Colloid Polym Sci 279:506–512 (2001)

SHORT COMMUNICATION

I. Schwarz
M. Stranz
M. Bonnet
J. Petermann

Changes of mechanical properties in cold-crystallized syndiotactic polypropylene during aging

Received: 18 September 2000
Accepted: 2 January 2001

I. Schwarz · M. Stranz · M. Bonnet
J. Petermann (✉)
Institute for Materials Science
Department of Chemical Engineering
University of Dortmund
Dortmund, Germany
e-mail: peterman@chemietechnik.uni-dortmund.de
Tel.: +49-231-7552479
Fax: +49-231-7552480

Abstract Many semicrystalline polymers undergo a process of aging when they are stored at temperatures higher than their glass-transition temperature (T_g). Syndiotactic polypropylene was quenched from the melt to −40 °C, crystallized from the glassy state at 20 or 40 °C and stored at the respective temperature for different aging times up to 7200 h. A significant increase in the tensile modulus and stress at yield and a decrease in strain at yield were observed for both aging temperatures. Differential scanning calorimetry (DSC) scans of aged material showed an endothermic annealing peak 15–30 °C above the previous aging temperature, the maximum temperature and enthalpic content of which increased with aging time. The position and the shape of the melting peak were not affected by aging. Scans of the storage modulus obtained from dynamic mechanical analyser measurements indicated a softening process starting at about 20 °C above the aging temperature and correlating with the annealing peak detected by DSC. Density measurements and wide-angle X-ray scattering investigations revealed that neither the crystallinity increased significantly nor did the crystal structure change. So the observed property changes induced by aging are attributed to microstructural changes within the amorphous phase. Furthermore, it could be shown by annealing experiments carried out at 60 °C, that aging above T_g is, analogous to aging below T_g (physical aging), a thermoreversible process.

Key words Cold-crystallized syndiotactic polypropylene · Aging · Mechanical properties · Density · Annealing

Introduction

Aging in polymers is a well-known phenomenon, whereas the term *physical aging* is usually used to describe changes of the material's physical properties with elapsed time due to the system's approach to thermodynamic equilibrium. Hence, any polymer being in a nonequilibrium state resulting from some kind of restriction in molecular mobility can undergo physical aging, which is obvious for polymers below their glass-transition temperature (T_g). In this case, an increase in density, yield stress, and elastic modulus has been observed, while impact strength, creep rate, and damping properties decrease with increasing aging time [1]. Property changes occurring on physical aging are generally attributed to the relaxation process in the amorphous phase, leading to a reduction in enthalpy and free volume, which will both be recovered at higher temperatures, implying that aging is a fully thermoreversible process.

Recently, numerous articles have been published reporting that the characteristics of physical aging had been observed in certain semicrystalline polymers above their nominal glass transition. In 1978, Struik [1] proposed a model founded on the concept of an extended glass transition in semicrystalline polymers. Owing to the constraining effects of the crystalline lamellae on neighbouring amorphous chains, the segmental mobility of these chains is greatly reduced, extending their glass transition to higher temperatures. Consequently, physical aging could occur above the nominal T_g of the unconstrained amorphous fraction.

