



Accuracy in locating glass transitions: aging and gamma sterilization of vulcanized thermoplastic elastomers

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Abstract: We have studied nine thermoplastic vulcanizate elastomers (TPVs) in four series: as made, after accelerated aging, after γ irradiation, after both irradiation and aging. The materials exhibit two glass transitions, one seen in cross-linked regions and the other in un-crosslinked amorphous regions. Three techniques of determination of glass transitions have been used and the results compared, all three based on dynamic mechanical analysis (DMA): as a peak in the loss modulus E'' ; as a peak in $\tan \delta$; and as the midpoint of the rapid decrease in the storage modulus E' . We recommend the last method for both fundamental and practical reasons.

Introduction

There has been a rapid rise in the use of polymer-based materials in medical applications ranging from drug-delivery systems to medical devices [1-3]. In particular, thermoplastic vulcanizate elastomers (TPVs) have found use in medical devices and implants due to their excellent combination of properties and processability. In order for such devices to be used, the materials from which they are made clearly must retain their mechanical properties not only after sterilization but also throughout their shelf life [4].

γ irradiation has now begun to replace traditional methods of sterilization (such as ethylene oxide) for medical devices - in part because γ -irradiation is safer to implement and does not leave malignant traces on the products as ethylene oxide does [2, 5]. Further, γ sterilization can be used after products are packaged, thus eliminating concern for recontamination introduced in packaging [3]. This is especially practical for disposable medical devices designed for one-time use, such as syringes and catheters. However, these products usually involve polymers, such as polypropylene (PP) and polyethylene (PE), which are known to suffer from degradation and loss of mechanical properties after γ irradiation [3, 6 - 8]. While there is information in the literature on the effects of irradiation on polymers [2, 3, 6 - 8], the information available is insufficient, for TPVs in particular [5]. Among the properties of TPVs not known well enough there are effects of gamma irradiation on thermophysical properties, especially on the glass-transition temperature T_g .

A second issue dealt with in the present paper goes far outside TPVs, in fact it concerns all amorphous and semicrystalline materials. In terms of thermophysical properties, T_g is one of the most important and useful material characteristics [9 - 20]. Indeed, T_g can be used to determine a material's maximal temperature of use, that is its material operational limit [21]: by definition, above T_g the material is soft and flexible; if not crosslinked, it is a melt (liquid). Further, T_g can also be used to evaluate many important properties in polymer systems such as assessment of compatibility and (im)miscibility, consequences of aging, and optimization of curing conditions [19].

While T_g is so important, different methods of its determination do not provide the same results. The most widely used technique is differential scanning calorimetry (DSC) [22 – 24]. However, Sperling [22] says that in determination of T_g by DSC "There is a hysteresis peak associated with the transition which appears frequently, but apparently not all the time". Along similar lines, Menard [24] says about the dynamic mechanical analysis (DMA) that "it is 10 to 100 times more sensitive to the changes occurring at the T_g " than DSC. A thorough investigation of a polymer liquid crystal including results from 18 laboratories around the world [25] has demonstrated the reliability of DMA and its advantages over some other techniques used. However, three distinct values of T_g can be obtained from each DMA run. These facts enable us to determine effects of γ sterilization and aging on selected polymeric materials and at the same time to compare T_g values obtained by three different DMA procedures.

Our work focuses on the VanishPoint automated retraction safety syringes manufactured by Retractable Technologies Inc (RTI) of Little Elm, TX. The design of the syringe has already been patented [26 – 33] and the principle discussed in [34]. In contrast to traditional syringes, the retractable syringes cannot be used for the second time. Outside the syringe is quite similar to the traditional ones and also the medication is dispensed through a needle-shaped small diameter tube into the body of the patient. However, at the time when all medication has just been dispensed, the plunger is depressed further into a small diameter nose portion of the syringe. The nose portion contains a compressed spring. The additional depression requires somewhat more thumb force against friction than the medication dispensation – and releases the spring that pushes the polymeric needle holder and the needle backwards. Retracting, the needle breaks the vacuum with the skin – so that blood or body fluids are not extracted from the patient. Since the spring was originally outside, it was not in contact with the medication before or during injection.

