

Carrier films behavior during thermoforming process studied using dynamic mechanical thermal analysis (DMTA)

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Abstract Dynamic mechanical thermal analysis was used to investigate the thermal transitions and modulus/temperature behavior of thermoformable carrier films, and to relate the information obtained to carrier film behavior during the thermoforming process. In this study the glass transition temperatures (T_g) and the temperatures at which crystallization occurred during heating (T_c) of four thermoformable carrier films were measured by using a dynamic mechanical thermal analyzer (DMTA). These films are good candidates for the automotive process, which uses painted carrier films as moldable automotive coatings (MAC). The modulus/temperature behavior of the films was also observed over a wide temperature range, which included thermoforming temperatures. Although films of PETG and PCTG 5445, co-polyesters based on poly(1,4-cyclohexylene dimethylene terephthalate), are thermoformable, their T_g values, 92 and 99 °C, respectively, are not high enough to allow current paint systems (with bake temperature of 100–110 °C) to cure on the films without causing severe film deformation.

Keywords Dynamic mechanical thermal analysis · Glass transition temperature · Carrier film · Modulus · Curing

Introduction

Presently employed automotive production techniques require that, in most cases, the vehicle body be fully assembled prior to spray painting. This method of painting, however, is capital, energy, space, and labor intensive. In

addition, paint solvents create health and environmental concerns. The increasing use of new polymeric materials as body panels and fascia also creates problems with color matching and with paint adhesion to the various substrates. Jones et al. have invented an automotive trim panel which has a thermoformable structural layer shaped into a non-flat contour with a pressure sensitive adhesive system applied to one side of the panel. Both the adhesive and release liner are capable of withstanding the high heat of thermoforming [1]. Space frame technology, such as that used in automotive industry, allows add-on plastic panels to be painted prior to mounting on the space frame [2]. A pressure sensitive adhesive is then applied to the back side of the film. This three-component laminate, the moldable coating, is drawn (vacuum formed), adhesive side down, onto an unpainted body panel [3]. A finished, “pre-painted” part is then ready for mounting to the space frame.

The moldable automotive coatings (MAC) process has many advantages with respect to conventional spray painting. For example, overspray is eliminated and solvent emissions substantially reduced since paint is applied to the carrier film by roll-coating. A uniform surface for painting (the film) is obtained for the entire vehicle regardless of body panel or fascia material, thus eliminating paint matching difficulties. Also, this is an automatable process. The appearance of the painted carrier films and pre-painted body panels have been shown to be comparable or, in the case of metal flake paints, superior to the appearance of conventionally painted parts [4]. Thus, MAC is a very attractive alternative paint process. The carrier film and the complete, painted laminate must meet several requirements to be used in the MAC process [5]. The first of these is that the cure, or bake temperature of the paint (basecoat and clearcoat) does not exceed the glass transition temperature (T_g) of the carrier film. Above T_g the softened film will sag

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and stretch during paint cure. On the other hand, the thermoforming of a painted laminate onto a molded part can only occur above T_g , after the film has softened and can deform. There is an upper limit to the forming temperature, however, and this is dictated by the temperature at which the paint fails or the film ruptures. For example, failure in a urethane clearcoat would mean loss of elongation and subsequent cracking during forming. The paint may also degrade (depolymerizes). Additionally, if an “as-received” amorphous film can crystallize, the crystallinity may interfere with the thermoforming process. The temperatures at which a film begins to crystallize (T_c) during heating, and subsequently melt (T_m), are usually well above T_g . However, it is possible for crystallization to occur during forming. The film may then become brittle or stiff, and with decreased elongation [6, 7]. This would necessitate temperature, or could even prevent thermoforming entirely [8]. Thus T_c and T_m are also important film properties.

Finally, to be used in the MAC process, a carrier film requires a particular modulus/temperature behavior. A typical amorphous, linear polymer exhibits four types of behavior (four domains of modulus values) when temperature is scanned at a fixed frequency. These are, in order of increasing temperature and decreasing modulus, a glassy phase (modulus values on the order of 1×10^9 Pa), a leathery region, a rubber plateau (modulus values on the order of 1×10^5 Pa), and viscous flow [9]. In the glassy state, the material is hard and brittle. The leathery region represents the transformation between glassy and rubbery behavior; it is the glass transition region. In the rubbery domain, rapid segmental chain motion occurs but long-range translational motion does not [10]. Viscous flow begins at still higher temperatures, when translational chain motion becomes possible. This is marked by a sharp decrease in modulus and a loss of structural integrity. At forming temperatures, which are above T_g , the film modulus must be high enough, that is, the material must retain enough strength, to permit the entire moldable coating to be self-supporting during the initial phase of the process. However, the film modulus must not be so high that the elongation necessary for the coating to conform to the shape of the part being fabricated is prevented. Therefore, a degree of chain mobility short of actual flow is desirable. These conditions are met if the forming temperature falls within the rubbery plateau.