Concerning isotactic polypropylene (iPP), it is now well established that rapid quenching leads to a third phase of intermediate order between crystalline and amorphous. The material undergoes pronounced aging, leading to an enhancement of mechanical properties, an increase in density, and a decrease of the permeation properties [2–6]. Differential scanning calorimetry (DSC) scans of quenched and annealed samples show a small endothermic peak [7], which was extensively investigated for semiflexible polymers such as poly(ether ether ketone) [8–11], poly(ethylene terephthalate), [12–15], or poly(phenylene sulphide) [16] and which can also be detected in cold-crystallized isotactic polystyrene [17]. Several attempts have been made to explain the origin of this annealing peak. It is either attributed to the melting of crystals differing in size, texture, or perfection from the higher melting crystal population [8–10] or associated with the enthalpic recovery of a physically aged constrained amorphous fraction (sometimes referred to as a third phase termed constrained amorphous, rigid amorphous, paracrystalline, pseudocrystalline or mesomorphic) [12, 15, 16, 18], or a combination of melting and relaxation processes [16, 17]. Romano et al. [2] speculate that the dimensions of the ordered smectic domains in iPP (intermediate phase) increase with aging time and the small endotherm may represent their disordering. They explain the changes in mechanical properties occurring on aging by a reduction in the free volume of the amorphous phase as well as a concomitant increase of the dimensions of the smectic domains. Also the physical properties of slowly cooled iPP crystallizing in the monoclinic form depend on the age of the material. From sorption and diffusion experiments Vittoria [19] concluded that aging involves two different mechanisms. The first, very rapid, consists of a decrease in the amorphous fraction and the second, superimposed on the first, consists of a progressive reduction in the mobility of the amorphous chains involved in the diffusion process.

Concerning syndiotactic polypropylene (sPP), crystallization proceeds comparatively slowly compared to iPP, making it possible to quench sPP into the glassy state. Here we present some results on the aging of cold crystallized sPP with respect to its mechanical and thermal properties and discuss the results with regard to proposed microstructural changes.

Experimental

The material investigated was sPP, kindly supplied by the Fina Oil & Chemical Company. Its pentadic syndiotacticity was determined by ^{13}C NMR spectroscopy to be 83%. For mechanical as well as for thermal investigations, sheets of 130×130 mm^2 were prepared in a hot press. The material was kept in the melt for 10 min at 170 °C to erase any memory effects due to previous thermal history and was subsequently quenched to −40 °C in an ethanol bath. The sheets were isothermally cold crystallized at 20 or 40 °C and stored at the respective temperature for various periods of aging time, t_a.

To examine the thermoreversibility of the observed aging effects, some specimens previously aged at 20 °C were annealed at 60 °C in an annealing chamber for different annealing times, t_{ann} (5 min up to 24 h).

For tensile testing, specimen of nominal dimensions $10 \times 0.4 \times 100$ mm^3 were deformed in a Zwick tensile testing machine at room temperature. Stress–strain diagrams were recorded at a constant deformation rate of 10%/min.

Dynamic mechanical analysis (DMA) was carried out using a TA Instruments DMA 2980 dynamic mechanical analyser. Samples of $4 \times 0.3 \times 30$ mm^3 (nominal length: 20 mm) were strained with a frequency of 1 Hz and an amplitude of 20 μm. A constant heating rate of 3 °C/min was applied from below T_g up to the melting region.

DSC was performed under nitrogen atmosphere using a TA Instruments MDSC 2910 differential scanning calorimeter. The temperature calibration was done with gallium, indium, and zinc. To reduce differences among samples due to thermal lag, similar discoid samples of 400 ± 50 μm thickness and 9.5 ± 0.5 mg mass were employed. Heating scans were recorded at a rate of 10 °C/min.

The density of the sPP (minimum sample size 15×15 mm^2) was determined by hydrostatic weighing in ethanol at room temperature. The density of ethanol was calculated on the basis of buoyancy measurements in a temperature range from 20 to 24 °C. Ethanol was used instead of water because of its better wetting properties concerning sPP, minimizing errors due to air bubbles adhering to the surface of the samples.

Results

Mechanical properties and density

The modulus revealed from tensile testing experiments is plotted in Fig. 1 versus aging time for samples aged at 20 and 40 °C, respectively. For both series a distinct increase with aging time can be observed. Compared to the value reached after 1 hour, the modulus has increased by 100% at 20 °C after 1000 h. If compared to a sample tested as soon as possible after quenching ($t_a = 15$ min), the tensile modulus after 1000 h is even 3 times as high as the "original" one.[1] For the samples aged at 40 °C, values belonging to shorter aging times are slightly higher but follow the same tendency, the increase showing a linear dependence of the logarithm of film age. The change in mechanical behaviour also manifests itself in a

---

[1] For comparison, in all other cases, a value obtained after $t_a = 1$ h is chosen as a reference, as the testing time can then be considered short compared to the aging time.

pronounced rise of stress at yield, σ_y, accompanied by a decrease of strain at yield, ε_y. Again, compared to the values reached after 1 h, σ_y has increased by 50% and ε_y has dropped by 25% at 20 °C after 1000 h. The characteristic values obtained after several aging times are listed in Table 1. The natural draw ratio remained constant for all specimens, independent of aging time and for both aging temperatures investigated. The stress–strain diagrams of a fresh and an aged specimen representing the change in deformation behaviour with aging time are shown in Fig. 2.