This technology has obvious consequences for containing spread of dangerous diseases among the drug addicts (who if only possible tend to use the same needles again and again) and also for accidental needle-sticks by medical professionals. However, materials for constructing the device have yet to be determined and optimized. There is no implication that the materials we studied are actually used by RTI.

The present study can also be considered as a continuation of earlier work. Extant tribological methods have been designed for flat surfaces moving against each other [34]. Since main parts of syringes are cylindrical, a new functionality test was developed for determining static and dynamic friction between rounded surfaces moving inside each other [1]. We have further evaluated effects of γ sterilization and aging on tensile behavior, friction and hardness of selected PP-based materials [5].

Our results show that the gamma irradiation from 18 kGy to 33 kGy and post-irradiation effects lead mostly to small to moderate changes in the hardness and in several mechanical properties of PP + ethylene-propylene-diene (EPDM) thermoplastic vulcanizates – except for larger changes in the elongation at break [5]. It has been also found that relatively small variations in the characteristics of TPVs used can affect significantly the final products.

The temperature of the glass transition is in fact a representative of the glass transition *region*. Applying three DMA-based procedures, we evaluate the effects of irradiation and aging and we compare the T_g values to those of non-irradiated and also irradiated but un-aged specimens. Under the circumstances we are looking first of all for directions and magnitudes of changes caused by various processes we study. Given the existence of several methods of locating T_g values, we would like to make a recommendation of a reliable method for the future.

Results

Zaharescu and his colleagues have shown that at doses from 40 or 50 up to 200 kGy there can be significant cross-linking [2, 10, 11]. We recall that our samples were irradiated following an ASTM standard, between 18 and 30 kGy, hence below the Zaharescu threshold. We demonstrate our procedures of location of T_g values in Figure 1.

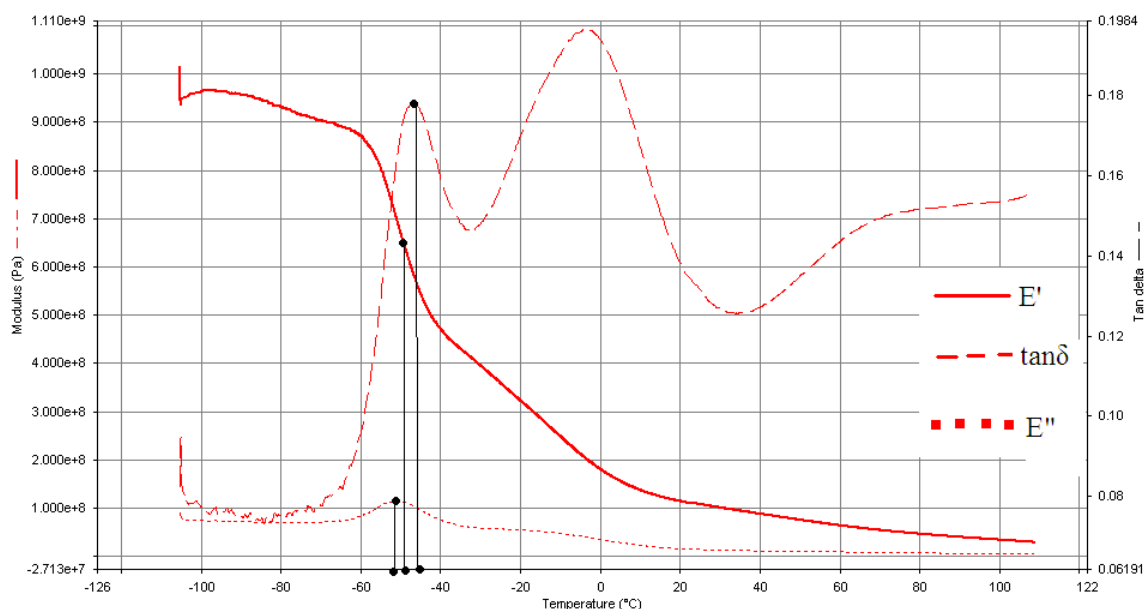


Fig. 1. DMA results for TPV-5 post-sterile aged specimen showing how T_g is determined by three methods (at 1.0 Hz).

