10 °C/min.

d From DMA, heating at 2 °C/min, f = 100 s^{-1}.
compared to DX, which was attributed to a higher comonomer concentration in MX and similar to our previous observations from polypropylene copolymers.\textsuperscript{29,30} A higher comonomer concentration also resulted in a higher plastification of MX, thereby, lowering its glass transition ($T_g$) as well.

While the $T_m$ was higher than 220 °C for both the grades, the onset of melting occurred at a much lower temperature ($T_{m,onset}$): 160 °C for MX and 190 °C for DX. A difference of 10 °C between $T_m$ but 30 °C between $T_{m,onset}$ of the two grades indicated that the MX grade had a smaller average size of the crystal but a much broader crystal size distribution. A low $T_{m,onset}$ might limit the use of a polymer film to temperatures much lower than $T_m$ due to its thermomechanical stability. For example, a stretched polymer film heated above its $T_{m,onset}$ might shrink, or experience considerable shrinkage stresses if spatially constrained. That occurs because the oriented polymer chains experience an entropic force to revert back to their coiled/unoriented configuration (commonly referred to as the “memory” effect). Simultaneously, melting of the smaller crystals and their recrystallization into bigger crystals abets the above process. Shrinkage of a dielectric polymer film or development of mechanical stresses during a capacitor operation is highly undesirable and should be avoided. It is because of this reason that the maximum operational temperature of BOPP dielectric film is restricted to 105 °C, the $T_{m,onset}$ and $T_m$ of PP being ~85–100 °C and ~162 °C, respectively. The capacitor then needs to be suitably deroated at higher temperatures. One of the methods to enhance the thermomechanical integrity of a polymer film beyond $T_{m,onset}$ is to stretch it at a temperature between $T_{m,onset}$ and $T_m$ and subsequently heat-set the film where the crystallinity is enhanced and oriented amorphous chains are relaxed. Such a procedure may ensure thermomechanical stability till the stretch temperature. An optimum stretch temperature can be measured using dynamic mechanical analysis and is discussed later. Heat-setting, however, was not pursued in this study and will be a subject of future studies.

The thermal degradation temperature ($T_{deg}$), which was defined as the temperature corresponding to a 1% mass loss in TGA, was >340 °C for both the grades (plots not shown). Although such a high degradation temperature seems promising for high-temperature dielectric applications, isothermal hold-up measurements suggested otherwise. Figure 3 shows the weight loss as a function of time for MX and DX grades from 180 to 280 °C. Both the grades exhibited reasonable thermal stability up to 240 °C but degradation accelerated beyond that temperature.

The dynamic mechanical storage modulus ($E'$) and loss tangent (tan $\delta$) in three flow regimes—glassy, rubbery and melt—are shown in Figure 4. In the glassy regime, $E'$ for both MX and DX grades was similar even though the crystalinity was higher for DX by 20%. This indicated an almost equivalent contribution from the crystalline and the amorphous domains in the glassy state. In the rubbery region, the amorphous regions were much softer and mobile compared to the crystals, which resulted in an increase in $E'$ for the DX grade. In the melt state, where the crystals were no longer present, $E'$ was again higher for DX due to a higher molecular weight. As most polymer films are required to be

![Figure 2: DSC endotherms for the MX and DX grades of P4MP. The curve for DX is shifted vertically for clarity. Inset shows the chemical structure of P4MP.](image)

![Figure 3: Isothermal TGA measurements for P4MP grades MX and DX. Both grades lose thermal stability above 240 °C. Thermal stability for DX is relatively higher compared to MX.](image)
mechanically wound under high tension in capacitors to ensure uniform contact between the wrapped layers without any air entrapment, they should possess good mechanical properties such as a high elastic modulus at room temperature. From Figure 4, the elastic modulus at room temperature (25 °C) is measured to be ~1.7 GPa for P4MP which is close to the value reported previously by us for PP.

The loss tangent showed three distinct thermal transitions for P4MP. These values are tabulated in Table 1. The β-relaxation peak at the lowest temperature \( T_β \) is associated with the localized thermal motion of the side-chains. \( T_β \) was similar for MX and DX grades indicating that the presence of copolymer did not affect the localized motion of the side-chains. The second peak corresponds to the glass-transition temperature, and a higher \( T_g \) for DX was consistent with the DSC results. The third peak corresponds to the \( α^* \)-transition that is generally observed in semi-crystalline polymers between the \( T_g \) and \( T_m \) and is associated with the slippage of crystal planes over one another or the motion of the crystallites. Practically, \( T_{α^*} \) provides an estimate of the processing temperature that is optimum for orienting the polymer chains through uniaxial or biaxial stretching. \( T_{α^*} \) was higher for the DX grade probably due to its higher crystallinity and bigger crystal size which required a higher thermal energy for producing crystal-crystal slip at a given frequency of deformation.