DMA measurements were performed to investigate the mechanical properties of the material over a broader temperature range including the glass-transition region. The storage modulus, E_{dyn}, and the loss tangent, tan δ, are presented for four samples of different age in Fig. 3a and b, respectively.

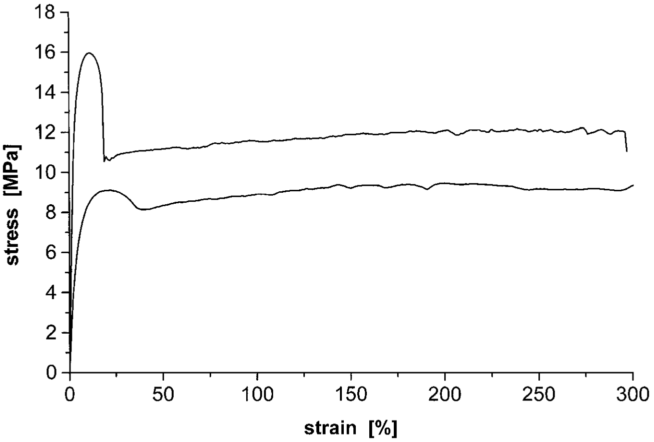

Fig. 2 Stress–strain diagrams of a fresh ($t_a = 0.3$ h, *lower curve*) and an old specimen ($t_a = 7200$ h, *upper curve*). The curves were not shifted

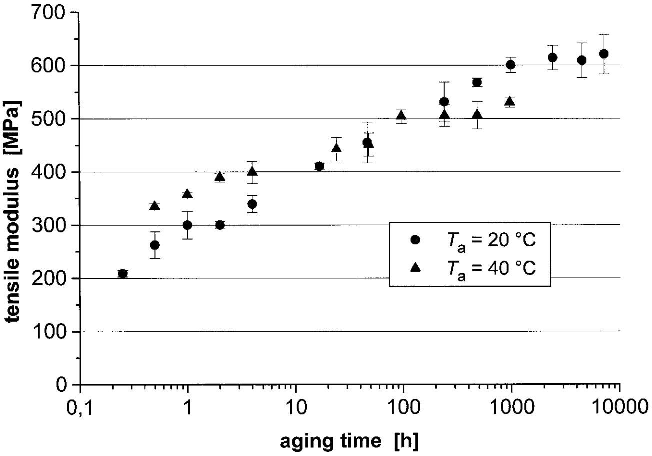

Fig. 1 Tensile modulus plotted versus aging time for samples aged at 20 °C (●) and 40 °C (▲)

Table 1 Characteristic values determined by tensile tests

t_a (h)	T_a = 20 °C			T_a = 40 °C		
	E [MPa]	σ_y [MPa]	ε_y [%]	E [MPa]	σ_y [MPa]	ε_y [%]
0.25	209	8.18	18.95			
0.5	262	8.83	15.56	335	11.39	15.44
1	300	9.36	13.94	357	11.85	15.34
2	300	9.26	15.01	389	12.40	13,23
4	339	9.95	13.56	399	12.90	13.32
17/24[a]	410	11.37	11.88	442	13.12	13.48
48	455	11.95	9.88	451	13.44	13.22
240	532	12.94	8.98	506	15.16	12.16
480	568	13.56	10.61	514	15.42	12.05
984/960[a]	601	14.11	10.32	531	15.81	11.48
2400	614	14.64	9.11			
7200	621	15.19	9.54			