Numerical results for all three methods used are presented in Tables 1 – 3. The post-sterile specimens show glass transition temperatures either practically the same or lower than T_g values for the pre-sterile specimens. Apparently in most samples during irradiation chain scissions dominate over cross-linking. Shorter chains created by scission provide *plasticization*, hence lowering T_g .

As for *aging*, a typical result is T_g lowering. However, sterile TPV-5 shows an increase in T_g after aging; all three methods we have used show this effect;

apparently during storage after irradiation some cross-linking occurs as well as densification.

Tab. 1. T_g /°C evaluated as $\max(\tan \delta)$.

Material	Pre-Sterile	Post-Sterile	Pre-Sterile Aged	Post-Sterile Aged
TPV-1	- 45	- 61	- 60	- 57
TPV-2	- 45	- 35	- 47	- 53
TPV-3	- 45	- 47	- 52	- 45
TPV-4	- 43	- 50	- 45	- 66
TPV-5	- 45	- 50	- 45	- 47
TPV-6	- 41	- 45	- 50	- 47
TPV-7	- 42	- 43	- 35	- 43
TPV-8	- 47	- 48	- 48	- 50
TPV-9	- 50	- 48	- 48	- 50

Tab. 2. T_g /°C evaluated as peak in E'' .

Material	Pre-Sterile	Post-Sterile	Pre-Sterile Aged	Post-Sterile Aged
TPV-1	- 47	- 62	- 64	- 60
TPV-2	- 45	- 45	- 47	- 53
TPV-3	- 47	- 50	- 57	- 50
TPV-4	- 45	- 52	- 47	- 75
TPV-5	- 47	- 57	- 50	- 51
TPV-6	- 42	- 47	- 55	- 50
TPV-7	- 45	- 43	- 45	- 45
TPV-8	- 50	- 52	- 50	- 55
TPV-9	- 50	- 55	- 50	- 55

Tab. 3. T_g /°C evaluate as midpoint of decrease in E' .

Material	Pre-Sterile	Post-Sterile	Pre-Sterile Aged	Post-Sterile Aged
TPV-1	- 45	- 55	- 64	- 60
TPV-2	- 45	- 44	- 47	- 53
TPV-3	- 47	- 50	- 55	- 50
TPV-4	- 45	- 50	- 47	- 75
TPV-5	- 47	- 55	- 50	- 50
TPV-6	- 42	- 47	- 55	- 50
TPV-7	- 45	- 45	- 43	- 45
TPV-8	- 50	- 50	- 50	- 55
TPV-9	- 50	- 55	- 50	- 55

The behavior of TPV-2 and TVP-4, which show relatively small T_g changes between pre-sterile, post-sterile, and pre-sterile aged specimens but significant decreases in

T_g of the post-sterile aged specimens, supports the notion that degradation induced by irradiation continues during subsequent storage. Because the T_g of the other samples did not change significantly during aging, we infer that the radiation-induced free radicals are only *partially* cross-linked during storage.

We cannot extend such generalization to all of our materials. Some materials are not affected much by solely the aging process or solely the sterilization process. However, the *combination* of both sterilization and aging produces larger effects on T_g .

Now consider graph taken from the run of TPV-5 post-sterile aged specimen (Figure 2). In addition to the peak in $\tan \delta$ observed at the reported T_g (-47 °C), we see that $\tan \delta$ peaks again at -5°C. This is a second thermal transition, which we shall denote as T_{g2} . This peak is related to the glass transition of uncross-linked portions of the amorphous PP in our samples. Our samples are blends of PP and EPDM elastomer, hence the first T_g transition is related to the cross-linked regions which upon radiation undergo significant chain scission and partial cross-linking while the second transition in the amorphous PP regions is the glass-to-liquid transition.

