PHYSICAL TRANSITIONS AND CRYSTALLIZATION PHENOMENA IN
POLY(ETHYLENE TEREPHTHALATE) STUDIED BY MICROHARDNESS

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SYNOPSIS

The crystallization behaviour of PET containing sodium montanate as crystal nucleating agent, as well as, PET without nucleating agent has been studied using the microhardness technique. The kinetics of crystallization from the glassy state was investigated in real time by measuring the microhardness (H) at different crystallization temperatures. Results are discussed in terms of the Avrami equation. Values of the Avrami exponent, n , of about 3 are observed for samples with and without nucleating agent. For the samples with nucleant two crystallization ranges are observed: A first range which corresponds to a fast crystallization from nucleating agent particles and a second range which is associated to a slow self-crystallization mode. New transitions evidenced by the presence of a small maximum in H as a function of annealing time and temperature are detected at temperatures higher than T_g for the physically aged samples. The kinetics of this transition has also been examined. It is further shown that the presence of nucleating agent induces a hardening at room temperature which is similar to the effect produced by the physical aging of the samples below T_g . Finally, it is found that aging reduces the rate of creep of the material under the indenter.

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INTRODUCTION

Microhardness, H , has emerged in recent years as a physical method which can offer a direct information on changes in morphology and microstructure of polymers (1,2). Many investigations on microhardness make reference to high crystalline polymer materials having glass transition temperatures well below room temperature (3-8). A few studies on the microhardness of low crystallinity materials and glassy polymers are also available (9,10). In particular, we have recently shown(11) that the microhardness of poly(ethylene terephthalate) (PET) can furnish a useful information about the different morphologies obtained during primary crystallization (involving an incomplete spherulitic growth) and secondary crystallization, i.e. after spherulitic growth is completed. The obtained results were quantita-

tively discussed in the light of three structural factors: a) The volume fraction occupied by spherulites. b) The value of crystallinity within the lamellar stacks. c) The average thickness of the crystals.

The mechanism of crystallization of PET from the glassy state, on the other hand, has been amply investigated by several investigators. The kinetics of crystallization from the glassy state was studied by Keller et al. (12) and Zachmann and Stuart(13) by measuring the density changes during crystallization and by Elsner et al. using time resolved small angle X-ray scattering (14,15). Günter and Zachmann examined the effect of catalysts on the kinetics of crystallization (16). Finally, one of us (T.A.) has recently analyzed the influence of catalysts on the rate of crystallization and on the crystalline lattice distortions in PET by means of wide angle X-ray scattering (17).

In the present study the crystallization of PET from the glassy state is examined by measuring the microhardness "in situ" during crystallization at different temperatures. It is shown that the effect of nucleating agents and of physical aging upon the crystallization behaviour from the glassy state are of primary importance. The occurrence of time and temperature dependent transitions observed at temperatures higher than T_g in physically aged PET is also reported.

EXPERIMENTAL

Samples of amorphous PET from Kalle(Germany) containing manganese acetate as catalyst were melt-pressed in the form of 200 μ m thick films. The molecular weight determined by viscometry was found to be 33000. Two types of samples were investigated:

a) Samples containing 0.075 percent sodium montanate as crystal nucleating agent. b) Samples without nucleant. The glassy polymers were investigated: i) immediately after quenching in ice-water (initial sample) and ii) after one year storage at room temperature.

The density of the samples was measured in a density gradient column containing a mixture of hexane and tetrachloroethane. From the density the volume degree of crystallinity α was calculated assuming for the crystal density a value of $\rho_c=1.4895$ g/cm³ and for the amorphous density a value $\rho_a=1.3379$ g/cm³. The data for the crystallinity determined in this way agree well with values obtained from wide angle X-ray scattering (18).