[a] Aging times for 20 and 40 °C, respectively

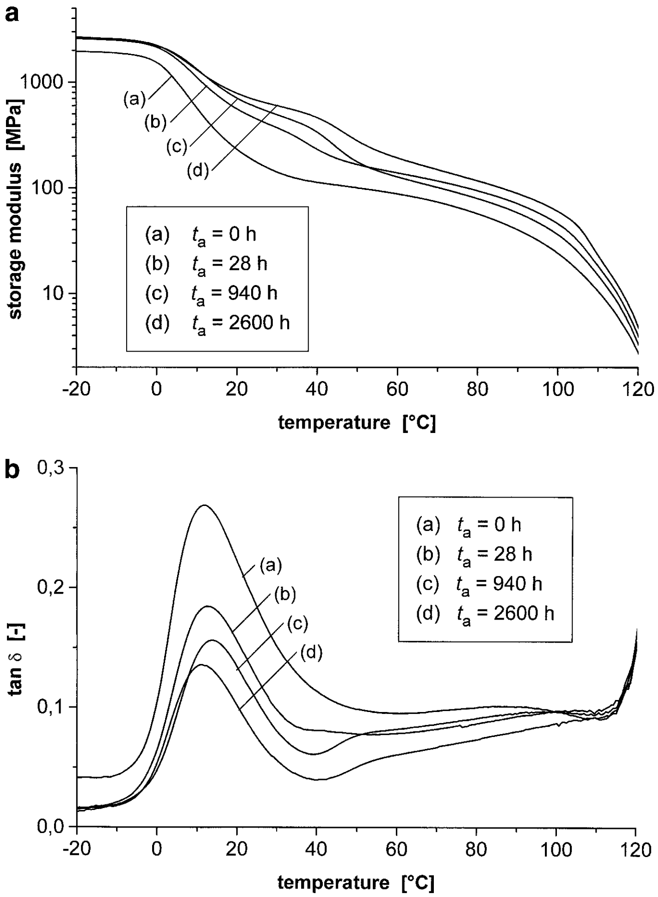

Fig. 3 a Storage modulus versus temperature for a specimen measured directly after quenching (*curve a*) and specimens aged for 28, 940, and 2600 h (*curves b, c, d*, respectively) at 20 °C, **b** Loss tangent versus temperature for a specimen measured directly after quenching (*curve a*) and specimens aged for 28, 940, and 2600 h (*curves b, c, d*, respectively) at 20 °C

At temperatures below T_g all samples exhibit the same thermomechanical behaviour, irrespective of previous aging time. Just the amorphous specimen measured directly after quenching shows a somewhat lower modulus and a higher loss tangent. This is probably due to inaccurate determination of the specimen dimensions, which had to be done at room temperature within a few seconds to prevent the material from "defrosting". In the temperature range from 0 to 40 °C the storage moduli of the aged samples decrease less than E_{dyn} of the amorphous one as is known from semicrystalline polymers. This decrease is less pronounced the longer the material has been aged and, accordingly, the maximum of tan δ declines with increasing aging time. At temperatures between 40 and 60 °C, a second drop in the modulus curves of the aged material occurs, indicating a second softening process. In the same temperature range tan δ increases markedly compared to the amorphous sample. The absence of a second maximum reveals the lack of an α-relaxation process which is well documented for iPP. The softening starts at about 20 °C above the aging temperature and is shifted to higher temperatures with longer aging times. It can be correlated with the endothermic annealing peak seen in the DSC scans in the same temperature region; this will be discussed later. Concerning melt-crystallized sPP, no comparable softening step can be detected by DMA measurements [20].

The density is plotted versus the aging time in Fig. 4.[2] The diagram shows a sharp increase within the first minutes of aging due to crystallization setting in as soon as the samples are heated above their T_g. Further aging induces just a slight linear increase in density with the logarithm of aging time. The functional relation obtained for both aging temperatures is comparable to that reported by other authors for the aging of iPP at room temperature [4, 6]. In contrast to the characteristic values describing the mechanical behaviour, the increase in density is not very pronounced and in no account is sufficient to attribute the significant enhancement of mechanical properties during aging just to secondary crystallization.