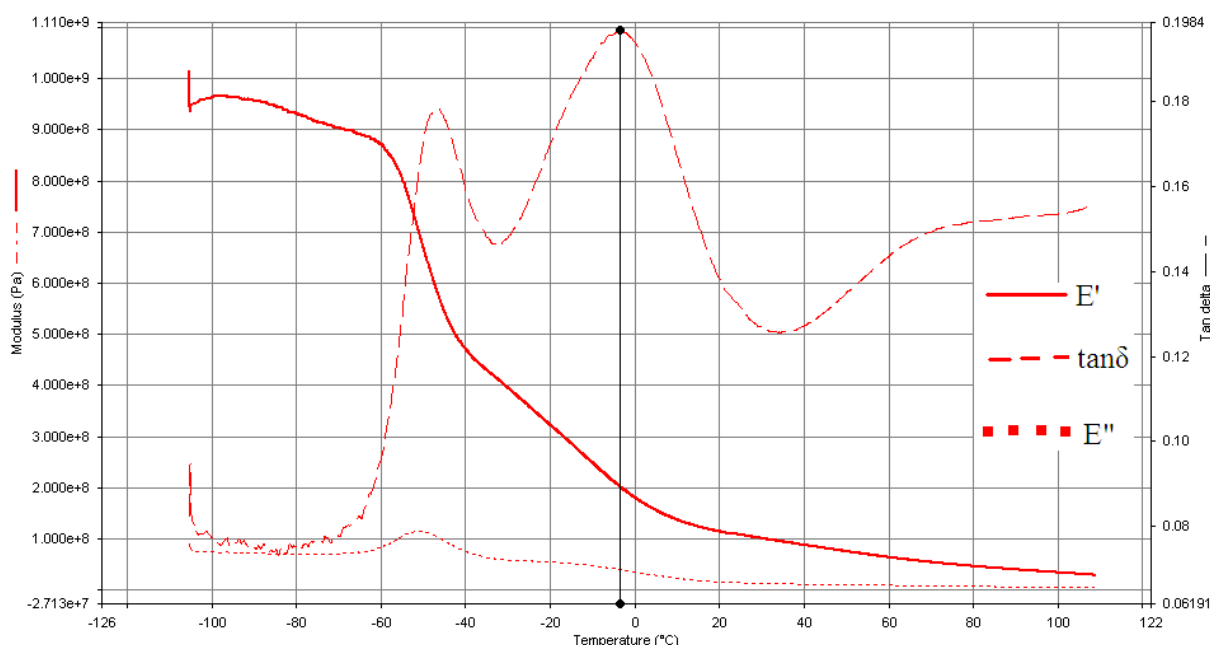


Fig. 2. DMA results for TPV-5 post-sterile aged specimen showing how T_{g2} is determined (at 1.0 Hz).

On the basis of $\tan \delta$ curves we tabulate the T_{g2} values for all samples in Table 4. In this case the other two methods do not lend themselves to providing a precise location of the glass transition T_{g2} .

We see that in general there is a decrease in T_{g2} between pre-sterile and post-sterile specimens – what is consistent with the known irradiation degradation observed in PP. Further, each of the observed T_{g2} is within the range consistent with known transitions in PP.

From the user standpoint, materials showing marked changes in T_g after sterilization and aging would not be useful, especially so in medical devices. For instance, TPV-4 shows large decreases in T_g after both sterilization and aging, thus significant effects

on properties. As another example, nanoindentation creep is at a minimum at T_g while going away from the glass transition in either direction increases the creep [41]. The reasons are understandable: far above T_g we are in the liquid state while far below T_g we have significant brittleness. Brittleness has been defined in [42] and analyzed further in [43]. As discussed before, brittleness increases further with aging [42].

Tab. 4. T_{g2} /°C obtained from a second peak in $\tan \delta$.