The results from Figures 2–4 show promise for the use of P4MP thin films at high temperatures up to at least 160 °C. The high temperature limit is controlled by the melting onset of the polymer which can be substantially increased by decreasing the comonomer content. In addition, the polymer film can be biaxially stretched above 200 °C in the molten state and thermally annealed in the stretched state to further raise the usage temperature.

**Rheological Properties and Processing Temperature**

The storage \( (G') \) and loss \( (G'') \) moduli obtained using small-amplitude oscillatory shear (SAOS) measurements are shown in Figure 5 for the two P4MP grades at a reference temperature \( (T_r) \) of 250 °C. Each curve is a master-curve constructed using time-temperature superposition (TTS) by shifting the isothermal data horizontally and vertically using the shift factors \( α_T \) and \( b_T \), respectively. The validity of TTS implied that the presence of 5–8 mol % comonomer did not affect the temperature scaling of relaxation times for the polymer chains, even though it had a plasticizing effect on the polymer flow behavior. Both elasticity and viscosity, that is, \( G' \) and \( G'' \), were higher for the DX grade. The relaxation time \( (τ_α) \), calculated from the inverse of the cross-over frequency of \( G' \) and \( G'' \), was also higher for DX \((0.10 \text{ s}) \) than MX \((0.05 \text{ s}) \). Higher \( G' \), \( G'' \), and \( τ_α \) for DX were attributed to its higher molecular weight and lower comonomer content than MX. The terminal regime (corresponding to a Newtonian-like behavior of the polymer chains, where \( G' \propto ω^2 \) and \( G'' \propto ω \)) was not observed for either of the polymers.

The flow activation energy, \( ΔE \), of the polymers was determined by using Arrhenius analyses, eqs 4 and 5, of the temperature dependence of the frequency shift factors \( (α_T) \) used to construct the LVE master-curves,

\[
τ_α = A e^{(ΔE/RT)}
\]

\[
ln(α_T) = ln(τ_r/τ_α) = ln(η_0/η_α) = \frac{ΔE}{R} \left( \frac{1}{T} - \frac{1}{T_r} \right)
\]

where \( τ_α \) is the terminal relaxation time, \( η_0 \) is the zero-shear viscosity, \( T \) is the temperature of interest, \( T_r \) is the reference temperature (250 °C).
temperature, and $R$ is the universal gas constant. $\Delta E$ is a measure of the potential energy barrier to translation of the monomer segments and should be independent of the molecular weight for a specific homopolymer above a critical molecular weight of 2–3 times the entanglement molecular weight, $M_e$.34–36 which is ~8.8 kDa for P4MP based on the value for poly(pentene)).37 The Arrhenius plots from the SAOS measurements and calculated values of $\Delta E$ are shown in Figure 6(a) for MX and DX. The linearity of the plots indicates an activated process for flow. Although an Arrhenius dependency was followed, two different values of $\Delta E$ were obtained depending upon the temperature range. $\Delta E$ was 77 kJ/mol for DX from 240–270 °C and 85 kJ/mol for MX from 230–280 °C. Above those respective temperatures, $\Delta E$ increased to 211 kJ/mol for MX and 157 kJ/mol for DX, which was attributed to the polymer degradation at higher temperatures. Although the SAOS measurements were made within a short time span of 10–20 min, polymer degradation was still possible above 270–280 °C in that time span, as indicated by the TGA data in Figure 3. It is interesting to note that the activation energy of other polyolefins (PE, PP, LDPE, etc.) is almost half that of P4MP,38,39 that is, the melt viscosity of P4MP is highly sensitive to a temperature change.