Thermal analysis

To investigate if the thermal behaviour of the material is also affected by aging, samples of different age were investigated by DSC measurements. The influence of aging time at 20 °C on the thermal behaviour is shown in Fig. 5 for two aged samples. In addition, a plot from a sample scanned directly after quenching is presented. Beside the glass transition at −2.7 °C, this scan shows an exothermic crystallization peak with its maximum at 30 °C. Integration of the peak areas belonging to crystallization and melting of the sample reveals the same enthalpic content of about 28 J/g, giving evidence to the sPP being fully amorphous after quenching. In accordance with the results from density measurements, no exotherms can be detected anymore after 10 min of aging, denoting that primary crystallization is completed after this time. Regarding the scans of the aged samples, the glass transition has slightly shifted to higher temperatures and a second endothermic peak (annealing peak) appears 15–30 °C above the aging temperature,

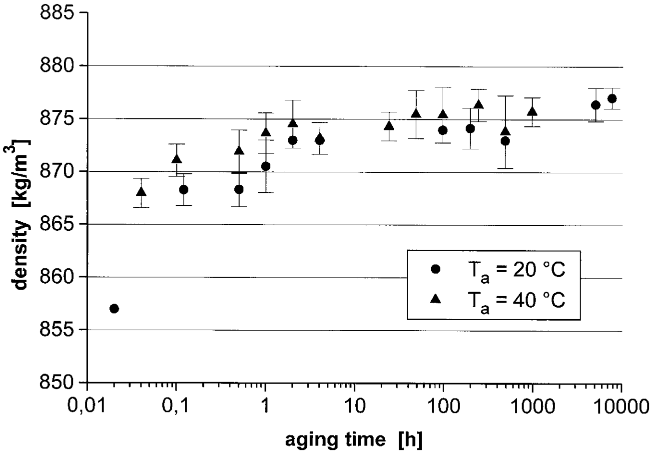

Fig. 4 Density plotted versus aging time for samples aged at 20 °C (●) and 40 °C (▲)

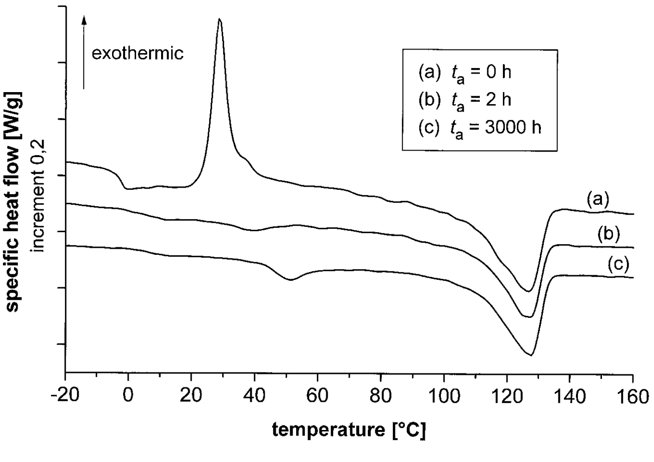

Fig. 5 Differential scanning calorimetry scans of an amorphous sample and of samples aged for 2 and 3000 h at 20 °C (heating rate 10 K/min). The curves are shifted along the y-axis for clarity

---

[2] For two reasons the crystallinity calculated from these values is not presented: not the absolute values are of interest but a tendency should be shown and calculating the crystallinity on the basis of density measurements implies the material consists of not more than two phases, which may be an undue assumption in our case. If a two-phase model is assumed, however, crystallinities within the scope of 20–30% would result from the measured densities.

whereas the position and the shape of the melting peak remain unchanged. The maximum temperature of the annealing peak, $T_{p,a}$, as well as its enthalpic content increase with aging time for both aging temperatures investigated. Corresponding observations have been made for amorphous [13, 21] and also for some semicrystalline [2, 8, 22] polymers, typically comprising a linear dependence of both, enthalpy and peak temperature, on the logarithm of annealing time.