Material	Pre-Sterile	Post-Sterile	Pre-Sterile Aged	Post-Sterile Aged
TPV-1	- 2	- 2	- 5	- 5
TPV-2	0	1	2	-15
TPV-3	- 1	- 1	- 22	- 1
TPV-4	0	- 20	5	-15
TPV-5	0	2	1	- 5
TPV-6	15	2	- 10	10
TPV-7	10	- 2	10	2
TPV-8	10	- 5	5	- 2
TPV-9	7	- 10	5	- 3

Our TPV-7 does not show much change in T_g after any combination of aging and sterilization. The changes are within ± 2 K, except for the value obtained from $\tan \delta$ for the pre-sterile aged specimen, namely $T_g = - 35$ °C. We recall the conclusion of Nielsen and Landel that the T_g peak of $\tan \delta$ curve can be 10 – 15 K higher than T_g values obtained by other methods [9]. Nielsen and Landel analyzed and quote in their book thousands of publications. In fact, their warning was one of the reasons for undertaking our comparative study. Thus, at least in terms of effects of sterilization and aging on the glass transition, TPV-7 is a worthwhile candidate for the intended application. It may potentially be used also for medical devices other than syringes.

General Discussion

Our results show that for certain TPVs γ sterilization does affect significantly properties of the materials from which medical devices are made. The changes that we observed in T_g and T_{g2} can be ascribed to the varying concentrations of PP in each of the samples. Indeed, in [5] we have shown effects of sterilization on tensile properties and hardness. We now see that glass transitions are affected as well – but the extent of changes depends on the specific composition of a TPV.

We have also observed that T_g continues to change as a result of aging. Similarly, Ishigaki and Yoshii [3] show the changes initiated during sterilization continue throughout the storage process. Considering our results jointly with those from previous studies on ultrahigh molecular weight polyethylene - a major component in prostheses - we see that sterilization-induced changes continue to propagate during storage after irradiation.

Clearly great care is needed in designing polymer-based medical devices; polymer degradation induced by sterilization and subsequent aging in storage may render the devices unusable or – worse - unsafe [4]. At the same time, our work has identified a material, TPV-7, that shows resistance to the changes brought on by sterilization and subsequent storage.

For evaluation of melting temperatures there is a variety of techniques [44]. Glass transitions are more difficult to locate also for the reason that a single glass transition temperature does not exist [45, 46]. As already noted above, it is always a temperature *region* – represented by a single number T_g for pure convenience. The fact that we are dealing with a region has been convincingly demonstrated by Kovacs more than half a century ago [46]. A recommendation of one of the three methods of T_g is not a simple task; there are reasons why the problem has not been solved yet. Let us proceed by elimination. A method based on the loss modulus E'' is not reliable. As seen in Figures 1 and 2, this function is not very sensitive and undergoes only relatively small changes at thermal transitions. As for $\tan \delta$, we have already quoted Nielsen and Landel [9] who have concluded from many hundreds of publications perused that the T_g determined this way can be 15 K away from T_g values determined by other techniques. Our own results for TVP-7 confirm their conclusion.

By a process of elimination, we are left with E' . Inspection of Figures 1 and 2 (and other diagrams obtained in this study but not included here for brevity) shows significant regions of fall of E' at glass transitions. However, there are also fundamental reasons for choosing E' . As noted, Kovacs in his unusually careful experiments has established the fact that there is a temperature interval at which the glass transition occurs [47]. The fall of E' corresponds to that interval. Midpoint of that interval is a good representation of the glass transition region.

There are two main ways of representation of structures of amorphous i.e. glassy materials: the binary radial distribution functions – from which coordination numbers can be obtained [48] and the Voronoi polyhedra [49, 50]. Duals to the Voronoi polyhedra are the Delaunay simplices [49, 50]. Molecular dynamics computer simulations show that the Delaunay simplices can be divided into those with high density (close in shape to perfect tetrahedrons) and those with low local density and large circumradii [51]. The former create a percolative cluster in the glassy state, the latter in the liquid state [51]. It is plausible to expect that half-way in the descent of the $E'(T)$ curve we are at or near the change from the percolative cluster present in the glassy state to the cluster percolating the material which is characteristic of the liquid state.