Microindentation hardness measurements were performed with a Leitz "Durimet" tester using a square based diamond. The microhardness value (in Pa) was derived from the residual projected impression using the equation:

$$H=Kp/d^2 \quad (1)$$

where d is the mean diagonal length of the indentation in meters, p the applied force in Newtons, and K a geometrical factor equal to 1.854 (19). The force is applied at a controlled rate, held for 0.1 min, and removed. The length of the impression is measured to $\pm 0.5 \mu\text{m}$ with a microscope equipped with a filar eyepiece. Further details concerning the test procedure are reported elsewhere (19). The temperature dependence of hardness was determined in the range of room temperature up to 140°C . The H -value in this temperature range was determined within $\Delta H/H \approx 0.5$. The penetration depth of the indenter is typically a few μm depending of temperature. The hardness was measured during heating of the sample every $3\text{--}4^\circ\text{C}$ up to 140°C . The isothermal crystallization of PET was followed, measuring H at various constant temperatures in the $90\text{--}117^\circ\text{C}$ range as a function of time every 45sec, using a hot stage with a heat-controller designed by Prof. T. Yoshida, Dr. T. Asano and Mr. K. Mizuno from Shizuoka University. The surface temperature of the samples was calibrated with organic compounds of known melting point. In order to obtain an adequate optical contrast of the impressions and to correct for a possible local elastic recovery a $100\text{\AA}$ thin layer of a Au/Pd alloy was evaporated onto the materials surface. Experiments were carried out during crystallization with the Au/Pd layer deposited on the PET surface. The Au/Pd alloy does not affect the H -values obtained.

RESULTS

Fig. 1 illustrates the DSC scans for the glassy PET samples without nucleating agent immediately measured after solidification (initial sample)(bottom) and after storage for one year at room temperature(top). All samples show the presence of a clear exothermic peak at about 120-140°C corresponding to the crystallization and a large endothermic peak at about 250°C corresponding to the melting of the polymer. In addition, the DSC scans of the glassy samples after immediate quenching (dashed lines) show the presence of a typical step corresponding to the T_g temperature. On the other hand, the T_g temperature in the aged material is revealed (solid lines) by the presence of a small endothermic peak which corresponds to a relaxation of the glass towards equilibrium (20). Enthalpic relaxation is associated to the onset of glass formation and restriction to segmental motion below this temperature region (20).

Figs. 2a and 3a show the kinetics of the microhardness variation during crystallization of the physically aged material as a function of time for different temperatures. Fig. 2 shows the H-data for the material without nucleating agent and Fig.3 presents the microhardness data for the material with nucleating agent. For samples without nucleating agent (Fig. 2a) one just observes one single rapid rate of H-increase at each crystallization temperature. In this case the final leveling-off value

of H is the same for all crystallization temperatures. On the other hand, for PET with nucleant (Fig. 3b) one clearly observes during crystallization at 95 and 100°C two well-defined regions corresponding respectively to a first rapid- and to a second slower crystallization rate. These two regions are not identified for temperatures of crystallization $T_C < 95^\circ\text{C}$ and $T_C > 100^\circ\text{C}$. In addition, for the samples with nucleating agent (Fig. 3a) the final leveling-off value of H increases from $H_M \sim 100\text{MPa}$ for $T_C = 90^\circ\text{C}^{(*)}$ up to $H_M \sim 160\text{MPa}$ for $T_C = 105^\circ\text{C}$.

Most interesting is the fact that the initial hardness variation with time (Fig. 2b) for the material without nucleating agent shows a hardness maximum after 8-9 minutes when measured both at 105 and 110°C, just before the onset of primary crystallization. These effects seem to be out of experimental error (denoted by the size of the symbols). In addition at 105°C also 'peaks' at ca. 20 and perhaps 24 minutes can be distinguished. For the material with nucleating agent a maximum in hardness as a function of time appears at lower temperatures (90-95°C) and after longer annealing times (12-25 minutes) (Fig. 3b). On the other hand, for crystallization temperatures of $T_C = 100^\circ\text{C}$ and 105°C solidification is so fast that it does not let this transition to be seen.

(*) This value not shown in Fig. 3a is obtained for $t_C > 400\text{min}$.

The above time dependent transition could suggest the occurrence of a certain ^{kind} of molecular ordering giving rise to a hardening effect which vanishes after 5-15 minutes, depending on temperature and on the presence of nucleant. In contrast, the fresh samples measured immediately after quenching do not seem to show the existence of such a transition, as evidenced in Fig.4.