While the glass transition, crystallization, and melt temperatures of the MAC carrier films may be determined by standard differential scanning calorimetry (DSC), the modulus/temperature behavior, especially above T_g , of these films and laminates cannot be obtained by using standard mechanical tests [11]. Neither Rheovibron nor rheometric techniques can obtain data at temperatures above T_g . Instron techniques are also unable to provide

data above T_g . It has been found, however, that the sample mounting and clamping arrangement of the particular dynamic mechanical thermal analyzer (DMTA) used in this work allows measurement of modulus/temperature profiles of polymer films throughout a wide range of temperatures, as well as T_g , T_c , and T_m of these materials. The DMTA, described in detail in the “Experimental” section, measures the dynamic storage and loss modulus (E' and E'') and the damping ($\tan \delta$) at a given test frequency as temperature is scanned. For the reasons described above, T_g , T_c , T_m , and the modulus/temperature profiles of MAC carrier films are of interest. In this work these properties of four carrier films and one complete moldable coating were studied by using the DMTA.

Experimental

Materials

Two co-polyester and two co-polyester blend carrier films were investigated. The carrier films, PETG, PCTG, PMB 10-231, and PMB 10-232, were used as received. Materials, suppliers, compositions, and comments are listed in Table 1. The film thicknesses for the carrier films prepared for this study were 0.25 mm.

Dynamic mechanical thermal analysis

A Polymer Laboratories, Ltd., dynamic mechanical thermal analyzer (DMTA) was used in this work [12]. Data acquisition and storage was handled by a Hewlett Packard 9816 microcomputer with 9122 disc drive.

The DMTA monitors the damping ($\tan \delta$) and dynamic storage (E') and loss (E'') moduli of a sample at a constant frequency and heating rate. From this, glass transition (T_g), crystallization (T_c), and melt (T_m) transition temperatures are determined. The dependence of sample modulus on temperature may be determined as well.

Rectangular samples, where sample thickness was 0.25 mm, were mounted in the DMTA mechanical head (see Fig. 1) using frame clamps to fix the positions of the ends of the rectangle and the drive shaft clamp to fix the position of the center of the rectangle. The specific clamps used depended on the type of material being tested [12]. The geometry constant for a given sample, which was necessary for modulus determinations, was calculated by, and stored in, the microcomputer. A sinusoidal stress was applied to the sample by the vibration of the drive shaft at a fixed frequency. The ensuing sample strain, proportional to the sample displacement, was monitored by a transducer. Temperature in the sample enclosure was monitored (± 0.2 °C) by a platinum resistance thermometer placed

Table 1 Description of carrier films

Material	Name	Supplier	Composition ^a	Comments
Carrier film	Kodar [®] PETG 6763	Eastman Chemical Products, Inc.	Based on poly(1,4- cyclohexylene dimethylene terephthalate)	Glycol-modified PET does not crystallize
Carrier film	Kodar [®] PCTG 5445	Eastman Chemical Products, Inc.	Based on poly (1,4- cyclohexylene dimethylene terephthalate)	Glycol-modified PET does not crystallize
Carrier film	PMB 10-231	Eastman Chemical Products, Inc.	PCTG 5445/styrene–maleic (Dylark ^{®b})	0.50/0.50 blend
Carrier film	PMB 10-232	Eastman Chemical Products, Inc.	PCTG 10179 ^c /styrene–maleic anhydride (Dylark ^{®b}) polycarbonate	0.33/0.33/0.33 blend

^a Provided by supplier

^b Acro Chemical Company

^c A different grade, with respect to PCTG 5445, of co-polyester based on poly(1,4-cyclohexylene dimethylene terephthalate)

directly behind the sample, and controlled by the universal temperature programmer. The sample chamber contained inlet and outlet ports for cycling inert gas during testing.