While we recommend the use of descent of E' for determining T_g , we have still used a second peak in $\tan \delta$ to determine T_{g2} . As discussed above, we are dealing with a second glass transition, occurring in amorphous and un-crosslinked regions of our materials. From our reasoning above, we would expect to use descent of E' again. However, as seen in Figure 2 (and others not included here for brevity), we simply do not observe a sharp descent in E' curve around T_{g2} . For this reason alone, then, we must resort to using peaks of the $\tan \delta$ diagram. Apparently the un-crosslinked regions constitute a minor part of the total volume. On the other hand, if T_{g2} were discernible on the E' diagram, then we would still recommend the use of descent of E' when determining locations of glass transition temperatures.

In earlier papers [19, 20] we have considered glass transitions from the point of view of their dependence on composition in binary polymer systems. Glass transitions are well known to affect surfaces and interfaces. Kopczyńska and Ehrenstein [52] discuss how interfaces determine properties of multiphase materials.

There seems to exist an opinion that irradiation causes polymer degradation. However, in cases where crosslinking prevails one obtains a material with enhanced mechanical properties and better dimensional stability. Brocka and her colleagues [53] have demonstrated how e- beam irradiation improves abrasion resistance of polymers.

Experimental

Materials

The investigated materials are based on isotactic PP (iPP) and its blends with an ethylene-propylene-diene (EPDM) rubber. Before processing the pellets of each material were dried in an oven at 80 °C for 4 h. An AB 100 injection molding machine (A.B. Machinery, Montreal, Quebec, Canada) was used at the adequate processing temperatures, thus between 182 °C and 220 °C.

DMA testing was performed using a DMA7e apparatus (Perkin Elmer Co.)

The TPV specimens were γ -irradiated at doses ranging from 18 to 30 kGy (1.8 to 3.3 Mrad), the most commonly validated doses for sterilization of medical devices. Sterilization was performed according to the ISO standard 11137:1995(E) “*Sterilization of Health Care Products*”. The samples were kept in a ⁶⁰Co gamma radiation chamber at room temperature in air. TPV samples prepared identically but not irradiated were tested as part of the shelf life determination in the absence of gamma radiation and were kept for comparison.

We also investigated the effect of aging on our samples. Since real-time aging is not practical, it was necessary to use accelerated aging techniques that can provide properties of interest for the shelf life of the product. We have incubated the specimens at a chosen elevated temperature for a determined period of time. This technique is used for qualification testing of polymeric medical devices. The specimens of each TPV material, sterilized and non-sterilized, were placed in a Lunaire Environmental Chamber Model CEO 932-4 (Thermal Product Solutions), at 50 °C \pm 3 °C and humidity 90 % for 15 weeks—similarly as in previous paper [5]. The procedure is based on the Arrhenius equation, widely used and also described in the literature—including an ASTM standard [35 - 37]. Thus, an oven test time of 15 weeks at 50 °C was equivalent to 2 years of storage at 22 °C.

We investigated 9 different commercially available TPVs. Because of a nondisclosure agreement our materials have code names, from TPV-1 to TPV-9.

The materials contained from 63 to 83 wt. % PP and from 13 to 26 wt. % EPDM. The contents of PP and EPDM is not additive since other minor components are present. For each material we studied four specimens, one for each of the combinations of aging and irradiation. Thus, we had four examples TPV-1 Pre-Sterile, TPV-1 Pre-Sterile Aged, TPV-1 Post-Sterile (= post-irradiated), and TPV-1 Post-Sterile Aged.

DMA testing

We have determined the storage modulus E' , the loss modulus E'' and $\tan \delta = E''/E'$. Physical significance of these quantities is discussed by Sperling [22], Lucas and her colleagues [23] and also by Menard [24]. Rectangular specimens with dimensions 3.10 x 6.9 x 15 mm (\pm 0.05 mm in each direction) were analyzed by three-point bending in temperature scan mode at the frequency of 1.0 Hz. Samples were heated

from -110 °C to 120 °C at 10 °C/min. We used the static force of 1100 mN and the dynamic force of 1000 mN.