Fig. 5a shows the variation of H as a function of temperature for quenched amorphous PET without (top) and with (bottom) nucleating agent before and after physical aging. One can distinguish two regions of behaviour:

In the high temperature region ($T > T_g$), in addition to the conspicuous softening range (from 120 MPa at T_g down to 5 MPa at 90°C) shown by aged PET without nucleant, it seems to emerge a faint hardness maximum at about 100°C (Fig. 5a). Fig. 5b illustrates a similar softening behavior for physically aged PET containing nucleating agent. In this case, owing to the decrease of the crystallization temperature the small H-maximum is shifted to $T \approx 90^\circ\text{C}$.

In the low temperature region ($T < T_g$) the aged samples (1 year storage at room temperature) without nucleant (Fig. 5a) clearly show larger microhardness values than the freshly prepared samples. On the other hand, aged samples with nucleant

(Fig. 5b) show the same H-values than fresh samples immediately examined after quenching.

To further characterize the physical aging of PET samples we investigated the creep behaviour under the indenter. Fig.6a shows the $\log(H)$ - $\log(t)$ plot for the PET samples without nucleant. A typical variation according to

$$H=H_0t^{-k} \quad (2)$$

is obtained, where H_0 is the hardness measured at $t=1\text{min}$ and k is the so-called creep constant. Here physical aging produces an equivalent increase of H for all loading times. As a consequence, the creep constant $k=0.06$ nearly remains unchanged after a long storage time of the material. On the other hand, the creep behaviour for PET with nucleating agent (Fig. 6b) is now totally different before and after physical aging. While at low loading times ($t \sim 0.1$ minutes) H is the same for the material with nucleating agent, before and after aging, after long loading times a clear difference is observed leading to a notable decrease of k after aging. Finally, it is worth noting that the creep constant is larger for the fresh material with nucleant, immediately examined after quenching ($k=0.12$) (see Fig. 6b), than for the material without nucleating agent ($k \sim 0.06$) (Fig. 6a).

DISCUSSION

Time and Temperature dependent transitions in physically aged PET

The study of molecular transition relaxation phenomena in amorphous polymers beyond T_g has been the object of intense activity (21). This has led to the concept of the existence of a liquid-liquid (T_{ll}) transition which has been observed by a variety of physical methods. In attempting to detect such relaxation phenomena we have followed the microhardness variation of PET as a function of time at temperatures well above T_g . One could expect, in principle, that the set up of segmental motions at these temperatures would give rise to distinct softening phenomena capable to be detected by microhardness. Instead, what we observe for physically aged PET, in Figs. 2b and 3b, is a local maximum in hardness versus time measured at 105-110°C for the material without nucleating agent and at 90-95°C for PET with nucleant.

To explain these transitions one may speculate about a possible restriction of segmental motions involving a time-dependent molecular "paracrystalline" ordering giving rise, in turn, to a hardening effect. This will be confirmed when real time X-ray diffraction experiments to observe such phenomena in PET are completed. This hardening of the material vanishes after 5-10 minutes for physically aged PET without nucleating agent and after 20-35 minutes for physically aged PET with nucleating

agent. This transition could be visualized as a precrystallization phenomenon involving larger segmental motions. In this sense, it seems reasonable the observed shift of the transition towards lower temperatures for the material with nucleating agent. Accordingly, the time at which the transition takes place is larger for PET with nucleating agent because the temperatures at which the transition occurs is lower. In case of high crystallization temperatures (higher than 110°C for aged PET without nucleating agent, and higher than 95°C for aged PET with nucleating agent) the crystallization rate is so fast that the transition cannot be detected. On the other hand, for the lowest temperatures investigated the transition cannot be either measured; the mobility of the molecules is probably not sufficiently high to initiate the first crystallization steps. Finally, it is to be noted that in the samples measured immediately after quenching none of these transitions is observed (Fig. 4). This could mean that a compact molecular arrangement and a reduced segmental mobility (obtained after long periods of physical aging) should be required for the onset of these transitions.

Concerning the temperature dependent effects shown in Fig.5, it is noteworthy that despite the large softening phenomenon occurring just above T_g the microhardness value does not vanish totally. Just before the onset of crystallization, a small hardness maximum seems to emerge. The corresponding H-values are comparable to those found at room temperature for short chain paraf-

finic compounds (22). This finding is in line with the above concept of a molecular ordering phenomenon before T_c .