Rectangular samples (approximately 25×12 mm) were cut from the films and mounted in the DMTA head using the spreader drive shaft clamps for thin samples. A single cantilever configuration, with the sample mounted only to one frame clamp and to the drive shaft clamp, was used. A slight tension was applied to the sample during mounting to prevent the thin films from buckling once the testing temperature exceeds T_g . Except where noted, samples were run at a heating rate of 4 °C/min and a frequency of 10 Hz under a nitrogen gas environment. The strain was approximately 60 μ m. T_g values were determined from the maxima in the $\tan \delta$ vs. temperature curves and T_c from the peak of the post- T_g modulus increase in the E' vs. temperature curves. Modulus/temperature behavior was also obtained from the E' vs. temperature curves. It should be noted that T_g values obtained by dynamic techniques are frequency dependent, i.e., they increase with increasing frequency. Therefore, when dynamic T_g values are compared to static T_g values (such as those obtained by

differential scanning calorimetry), it is usually observed that the dynamic T_g is higher.

Results and discussion

Glass transition temperatures

PETG and PCTG

The T_g values of the (initially) amorphous carrier films tested in this work are listed in Table 2. PETG and PCTG 5445 each had a single T_g at 92 and 99 °C, respectively. The $\tan \delta$ vs. temperature DMTA curves for these materials are shown in Fig. 2. The small peak at 152 °C for PCTG will be discussed in the next section. Both of these films may be readily thermoformed but, on the basis of their T_g values, neither is suitable for the MAC process. That is, the T_g values of these films are below the paint cure temperatures (100–110 °C) of the proposed paint system and the films would sag and deform during cure.

PMB 10-231

The first of the blend films, PMB 10-231, exhibited two clearly defined glass transitions at 97 and 137 °C (Fig. 3), indicating that the blend components, PCTG 5445 and

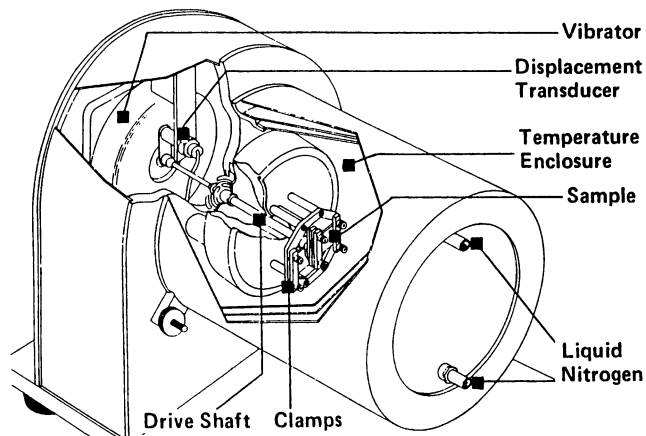


Fig. 1 Mechanical head of the dynamic mechanical thermal analyzer [12]

Table 2 Transition temperatures for carrier films

Sample	T_g (°C) ^a	T_c (°C) ^b
PETG	92	–
PCTG 5445	99	165
PMB 10-231	97, 137	155
PMB 10-232	124, 153	190

^a Obtained at 10 Hz and a heating rate of 4 °C/min

^b These values are estimated transition maximum

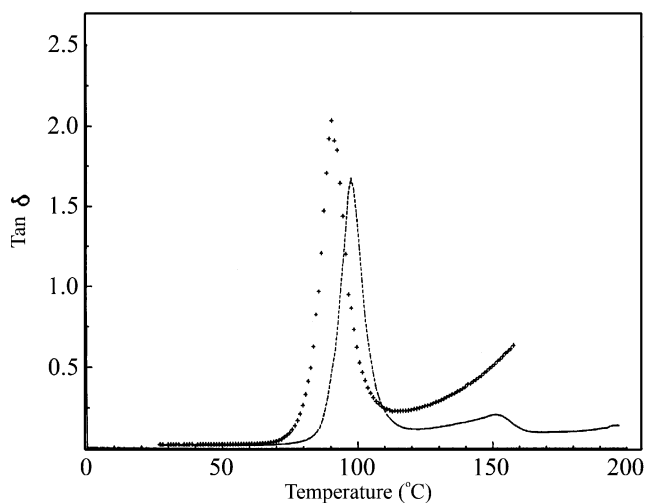


Fig. 2 Tan δ versus temperature for PETG (+) and PCTG 5445 (– –)