The shear viscosity for the two grades at a reference temperature of 250 °C is compared in Figure 7. The steady-shear viscosity $(\eta(\dot{\gamma}))$ was obtained from the cone-and-plate and capillary flow measurements. The dynamic viscosity $(\eta^*(\omega))$ was calculated from SAOS measurements using the equation,

$$\eta^*(\omega) = \frac{G^*}{\omega} = \sqrt{\left(\frac{G'}{\omega}\right)^2 + \left(\frac{G''}{\omega}\right)^2} \quad (6)$$

Each curve in Figure 7 is a master curve that was constructed using time-temperature superposition (TTS) by shifting the isothermal data horizontally and vertically using the shift factors $a_T$ and $b_T$, respectively. Both the polymers displayed a plateau in the shear viscosity at low shear rates, called the zero-shear viscosity $(\eta_0)$, beyond which a shear-thinning behavior was observed. $\eta_0$ was higher for DX (9621 Pa s) compared to MX (6356 Pa s) which was consistent with a higher molecular weight of DX. An overlap of the viscosity data at 250 °C in Figure 7 indicated consistency between the three independent rheological measurements, and validity of the Cox–Merz rule40 for P4MP. An Arrhenius temperature-dependency described by eq 4 was also observed from the steady-shear measurements, and the Arrhenius plots are shown in Figure 6(b). The calculated activation energies and the degradation temperatures for MX and DX grades were consistent with those obtained from the SAOS measurements within experimental error.
The rheology data for P4MP indicates that a precise temperature control in the extruder is required while processing P4MP in the melt state, and that the melt extrusion temperature should be restricted to <270 °C. Given the viscous and elastic behavior of P4MP, its processing into thin films is clearly possible but care has to be taken to prevent any polymer degradation to maintain reproducibility and consistency in the final product.

**Real-Time Dynamics during Drying of Thin Films**

While melt-processing is a viable and easy route for preparing thin P4MP films, another route is solution-processing. Solution processing can yield free-standing P4MP films as thin as 3–5 μm besides providing a better control on the thickness uniformity. Figure 8 shows the drying behavior of a P4MP (MX) film cast from a 5 wt % cyclohexane solution at 22 °C. The mass and thickness changes were nearly linear for the first ~300 s after casting the film [Fig. 8(a)]. The surface temperature dropped by 1–2 °C due to convective cooling by solvent diffusion, but reached back to the initial cast temperature. The film was optically clear until that time as can be observed from the transparent circular region in Figure 8(b). A pseudo “steady-state” was reached after ~500 s of casting the film, where the rate of reduction in the weight and thickness dropped drastically. This was attributed to the formation of a polymer-rich skin layer at the film–air interface as shown by the pictographs in Figure 8(b) (note the change in color of the circular region from transparent to opaque white). That observation was also supported by a decrease in the light transmission through the polymer film from an initial 100% to 43% at 500 s. The diffusion mechanism at $t \sim 400$ s changed from Case I diffusion, which is governed by linear Fick’s first and second law, to a Case II diffusion, which is described by a nonlinear diffusion equation also referred to as the Thomas–Windle model.41,42

The in-plane ($\Delta n_{12}$) and the out-of-plane ($\Delta n_{23}$) birefringence were zero before the skin formation indicating an isotropic state of polymer chain orientation in the cast film [Fig. 8(c)]. However, during and after the skin formation, $\Delta n_{12}$ remained negligibly small, whereas $\Delta n_{23}$ increased to 0.003 (intrinsic birefringence for isotactic P4MP $\sim 0.01$).43 A nonzero $\Delta n_{23}$ might suggest that the polymer chains aligned preferentially in the thickness direction while drying. However, several factors such as the skin layer morphology, skin layer thickness, and the tendency of the polymer to crystallize or phase-separate while drying complicate this observation.

Similar measurements as above were made for different systems involving a combination of polymer concentration, casting temperature, and type of solvent. The results for both MX and DX grades were qualitatively similar. The birefringence values for three different systems—P4MP (MX) films cast with cyclohexane at 22 °C and 65 °C, and with cyclopentane at 22 °C—are compared in Figure 9(a). The in-plane birefringence ($\Delta n_{12}$) for all the systems was low, but the out-of-plane birefringence ($\Delta n_{23}$) increased upon the formation of the skin. However, unlike in the case of cyclohexane at 22 °C, $\Delta n_{23}$ decreased after the skin formation for the other systems. The surface morphology at the skin–air interface observed using scanning electron microscope (SEM) is shown in Figure 9(b) for all the systems. The surface roughness decreased with faster drying conditions that may delay the polymer phase separation for kinetic reasons. A lower surface roughness also explains the higher light transmission through those polymer films, as shown in Figure 9(b), due to lower scattering of light at the skin–air interface. In addition, periodic asperities at the polymer–air interface with an average length-scale comparable to the wavelength of light can give rise to form-birefringence, which may be the case in Figure 9(a). Hence, a nonzero $\Delta n_{23}$ for P4MP film cast with cyclohexane at 22 °C was an artefact caused by the surface (skin) morphology and not due to any preferential chain alignment in the thickness direction. Overall, P4MP thin films had negligible anisotropy in the polymer chain orientation and could be considered isotropic. The isotropy was also confirmed from wide-angle X-ray diffraction (WAXD) measurements discussed in the next section.