As already noted, we were up against a problem. T_g values located at the maximum of the peak of $\tan \delta$ are known to be higher than those at the maximum of the peak of E'' as much as 10 – 15 K [9, 38]. Rotter and Ishida recommend using $\max(\tan \delta)$ to locate T_g because it is independent of sample geometry and more easily located than E'' [39]. Still others propose using E' to determine T_g , either by mid-point approximations or more sophisticated methods involving changes in slope of E' curve [40]. In short, there is no one set standard for reporting T_g ; it appears to be the authors' preference how to report the values. Here we have determined T_g values in three ways: as a peak in E'' , as a peak in $\tan \delta$, and as the midpoint of the rapid decrease in E' . We believe it is instructive to compare T_g values reported in all three ways – so as to achieve a better perspective on their merits.

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References

- [1] Brostow, W.; Pietkiewicz, D.; Wisner, S.R. *Adv. Polym. Tech.* **2007**, 26, 56.
- [2] Zaharescu, T.; Setnescu, R.; Jipa, S.; Setnescu, T. *J. Appl. Polym. Sci.* **2000**, 77, 982.
- [3] Ishigaki, I.; Yoshii, F. *Rad. Phys. & Chem.* **1992**, 39, 527.
- [4] Gopferich, A. *Biomaterials* **1996**, 17, 103.
- [5] Brostow, W.; Deshpande, S.; Fan, K.; Mahendrakar, S.; Pietkiewicz, D.; Wisner, S.R. *Polym. Eng. Sci.* **2009**, 49, 1035.
- [6] Lewis, G.; Rogers, C.; Trieu, H.H. *J. Biomed. Mater. Res.* **1988**, 43, 249.
- [7] Roe, R.; Grood, E.; Shastri, R.; Gosselin, C.A.; Noyes, F.R. *J. Biomed. Mater. Res.* **1981**, 15, 209.
- [8] Rimnac, C.M.; Klein, R.W.; Betts, F.; Wright, T.M. *J. Bone & Joint Surgery*, **1994**, 76, 1052.
- [9] Nielsen, L.E.; Landel, R.F. “*Mechanical Properties of Polymers and Composites*”, Marcel Dekker, New York **1994**.
- [10] Modine, Z.F.A.; Duggal, A.R.; Robinson, D.N.; Churnetski, E.L.; Bartkowiak, M.; Mahan, G.D.; Levinson, L.M. *J. Mater. Res.* **1996**, 11, 2889.
- [11] Giruginca, M.; Zaharescu, T. *Polymer* **2000**, 41, 7583.
- [12] Brostow, W., editor. “*Performance of Plastics*”, Hanser, Munich – Cincinnati **2000**.
- [13] Gryshchuk, O.; Jost, N.; Karger-Kocsis, J. *J. Appl. Polym. Sci.* **2002**, 84, 672.
- [14] Grosu, E.; Rapa, M.; Tomescu, A.; Nemes, E.; Zaharescu, T.; Jipa, S.; Setnescu, R.; Vasile, C. *Nucl. Instr. Methods B* **2003**, 208, 220.
- [15] Roslaniec, Z.; Broza, G.; Schulte, K. *Compos. Interfaces* **2003**, 10, 95.
- [16] Gryshchuk, O.; Karger-Kocsis, J. *J. Polym. Sci. Chem.* **2004**, 42, 5474.
- [17] Jose, S.; Thomas, S.; Lievana, E.; Karger-Kocsis, J. *J. Appl. Polym. Sci.* **2005**, 95, 1376.
- [18] Bismarck, A.; Hofmeier, M.; Doerner, G. *Composites A* **2007**, 38, 407.