styrene–maleic anhydride (SMA), were incompatible [13–15]. On a molecular level the glass transition marks the onset of large-scale motion of the polymer backbone. This chain (segmental) mobility is a function of local environment. If a blend is compatible, the environment is homogeneous and a single T_g is observed. This T_g is usually intermediate to the T_g values of the component polymers, and is composition dependent. If the blend is incompatible, however, two separate environments (phases) exist, and two T_g values, one for each phase, will be observed [13]. Thus, for the PMB 10-231, the T_g of 97 °C represents the PCTG 5445 and the T_g of 137 °C represents the SMA. SMA has a T_g , by static measurement, of 109–129 °C depending on the grade. The dynamic T_g , as noted in the “Experimental” section, is expected to be slightly higher. The PMB 10-231 film has been shown to be capable, marginally, of withstanding paint cure temperatures [16]. Evidently, the SMA phase of the blend, with its higher T_g , was able to maintain film integrity during paint cure. This film thermoforms well at temperatures that do not cause paint damage and is, therefore, a good MAC candidate.

PMB 10-232

Along with the two types of blend behavior described above (compatible and incompatible) is a third, intermediate category. The behavior of such “marginally” or “partially” compatible blends is dependent on composition, blending method, temperature, and the thermal history of the specific sample. A marginally compatible blend may exhibit one intermediate, but broadened transition, or the original component T_g values may be broadened and/or shifted towards each other. The second blend film, PMB 10-232, appears to be in this third category of blend behavior. PMB 10-232 exhibited a broad T_g centered at

124 °C with a slight shoulder at 153 °C (Fig. 3). The shoulder represents a polycarbonate transition in this PCTG 10179/SMA/polycarbonate blend. The single, broad peak at 124 °C, intermediate to the separate PCTG 5445 and SMA peaks for the PMB 10-231 blend (Fig. 3), indicates that the PCTG 10179 and SMA in the PMB 10-232 are at least partially compatible. The difference in the behavior of these components in the two blends may be caused by the use of two different grades of PCTG. PCTG is a co-polyester prepared from two glycols, ethylene glycol and cyclohexanedimethanol (CHDM) (Table 1). It is likely that the ethylene glycol/CHDM ratio is different for the two grades of PCTG and this could affect PCTG/SMA compatibility. Additionally, the presence of a third component, polycarbonate, may increase PCTG/SMA compatibility by altering the net interactions between these blend components. Determination of specific PCTG/SMA/polycarbonate interactions is beyond the scope of this work. Because of the high polycarbonate T_g , the PMB 10-232 film is, of the four films tested here, best able to withstand paint cure temperatures (100–110 °C). However, presumably because of the high polycarbonate T_g , this film was found difficult to thermoform at a temperature below 165 °C [17].

Crystallization and melting

PETG and PCTG

Using differential scanning calorimetry (DSC), PCTG 5445 and PCTG 10179 were found to crystallize over a range of 140–180 °C when heated at either 10 °C/min or 20 °C/min. The melting points were then 240 and 260 °C for the 5445 and 10179, respectively [18]. Thus, the small peak at 152 °C seen in the DMTA tan δ vs. temperature curve for PCTG 5445 (Fig. 2) represents crystallization. Figure 4b, the modulus vs.

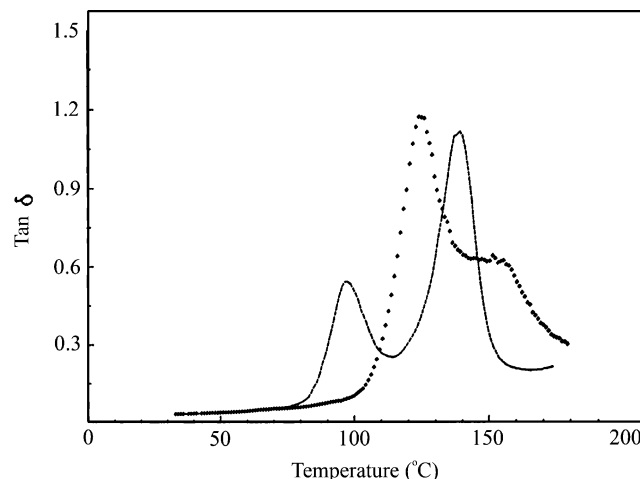


Fig. 3 Tan δ versus temperature for PMB 10-231 (– –) and PMB 10-232 (•)

temperature curve for PCTG 5445, also shows clear evidence of the film's crystallization (labeled T_c). There is a drop in E' at approximately 98 °C due to the glass transition, followed by a sharp increase. As noted earlier, an increase in post- T_g modulus indicates that crystallization has occurred. The PCTG modulus reached a maximum at about 165 °C, and this temperature, T_c , is within the range of crystallization temperatures found by the DSC. The $\tan \delta$ vs. temperature and E' vs. temperature curve for PETG, Figs. 2 and 4a, showed no evidence of PETG crystallization.