**Surface Morphology and Crystal Structure**

Based on the results discussed in previous section, thin films (10–20 μm) of P4MP were prepared on a R2R platform by varying casting conditions such as the temperature of casting (substrate and/or the solution temperature), type of solvent, and the initial polymer concentration in the solution. The surface morphology of these films was characterized using scanning electron microscopy (SEM). Figure 10 shows the effect of varying the casting conditions on the surface morphology of P4MP films at the polymer–air interface. A smoother surface morphology was obtained under faster drying conditions, which was a result of the delay in phase separation of P4MP from the polymer solution due to kinetic reasons.

In addition to the surface morphology, P4MP films exhibited a number of crystal structures that were studied using wide-angle X-ray diffraction (WAXD) and the diffractograms are shown in Figure 11. These diffractograms confirm the overall isotropy of solution-cast films. P4MP exists in 5 crystal modifications with differing crystal structure and/or chain conformation,44–49 which are summarized in Table 2. All 5 modifications were obtained by varying the casting conditions. However, good-quality films were obtained only for crystal modifications I, II, and III. Crystal structure and morphology is known to affect the dielectric properties of ferroelectric polymers such as poly(vinylidene fluoride) (PVDF) and PVDF-based copolymers.8,50 An interesting question, therefore, is the effect of surface morphology and the crystal structure on the dielectric properties of P4MP, which is discussed below.

**Dielectric Properties**

Dielectric properties for the dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), and the loss tangent (tan δ = $\varepsilon''$/$\varepsilon'$) of solution-cast P4MP films is shown in Figure 12. The sample used in Figure 12 is a MX film cast with cyclopentane at 25 °C; the dielectric data for other films were qualitatively similar. The
thermal transitions for this film, obtained from DSC (exo-therm not shown), were a glass-transition ($T_g$) of 27 °C, peak melting point ($T_m$) of 225 °C, and a crystallinity ($\phi_m$) of 18%. The dielectric constant [Fig. 12(a)] varied from 2.8 to 3.0 upon increasing the temperature from RT to 150 °C, but was very stable as a function of frequency and temperature, which is desirable for the capacitor application. A higher $\varepsilon'_c$ than the reported value of 2.122 could be due to the presence of copolymer or some residual solvent in the polymer film. The absence of an upturn in $\varepsilon'_c$ at lower frequencies ($\omega < 1$ Hz) indicates that the interfacial polarization (i.e., electrode polarization (EP) or Maxwell–Wagner–Sillars
FIGURE 9  A comparison of the (a) in-plane ($\Delta n_{12}$) and out-of-plane ($\Delta n_{23}$) birefringence and (b) 0° transmission for P4MP thin films under different casting conditions. The pictures on the right plot are SEM micrographs of the surface morphology (scale bar = 5 µm). [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 10  The effect of varying solution-casting conditions on the surface morphology of P4MP (MX) thin films at the polymer-air interface. A smoother surface morphology was obtained under faster drying conditions. Scale bar corresponds to 5 µm. [Color figure can be viewed at wileyonlinelibrary.com]
(MWS) polarization) was absent in this sample and, therefore, would not contribute to the dielectric loss.

The loss tangent [Fig. 12(c)] was restricted to <0.4% for \( \omega > 1 \) Hz, which is again a desirable characteristic from a capacitor film. A dispersion peak at \( \omega = 5 \) s\(^{-1} \) at RT was attributed to the relaxation by segmental motion of polymer chains as \( T_g \) was close to RT. Upon increasing the temperature above \( T_g \), this dispersion peak moved to higher frequencies, or lower relaxation times, as indicated in Figure 12(c), but the losses were still limited to <0.4%. At lower frequencies, \( \omega < 1 \) Hz, the loss tangent was much higher and increased upon decreasing the frequency and increasing the temperature. In the same frequency range, \( \varepsilon'' \) approached a slope of –1 as shown in Figure 12(b), which suggested that the losses occurred due to DC conduction.