Thermoreversibility

Considering the physical aging of glassy polymers, microstructural changes (and property changes) can be fully revoked, if the material is heated above its T_g [1]. To examine if sPP aged well above T_g shows similar behaviour, annealing experiments were carried out. An annealing temperature of 60 °C was chosen, because it corresponds to the upper end of the annealing peak and from that temperature on DSC measurements revealed no alteration in the scans of samples aged for different periods of time.

Tensile testing of the aged and annealed specimens indeed shows that the change in mechanical properties due to aging is reversible and can be erased by annealing. Storage of an "old" sample ($t_a = 4600$ h) at 60 °C for $t_{ann} = 5$ min causes the modulus as well as the stress at yield to drop and the strain at yield to increase again. The values obtained then are comparable to the ones of a sample aged for a short time where primary crystallization has finished. When samples of distinct age ($t_a = 24$ h up to 4600 h) are annealed for 1 h, the dissimilarity in their mechanical behaviour resulting from different aging times disappears and the characteristic values, i.e., E, σ_y, and ε_y, turn to constant levels, irrespective of previous aging time (Fig. 6a, b, c).

Consistent results are obtained from thermal analysis. A few seconds at 60 °C is sufficient to erase the annealing peak which characterizes the previous thermal history of the sample.

If the annealing time is extended, a new aging process sets in: A peak corresponding to an annealing temperature of 60 °C arises in the DSC scans, E and σ_y increase, and ε_y decreases with ongoing annealing time. This is why the property changes due to aging at 20 °C cannot be fully revoked by annealing at higher temperatures. Any thermal treatment of cold-crystallized material at temperatures between its crystallization temperature and T_m induces a new aging process.