PMB 10-231 and PMB 10-232

Although crystallization peaks were not visible in the $\tan \delta$ vs. temperature curves of PMB 10-231 and PMB 10-232, increases in E' due to crystallization were observed in the E' vs. temperature curves of these films (Fig. 4c, d). T_c , the temperature of the post- T_g modulus maximum, was 155 °C for PMB 10-231 and 190 °C for PMB 10-232 (Table 2). The magnitude of the increase in E' was smaller for the PMB 10231 and PMB 10-232 films than for the PCTG film

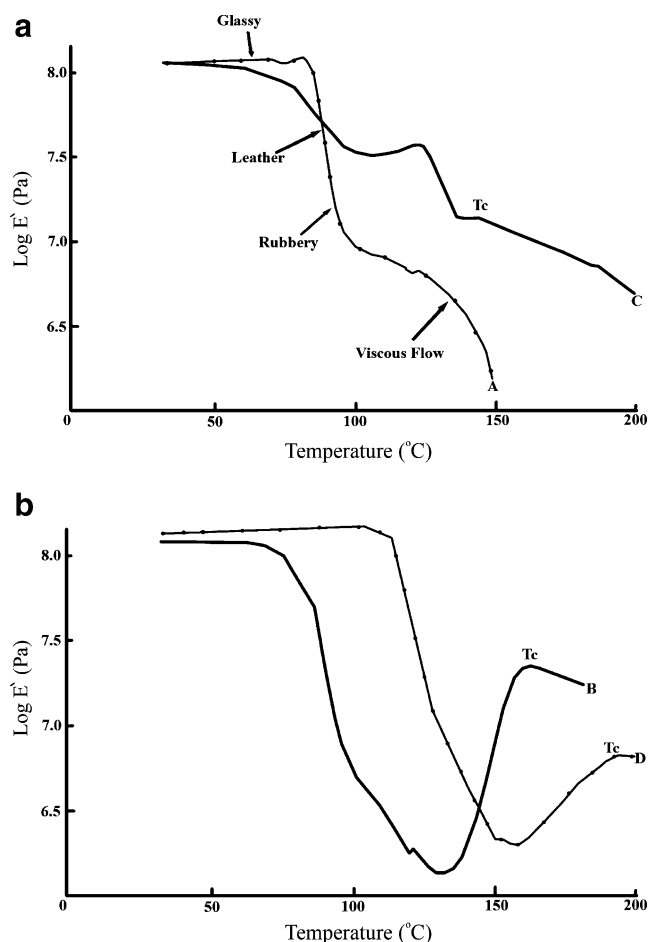


Fig. 4 Log E' (Pa) versus temperature (°C) for **a** PETG and **c** PMB 10-231. Log E' (Pa) versus temperature (°C) for **b** PCTG 5445 and **d** PMB 10-232

(Fig. 4b). Crystallinity, and the effect of crystallinity on E' , should be smaller for the blends than for the PCTG copolyester alone since only one of the blend components, the PCTG, can crystallize. It has also been shown that, for compatible systems, if only one blend component can crystallize, its crystallization is hindered by the presence of amorphous material [13].

Crystallization and thermoforming

Despite the ability of three of the four carrier films to crystallize during heating at 4 °C/min in the DMTA, no crystallization was observed for any of the films during the initial phases of thermoforming. This is presumed to be an indication of a rate dependence of crystallization. That is, heating during thermoforming is too rapid (approximately 200 °C/min) to allow the polymer chains time to reorganize and therefore crystallize. Indeed, subsequent DMTA runs of PCTG samples showed a dependence of T_c on heating rate, with T_c increasing with increasing heating rate. It is, of course, possible for crystallization to occur as the films or laminates cool if cooling is slow enough.