### TABLE 2

<table>
<thead>
<tr>
<th>Crystal Modification</th>
<th>Unit Cell Structure</th>
<th>Unit Cell Dimensions</th>
<th>Chain Conformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Tetragonal</td>
<td>( a = 18.66 ) Å ( c = 13.8 ) Å</td>
<td>7/2 helix</td>
</tr>
<tr>
<td>II</td>
<td>Tetragonal</td>
<td>( a = 19.16 ) Å ( c = 7.12 ) Å</td>
<td>4/1 helix</td>
</tr>
<tr>
<td>III</td>
<td>Tetragonal</td>
<td>( a = 19.36 ) Å ( c = 6.94 ) Å</td>
<td>4/1 helix</td>
</tr>
<tr>
<td>IV</td>
<td>Hexagonal</td>
<td>( a = 22.17 ) Å ( c = 6.69 ) Å</td>
<td>–</td>
</tr>
<tr>
<td>V</td>
<td>Hexagonal</td>
<td>( c = 6.5 ) Å</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 13 compares the dielectric constant and the loss tangent as a function of temperature at $\omega = 100$ Hz for different P4MP films. These films were prepared under varying casting conditions, and the associated crystal structures as well as the surface morphology are indicated in Figure 13. $\varepsilon'$ varied from 2.6 to 2.8 depending upon the film but the overall variation in $\varepsilon'$ was not large. A slight increase in $\varepsilon'$ upon increasing the temperature could be related to the increased polymer chain mobility at higher temperatures. The dielectric losses were restricted below 0.4% and decreased upon increasing the temperature due to a shift of the dispersion peak to higher frequencies at a higher temperature (Fig. 12).

Figure 13 Dielectric constant and loss tangent as a function of temperature at $\omega = 100$ Hz for various P4MP thin films. The crystal modification and the surface morphology of the film for each data are indicated with arrows. Crystal modifications II and II undergo an irreversible transition to a more stable crystal modification I upon annealing at 80 °C and (55–73) °C, respectively.62,63

[Color figure can be viewed at wileyonlinelibrary.com]
12(c)]. For P4MP, an irreversible crystal–crystal transition occurs from modifications II and III into a more stable modification I upon thermal annealing at 80 °C and (55–73) °C, respectively, which essentially changes the polymer chain conformation from a 4/1 to a 7/2 helix without changing the tetragonal crystal structure (Table 2). A change in the crystal modification did not influence the dielectric constant or the loss. This result was not very surprising considering that P4MP is a nonpolar polymer with an overall isotropic dipole orientation in contrast to PVDF, for example, where a change in the polymer chain conformation between different crystal modifications (α, δ, γ, β) causes a change from a nonpolar (α) to a ferroelectric behavior (δ, γ, β). Unfortunately, good-quality P4MP films containing crystal modifications IV and V could not be obtained to compare the effect of tetragonal versus hexagonal unit crystal structure on the bulk dielectric properties in P4MP.

The breakdown strength variation in P4MP films was described by the Weibull distribution shown in Figure 14 with the solid lines being a nonlinear least squares fit of eq 2 to the experimental data. The values of Weibull breakdown strength (η) and the Weibull slope parameter (β) along with the film characteristics are summarized in Table 3. Film surface morphology was the most important factor that affected the breakdown field strength. In general, η was higher for P4MP films with a more uniform surface morphology which is clearly evident from the comparison in Figure 15 for three films. P4MP films prepared by compression-molding without any smooth substrate possessed the least uniform surface morphology and, therefore, had the lowest breakdown strength. Compression-molding with a smooth Kapton (polyimide) substrate reduced some of the surface defects, but few defects such as pits and cavities (encircled in the micrograph) still remained. Therefore the breakdown strength slightly improved. Solution-casting produced films with the most uniform surface morphology and η for those films was almost three times that of compression-molded films without a substrate. This shows that uniformity, and not flatness (height variations), of the surface morphology controlled the breakdown strength of P4MP thin films. While η increased for the solution-cast films, β decreased compared to the compression-molded films indicating a wider dispersion in the breakdown data. However, simultaneous increases in the minimum and maximum breakdown strength of the solution-cast films suggested that there is vast potential for increasing β by further improving the film quality. One method to achieve this, for example, would be to eliminate any external contamination by preparing films in a controlled environment such as in a Clean Room. Overall, even though the solution-casting improved the breakdown strength of P4MP films compared to compression-molding, their characteristic breakdown strength was still one-half compared to that of BOPP (T(BOPP) ~ 700 V/μm) and the slope parameter was even lower (β(BOPP) ~ 15).54

It should be noted that thickness of the solvent-cast films was smaller than the compression-molded films, which itself could result in a higher breakdown strength of solvent-cast films due to less pronounced volume effects.55–57 However, in this study, it was not possible to decouple the surface and volume effects in P4MP films.