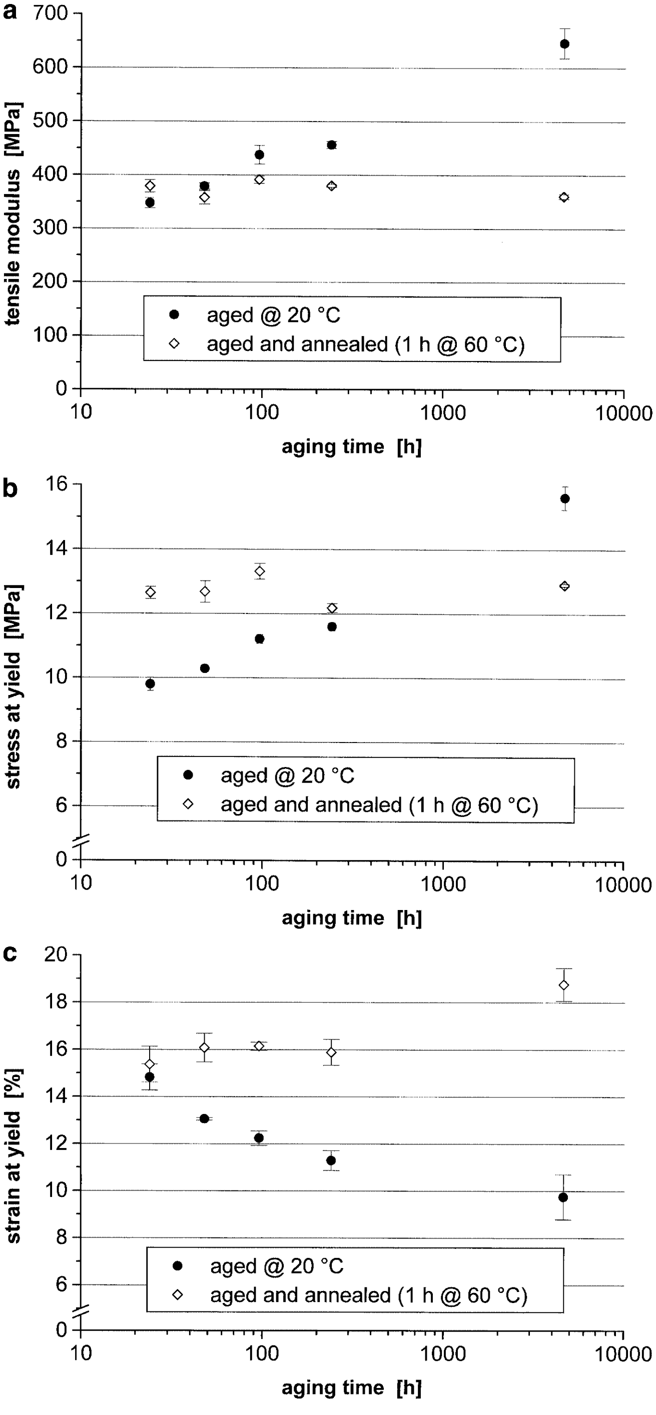

Fig. 6 a Tensile modulus plotted versus aging time for samples aged at 20 °C (●) and for samples aged for indicated times at 20 °C and subsequently annealed for 1 h at 60 °C (◇). **b** Stress at yield plotted versus aging time for samples aged at 20 °C (●) and for samples aged for indicated times at 20 °C and subsequently annealed for 1 h at 60 °C (◇). **c** Strain at yield plotted versus aging time for samples aged at 20 °C (●) and for samples aged for indicated times at 20 °C and subsequently annealed for 1 h at 60 °C (◇)

Discussion

The observed changes in the mechanical properties with aging time indicate that some kind of microstructural reorganization takes place within the material. As, apart from the first minutes where structural arrangement is dominated by crystallization, the density does not increase considerably, the enormous enhancement of the modulus cannot be attributed to secondary crystallization. Moreover, the possibility of more than two phases being present in the aged material implies that an increase in density does not necessarily denote an increase in crystallinity. As another possible explanation for the development of the mechanical properties with time one might assume changes within the crystal, with the overall crystallinity staying almost constant. Phenomena such as crystal perfecting or lamellar thickening, being a typical feature of many polymers in the temperature range between T_α and T_r, can be excluded for sure.[3] As is evident from our DMA measurements and as was shown earlier by other authors [25, 25], sPP exhibits no α-relaxation, allowing no crystalline mobility at temperatures far below the melting region. A change in the crystalline structure (chain packaging) can be excluded as well, which was revealed by wide-angle X-ray scattering (WAXS) experiments showing no additional peaks in the diffractograms of aged samples. So we conclude that the structural changes induced by aging do not affect the crystalline phase but take place within the amorphous regions or parts of the amorphous regions of the material. This assumption is strongly supported by DMA results which clearly show that the mechanical properties at temperatures lower than T_g are not influenced by aging. Whether all the amorphous phase is affected in the same manner or the aging process is concentrated to specific regions cannot be clearly determined by one experiment. It is evident that a reduction in the free volume as in physical aging of amorphous polymers would explain the slight increase in density with time and would also affect the mechanical properties of the material; however, it would not account for such an enormous increase of the modulus. Also a uniform change in the amorphous phase would cause a more pronounced shift of the glass transition than we observed it in our DSC and DMA scans and, what is more, would not provoke an endothermic peak in the DSC heat flow. Therefore, we favour the idea that cold-crystallized sPP might contain a third phase besides crystalline and "classical amorphous", becoming more and more conspicuous the longer the material has been aged and significantly enhancing the mechanical properties of the material, which does not mean that we suppose the "classical amorphous" phase to be totally unaffected by aging. As demonstrated by DSC experiments and tensile tests, the effects of aging can be erased by annealing, which causes the destruction or reordering of this phase.[4] So the aging-induced changes within the material can be seen as a thermoreversible process, whereas one should note that by annealing a new aging process is induced at once.