Modulus/temperature behavior

PETG, PCTG, PMB 10-231, and PMB 10-232

As mentioned earlier, the E' vs. temperature curves obtained by DMTA for the four carrier films are shown in Fig. 4. The four types of modulus/temperature behavior described in the "Introduction" can be seen in Fig. 4a for PETG. The other films (Fig. 4b–d) exhibit similar behavior as well as post- T_g increases in modulus indicating crystallization. In the glassy region, E' increased slightly with temperature just prior to T_g (PMB 10-231 excepted). This increase in modulus may result from the pre-tension placed on each sample prior to mounting it in the DMTA head. The drop in E' at the glass transition was quite sharp for the PETG and PCTG 5445 films (Fig. 4a and b). This indicates, as noted in the earlier discussion of $\tan \delta$ vs. temperature data, that both these films are homogenous materials. Figure 4c, however, shows that PMB 10-231 is a heterogeneous material, an incompatible blend with the two separate drops in the modulus vs. temperature curve corresponding to the two peaks in the $\tan \delta$ vs. temperature curve (Fig. 3). The transition for the partially compatible PMB 10-232 film (Fig. 4d) was broadened with respect to the transition for PCTG. The PMB 10-232 glass transition occurred over a temperature range of approximately 40 °C. The greatest decrease in modulus for the four films was about two orders of magnitude for PMB 10232, and the smallest modulus decrease was slightly less than one order of magnitude for PMB 10-231.

Modulus/temperature behavior and thermoforming

PCTG 5445 is thermoformed at 150 °C, while PMB 10-231 and PMB 10-232 are both formed at about 165 °C, although unpainted PMB 10-232 is more difficult to form at this temperature. The forming temperature of a painted laminate cannot be increased, as paint failure would occur. Referring to Fig. 4b–d, the values of E' at the different forming temperatures for PCTG, PMB 10-231, and PMB 10-232 are 5.0×10^6 , 7.9×10^6 , and 2.0×10^6 Pa, respectively ($\log E'$ of 6.7, 6.9, and 6.3, respectively). A rubbery plateau is not evident in the E' vs. temperature curves of PCTG and PMB 10-232 because of the onset of crystallization. Recall, however, that there is no crystallization of these films during the initial (heating) phase of thermoforming due to the rapid heating rate. During the forming process it is then likely that the modulus of the material is within the rubbery plateau region of the modulus/temperature curve. Deformation (elongation) is possible since the material is above T_g , but extensive flow, film rupture, and/or other film failure would not be likely to occur. For PMB 10-231, which exhibited (Fig. 4c) only a slight degree of crystallization, the forming temperature 165 °C does appear to be within the plateau region.

PETG, like PCTG, would likely be thermoformed at 150 °C. The modulus of PETG at this temperature was found to be approximately 2×10^5 Pa ($\log E'$ of 5.3, Fig. 4a), somewhat low in comparison to the E' values of the other three carrier films. A forming temperature of 117 °C, however, corresponds to an E'' of 2×10^6 Pa ($\log E''$ of 6.3) for PETG, which would provide a stronger film for the process. Another chemically similar polymer material, poly(ethylene terephthalate) (PET) is currently being investigated. Preliminary results show that crystalline PET, a film difficult to thermoform at 165 °C, has a modulus higher than that of either PMB 10-231 or PMB 10-232 at that temperature. Apparently, this is too high a modulus for the forming temperature. Again, for the current paint system, with paint cure temperatures of 100–110 °C, the forming temperature cannot be increased.

Conclusions

Requirements for MAC carrier films include a carrier film T_g greater than the paint cure temperature. Therefore, for the current paint system, its T_g must be greater than 110 °C. Also, the temperature at which the film may be thermoformed must not be greater than about 165 °C, the temperature at which paint damage ensues. A carrier film will meet these requirements if, in the temperature range of

110–165 °C, it behaves as a rubbery material. That is, the forming temperature of a MAC carrier film should be in the rubbery plateau of the film's modulus/temperature profile. Additionally, DMTA results suggest that the film modulus during forming should be in the range of 1×10^6 – 1×10^7 Pa. The DMTA was found to be an excellent instrument for the determination of the glass transition and crystallization temperatures of MAC carrier films, and to study the modulus/temperature behavior of the films. DMTA data can also be used to monitor film heterogeneity. From this information the optimum forming conditions of a given film can be determined, the behavior of the films during thermoforming can be better understood, and various new MAC candidates evaluated.

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