Similar to our observations from Figure 13, the type of crystal structure had no effect on the breakdown field strength. Interestingly, percent crystallinity also did not influence the breakdown field strength as observed for compression-molded versus solution-cast films and MX versus DX grades. For example, MX film cast from a 6 wt % cyclopentane solution at 25 °C had a similar Weibull breakdown strength as a DX film cast from 4 wt % cyclopentane solution at 25 °C even though their crystallinities were 18% and 33%, respectively. This result is contrary to the observations made for other polyolefins such as polypropylene58 or polyethylene,59 where the breakdown field strength is observed to increase with increasing crystallinity and that is also consistent with the predictions from the free-volume theory60,61 of dielectric breakdown in polymers. The solution-cast films with lower crystallinity also had a smoother surface morphology indicating that the two were coupled, that is, faster drying conditions that kinetically inhibited phase-separation of P4MP from its solution producing a smoother surface morphology also inhibited regular chain folding into a crystal structure resulting in a lower crystallinity.

**Breakdown-Induced Surface Morphology and Mode of Breakdown**

Examination of the surface morphology after the occurrence of dielectric breakdown revealed an interesting phenomenon that occurred during and after the breakdown. Figure 16 compares the surface morphology of P4MP thin films that were prepared by compression molding at 260 °C without a substrate (a–c) and solution casting at 25 °C with cyclopentane (d–f). The breakdown area appeared to be closer to a
TABLE 3 Summary of the Weibull Breakdown Strength and the Slope Parameter for P4MP Films Along With Their Crystallinity, Crystal Structural, and Surface Morphology

<table>
<thead>
<tr>
<th>Film Preparation</th>
<th>Sample</th>
<th>Crystal Structure</th>
<th>Surface Morphology</th>
<th>Crystallinity $\phi_m$ (%)</th>
<th>Breakdown Strength (V/μm)</th>
<th>Weibell Slope Parameter $b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression-molding MX</td>
<td>260 °C</td>
<td>I</td>
<td></td>
<td>23</td>
<td>64 105</td>
<td>93 10.3</td>
</tr>
<tr>
<td>Solution-casting MX</td>
<td>Cyclohexane 50 °C</td>
<td>III</td>
<td></td>
<td>21</td>
<td>84 365</td>
<td>309 5.5</td>
</tr>
<tr>
<td>Solution-casting MX</td>
<td>Cyclohexane 35 °C</td>
<td>III</td>
<td></td>
<td>20</td>
<td>196 405</td>
<td>355 3.2</td>
</tr>
<tr>
<td>Solution-casting MX</td>
<td>Cyclohexane 25 °C</td>
<td>III</td>
<td></td>
<td>21</td>
<td>134 390</td>
<td>312 4.0</td>
</tr>
<tr>
<td>Solution-casting DX</td>
<td>Cyclohexane 25 °C</td>
<td>III</td>
<td></td>
<td>38</td>
<td>83 330</td>
<td>239 2.0</td>
</tr>
<tr>
<td>Solution-casting MX</td>
<td>Cyclopentane 35 °C</td>
<td>II</td>
<td></td>
<td>17</td>
<td>48 407</td>
<td>193 1.2</td>
</tr>
<tr>
<td>Solution-casting MX</td>
<td>Cyclopentane 30 °C</td>
<td>II</td>
<td></td>
<td>19</td>
<td>72 535</td>
<td>311 1.9</td>
</tr>
<tr>
<td>Solution-casting MX</td>
<td>Cyclopentane 25 °C</td>
<td>II</td>
<td></td>
<td>18</td>
<td>206 445</td>
<td>362 3.5</td>
</tr>
<tr>
<td>Solution-casting DX</td>
<td>Cyclopentane 25 °C</td>
<td>II</td>
<td></td>
<td>33</td>
<td>146 408</td>
<td>336 4.3</td>
</tr>
</tbody>
</table>
circle rather than depicting a lateral tree growth as has been observed for several polymers. In general, it was observed that the overall breakdown coverage area was higher for the film with a lower Weibull breakdown strength. Magnification of the surface features in Figure 16(b,e) revealed fractals with a fourfold (tree fractals) or a sixfold symmetry (snow fractals) which corresponds well with the tetragonal or the hexagonal shape of the crystalline unit cell of P4MP, refer Table 2. The branches [shown in yellow color in Fig. 16(c,f)] emanating from the trunk [shown in green color in Fig. 16(c,f)] also followed a similar symmetry as the trunk, that is, the growth symmetry was hierarchal so that the surface features resembled a dendritic pattern. Such self-similar fractal growth has been attributed to a diffusion-limited process.62