Conclusion

The changes in the mechanical and thermal properties of cold-crystallized sPP during aging have been investigated for aging temperatures of 20 and 40 °C. The enormous increase in the tensile modulus and the shift of the yield point towards higher stresses and lower strains as well as the appearance of an aging time dependent annealing peak in DSC scans point towards microstructural changes within the material. Density measurements revealed just a slight increase in density with time, being insufficient to attribute the significant enhancement of mechanical properties during aging to secondary crystallization. As sPP exhibits no α-relaxation, the observed property changes cannot originate from changes within the crystals built during primary crystallization either. WAXS experiments revealed that a change in the crystalline structure (chain packaging) can be excluded as well. Thus, we presume that aging does not affect the crystalline phase, but microstructural changes take place within parts of the amorphous regions of the material. DMA measurements clearly show that the mechanical properties at temperatures lower than T_g are not influenced by aging, giving further evidence to this assumption. We also support the idea that cold-crystallized and aged sPP contains a third phase besides crystalline and "classical amorphous". The growth of this phase with time might contribute to the slight increase in density and lead to the observed enhancement of the mechanical properties of the material. As revealed by DSC experiments and tensile tests, the buildup of this phase is a thermoreversible process and the effects of aging can be erased by annealing, which, however, simultaneously induces a new aging process.

Acknowledgements This work was supported financially by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

---

[3] T_α (50–100 °C for iPP) is correlated to the α-relaxation process; T_r (145–160 °C for iPP) characterizes the onset of the recrystallization processes at the beginning of the melting region [23].

[4] Temperature-modulated DSC measurements, being an appropriate method to get a deeper insight into the nature of this process, are in progress for several materials.

References

1. Struik LCE (1978) Physical aging in amorphous polymers and other materials. Elsevier, Amsterdam
2. Romano G, Russo R, Vittoria V (1998) J Macromol Sci Phys B 37:841–850
3. Vittoria V (1988) Polymer 29:1118–1123
4. Baum JS, Schultz JM (1981) J Appl Polym Sci 26:1579–1584
5. Gezovich DM, Geil PH (1968) Polym Eng Sci 8:210–215
6. Schael GW (1966) J Appl Polym Sci 10:901–915
7. Busfield WK, Blake CS (1980) Polymer 21:35–40
8. Velikov V, Marand H (1997) J Therm Anal 49:375–383
9. Verma R, Marand H, Hsiao B (1996) Macromolecules 29:7767–7775
10. Bassett DC, Olley RH, Al Raheil AM (1988) Polymer 29:1745–1754
11. Blundell DJ (1987) Polymer 28:2248–2251
12. Bonnet M, Rogausch K-D, Petermann J (1999) Colloid Polym Sci 277:513–518
13. Cañadas JC, Diego JA, Mudarra M, Belana J (1998) Polymer 39:2795–2801
14. Qian R, Shen D, Sun F, Wu L (1996) Macromol Chem Phys 197:1485–1493
15. Montserrat S, Cortés P (1995) J Mater Sci 30:1790–1793
16. Lu SX, Cebe P (1996) Polymer 37:4857–4863
17. Liu T, Yan S, Bonnet M, Lieberwirth I, Rogausch KD, Petermann J (2000) J Mater Sci 35:5047–5055
18. Cheng SZD, Cao M-Y, Wunderlich B (1986) Macromolecules 19:1868–1876
19. Vittoria V (1987) Polym Commun 28:199–201
20. Bonnet M (1999) PhD thesis. Universität Dortmund
21. Hutchinson JM (1995) Prog Polym Sci 20:703–760
22. Alizadeh A, Richardson L, Xu J, McCartney S, Marand H, Cheung YM, Chum S (1999) Macromolecules 32:6221–6235
23. Gahleitner M, Fiebig J (1999) In: Karger-Kocsis J (ed) Polypropylene: an A–Z reference. Kluwer, Dordrecht, pp 392–398
24. Uehara H, Yamazaki Y, Kanamoto T (1996) Polymer 37:57–64
25. Sakata Y, Unwin AP, Ward IM (1995) J Mater Sci 30:5841–5849