- [19] Brostow, W.; Chiu, R.; Kalogeras, I.M.; Vassilikou-Dova, A. *Mater. Lett.* **2008**, *62*, 3152.
- [20] Kalogeras, I.; Brostow, W. *J. Polym. Sci. Phys.* **2009**, *47*, 80.
- [21] Herzog, B.; Gardner, D.; Lopez-Anido, R.; Goodell, B. *J. Appl. Polym. Sci.*, **2005**, *97*, 2221.
- [22] Sperling, L.H. *Introduction to Physical Polymer Science*, 2nd edn., Wiley, New York **1992**.
- [23] Lucas, E.F.; Soares, B.G.; Monteiro, E. *Caracterização de polímeros, e-papers*, Rio de Janeiro **2001**.
- [24] Menard, K.P. *Dynamic Mechanical Analysis – An Introduction*, 2nd edn., CRC Press, Boca Raton, FL **2008**.
- [25] Brostow, W.; Hess, M.; López, B.L. *Macromolecules* **1994**, *27*, 2262.
- [26] Shaw, T.J. *U.S. Patent 5,120,310*, **1992**.
- [27] Shaw, T.J. *U.S. Patent 5,385,551*, **1995**.
- [28] Shaw, T.J. *U.S. Patent 5,389,076*, **1995**.
- [29] Shaw, T.J. *U.S. Patent 5,578,011*, **1996**.
- [30] Shaw, T.J. *U.S. Patent 5,632,733*, **1997**.
- [31] Shaw, T.J. *U.S. Patent 6,090,077*, **2000**.
- [32] Shaw, T.J.; Zhu, J. *U.S. Patent 6,221,055 B1*, **2001**.
- [33] Shaw, T.J.; Zhu, J.; Rutherford, D. *U.S. Patent 6,572,584*, **2003**.
- [34] Brostow, W.; Deborde, J.-L.; Jaklewicz, M.; Olszynski, P. *J. Mater. Ed.* **2003**, *25*, 119.
- [35] F1980-99 “Standard method for accelerated aging of sterile medical device packages”, ASTM, West Conshohocken, PA **1999**.
- [36] Sauer, B.B. Ch. 10 in “Performance of Plastics”, Brostow, W.; editor; Hanser, Munich - Cincinnati, **2000**.
- [37] Eklund, M.; Edin, H.; Gedde, U.W. *Polym. Degrad. & Stab.* **2007**, *92*, 617.
- [38] Aklonis, J.J.; MacKnight, W.J. “Introduction to Polymer Viscoelasticity”, Wiley, New York **1993**.
- [39] Rotter, G.; Ishida, H. *Macromolecules* **1992**, *25*, 2170.
- [40] Wolfrum, J.; Ehrenstein, G.W.; Avondet, M.A. *J. Compos. Mater.* **2000**, *34*, 1788.
- [41] Beake, B.D.; Bell, G.A.; Brostow, W.; Chonkaew, W. *Polym. Int.* **2007**, *56*, 773.
- [42] Brostow, W.; Hagg Lobland, H.E.; Narkis, M. *J. Mater. Res.* **2006**, *21*, 2422.
- [43] Brostow, W.; Hagg Lobland, H.E. *Polym. Eng. Sci.* **2008**, *48*, 1982.
- [44] Svamy, Y.V.; Dubrovinskaya, N.A.; Dubrovinsky, L.S. *J. Mater. Res.* **1999**, *14*, 456.
- [45] Privalko, V.P. *J. Mater. Ed.* **1998**, *20*, 57.
- [46] Privalko, V.P. *J. Mater. Ed.* **1998**, *20*, 373.
- [47] Kovacs, A.J. *J. Polym. Sci.* **1958**, *30*, 131.
- [48] Brostow, W. *Chem. Phys. Letters* **1977**, *49*, 285.
- [49] Brostow, W.; Chybicki, M.; Laskowski, R.; Rybicki, J. *Phys. Rev. B* **1998**, *57*, 13448.
- [50] Brostow, W.; Castaño, V.M. *J. Mater. Ed.* **1999**, *21*, 297.
- [51] Medvedev, N.N.; Geiger, A.; Brostow, W. *J. Chem. Phys.* **1990**, *93*, 8337.
- [52] Kopczyńska, A.; Ehrenstein, G.W. *J. Mater. Ed.* **2007**, *29*, 325.
- [53] Brocka, Z.; Schmachtenberg, E.; Ehrenstein, G.W. *Proc. Ann. Tech. Conf. Soc. Plast. Engrs. (ANTEC-SPE)* **2007**, *67*, 1690.