An explanation for the occurrence of such features is the melting of polymer at the surface in contact with the electrode due to extreme heat and high temperatures produced during the electrical breakdown, which is followed by slow and homogeneously nucleated recrystallization of the polymer. A slow and homogeneous growth of the crystals at the surface is also supported by the observation from Figure 16 that these crystals are nonpervading over the breakdown area and consistent with the diffusion-limited growth of such fractals.52

While the growth of crystal modification I upon cooling from the melt state was expected as it is the most stable among all five modifications, the growth of crystal modifications IV or V is not obvious. It is interesting to note that Hasegawa et al.49 have reported a transition from crystal modification I (tetragonal crystal structure) → IV (hexagonal crystal structure) for P4MP at temperatures above 200 °C and a pressure of 456 MPa. It is also known that the local temperature rise at the breakdown site can achieve values as high as 1000 °C which is much higher than the melting point of the polymer (224–235 °C). Considering the above data, it appears that the electrical breakdown in P4MP films is not only accompanied by high temperatures but also high pressures, which suggests that the breakdown is electromechanical in nature. Additionally, data from Figure 16 indicate that the mode of electrical breakdown is same for all the films even though the breakdown strength differs based on the processing method.

**Effect of Biaxial Stretching on Dielectric Properties**

Polymer chain orientation through uniaxial or biaxial stretching affects several polymer properties such as mechanical, thermal, optical, and dielectric and induces anisotropy in these properties.53–68 Polymer film orientation is known to improve the dielectric breakdown strength of polymers due to several factors such as an enhancement in crystallinity, increase in the amorphous phase density, improvement in mechanical properties such as the tensile modulus, and reduction in the surface defects and thickness variations.15,58,59,69 Therefore, the P4MP thin films prepared by
solution-casting were also biaxially stretched to evaluate its effect on the dielectric properties. Figure 17 shows the dielectric constant ($\varepsilon'$) and loss tangent (tan $\delta$) for P4MP (MX) films that were solution-cast with cyclopentane at 25 °C and then biaxially stretched by an elongation ratio ($\lambda_1 = \lambda_2$) of 1.3 and 1.6 at 50 °C. An ideal temperature for biaxial stretching of the MX film would be $T > T_a^* (=200$ °C from Fig. 4), but such a high temperature was not possible with our current instrumental set-up. The dielectric constant reduced from a value of $\sim 3$ for the solution-cast film (Fig. 12) to a value of $\sim 2$ for the stretched films. All films were completely dried before TDDS measurements, and the TGA measurements did not detect the presence of any moisture or solvent in these films, hence the influence of residual solvent is less likely. The dielectric constant was very stable as a function of frequency and temperature as high as 150 °C and the dielectric losses were restricted to <1-2% above 1 Hz for the biaxially stretched films, which are the desired properties for the capacitor application.

Although the low-field dielectric properties remained unchanged upon biaxially stretching the P4MP thin films, significant effect was observed on the breakdown field strength. Figure 18 compares the Weibull breakdown characteristics, surface morphology and crystallinity of P4MP (MX) film solution-cast with cyclopentane at 25 °C, and the same film after biaxial stretching by an elongation ratio ($\lambda_1 = \lambda_2$) of 1.3 and 1.6 at 50 °C. The Weibull breakdown strength ($\eta$) increased for the biaxially stretched films compared to the unstretched film, although not much effect was observed on the Weibull slope parameter. Furthermore, $\eta$ increased with an increase in the elongation ratio and an increase of 65%
was obtained at an elongation ratio of only 1.6. The breakdown strength is expected to increase even more at higher elongation ratios. From Figure 18, the surface morphology of the biaxially stretched film appeared coarser but more uniform than the solution-cast film. Considering that the electrical breakdown is a localized phenomenon, one hypothesis for an increase in the dielectric breakdown strength of biaxially stretched films over solution-cast films is the improvement in their surface morphology by elimination of topological defects such as pits or cavities, which otherwise may cause a nonuniform localized concentration of electric field around the defects and, hence, precipitate breakdown at lower voltages. The same factor is responsible for a higher breakdown strength of solution-cast films compared to compression-molded films as shown in Table 3.

As the energy density of a film capacitor is directly proportional to square of the breakdown strength of the dielectric film, our results suggest that solution-processing a P4MP film followed by biaxial stretching can increase the energy density by a factor of 20 over a conventional melt-processed film.

![Figure 17](image1.png)

**FIGURE 17** Dielectric constant and loss tangent as a function of frequency and temperature for P4MP (MX) film cast from cyclopentane at 25 °C and biaxially stretched at 50 °C by an elongation ratio of (a) $1.3 \times 1.3$ and (b) $1.6 \times 1.6$. [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 18](image2.png)

**FIGURE 18** SEM surface micrographs of solution-cast and biaxially stretched P4MP films along with their crystallinity, Weibull breakdown strength, and Weibull slope parameter. [Color figure can be viewed at wileyonlinelibrary.com]
Quality of Base Resin
The effect of cleanliness or purity of the base resin on the breakdown strength of polypropylene is well known. Residual catalyst, residual monomer, and contaminants present in the base resin or introduced during the manufacturing process result in a significant decrease in the dielectric strength. On the other hand, producing a base resin that meets the stringent purity requirement of a capacitor film is difficult and expensive. Current state-of-the-art thin film manufacturing for dielectric capacitor involves using a high purity “capacitor-grade” base resin along with processing and metallization of films in a clean environment. A capacitor-grade BOPP film exhibits a higher Weibull breakdown strength (η) and slope parameter (b) than a packaging-grade BOPP film. A Weibull strength of 514 V/μm for a biaxially oriented P4MP (BOP4MP) film in Figure 18 is comparable to that of a BOPP film made from a packaging-grade base resin. Therefore, a further increase in the dielectric strength of BOP4MP is expected upon switching to a capacitor-grade resin, and BOP4MP could be a viable high-temperature alternative to state-of-the-art BOPP capacitor films.

CONCLUSIONS
Studies were conducted to assess the viability of poly(4-methyl-1-pentene) (P4MP) as a suitable candidate for high-temperature capacitor applications. Thermal stability to degradation at high temperatures (>200 °C), melting onset at 190 °C and a high thermal transition for crystallite motion (200–216 °C) suggested that P4MP thin films should withstand operating temperatures up to at least 190 °C in dielectric capacitors. Investigation of the rheological behavior of P4MP indicated that it could be melt-processed below 270 °C in the extruder without degradation. In addition to melt processing, P4MP offers a much higher flexibility toward thin film manufacturing by solution processing due to favorable solubility characteristics, which provides an advantage over other polyolefins such as PP. Isotropic, freestanding films as thin as 10 μm were successfully obtained using different solvents and casting temperatures in this study, although the thickness could be easily reduced to 3–5 μm. The solution processing route also enabled a control of the film surface morphology, percent crystallinity and different crystal structures by controlling the casting conditions. The surface morphology had the biggest influence on the dielectric strength of P4MP films, while the unit crystal structure or the percent crystallinity had a negligible influence. The mode of electrical breakdown in both melt-processed and solvent-cast films appeared to be electromechanical. Biaxial stretching of the solution-cast films further increased the breakdown strength due to improvement in the surface morphology. Compared to the melt-processed films, the Weibull breakdown strength increased by 290% for solution-processed films, and 450% for solution-processed films that were biaxially stretched to an elongation ratio of 1.6×. This implies that an increase in the energy density by up to 20 times over conventional melt-processed films could be theoretically obtained. In addition, P4MP has a dielectric constant and loss similar to PP and very stable as a function of frequency and temperature. It has been recently reported that ionic functionalization of P4MP can further increase the dielectric constant and breakdown strength while maintaining low dielectric losses. Therefore, a similar or an even higher energy density than BOPP can be obtained from biaxially oriented P4MP films with an added advantage of operating at much higher temperatures than PP.

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