Influence of the nucleating agent on physical aging

In agreement with previous investigations (9), the results shown in Fig.5 indicate that the hardness values obtained below T_g depend on the physical aging of the samples. Physical aging below T_g is connected to local molecular motions (conformational changes) (23). One may speculate that these changes may involve, in our case, ordering or parallelization of PET benzene rings reducing segmental mobility. Physical aging could be, thus, visualized as a slow "nucleation mechanism" below T_g which is accompanied by a hardening of the material. Beyond T_g the hardness values show a unique variation with a loss of memory of the previous aging effects.

Most interesting is the observation that the hardness value below T_g is larger for the materials with nucleating agent than for the samples without nucleating agent and equals the hardness of the aged material (Fig. 5b). This result suggests that, the presence of nucleating particles within the polymer induces a similar hardening effect as that occurring in the material after physical aging. The effect of aging is, thus, hidden by the agent.

Finally, the study of microhardness as a function of loading time (Fig. 6) further illuminates the aging behaviour for these materials. The H-variation with loading time is described by equation 2, where k provides a measure of the rate of creep of the material under the indenter. It is known that k depends on molecular packing and crystallinity (24,25). Thus, the results of Fig. 6a suggest that while physical aging for PET without nucleating agent involves a similar H-increase for all loading times, the rate of creep of the material does not substantially change after long storage times at room temperature; i.e., although free volume is reduced and chain packing improves, the rate of creep after aging is nearly unchanged. On the other hand, the freshly solidified material containing nucleating agent (Fig. 6b) shows a higher rate of creep than PET without nucleating agent (Fig. 6a). This finding could suggest that although nucleating particles impose the requirement of less free volume at short loading times (higher H-values) they induce a higher creep rate on the material. The effect of aging in case of longer loading times shows up the difference between fresh and aged samples containing nucleating agent. It is seen that the aging effect reduces the free volume and, thus, counterbalances the initial fast rate of creep.

Isothermal crystallization of PET

It is well known that the increase of crystallinity with time at a constant crystallization temperature follows Avrami equation (26):

$$\alpha(t) = \alpha_c [1 - \exp(-Gt^n)] \quad (3)$$

where $\alpha(t)$ is the degree of crystallinity at time t , α_c is the final degree of crystallinity, G is the Avrami constant which is proportional to the number of nucleating sites and n is the Avrami exponent which determines the type of crystallization which is taking place. Since in previous investigations(11) the increase in the H -value of PET during primary crystallization was shown to be directly proportional to the increase of crystallinity, one may expect that the increase of the H -values will follow a similar relationship as a function of time

$$H(t) = H_m + (H_M - H_m) [1 - \exp(-Gt^n)] \quad (4)$$

where H_m and H_M represent the lowest and highest H -values obtained during the crystallization process respectively.

In Fig. 7 $\log\{-\ln[1 - (H(t) - H_m)/(H_M - H_m)]\}$ is plotted as a function of $\log(t)$ for the different crystallization temperatures and for the samples with and without nucleating agent. From the

evaluation of such curves one obtains directly the n and G values from the slope and from the intercept of the straight line respectively. Fig. 7a shows the data obtained for the samples without nucleating agent. A value of about 3 in the Avrami exponent is observed for all the temperatures investigated (see table 1). The obtained value of $n=3$ is consistent with the concept of a three-dimensional growth with a fixed number of nuclei born at $t=0$. It is known that PET crystallization from the glassy state gives rise to spherulitic materials (27,28). The present PET samples consist of small spherulites, a few microns in size, when observed under the optical microscope. On the other hand, for the samples with nucleant (Fig. 7b) crystallized at $T_C=95^\circ\text{C}$ and $T_C=100^\circ\text{C}$ one clearly observes in Fig. 3a two regions corresponding to an independent contribution of a fast and a slow crystallization rate for each temperature. These two regions correspond in Fig. 7b to the two pair of straight lines denoted as "fast" and "slow". These two regions could be interpreted in terms of a simultaneous crystallization from $t=0$ due to two independent modes: i) A fast crystallization mode starting from the nuclei provided by the nucleating agent which appear at $t=0$ within the sample. Spherulites would grow from these nuclei up to a limited value when the nucleating agent is saturated. At this stage, the spherulites do not fill yet the whole volume of the sample. ii) A slow crystallization mode starting spontaneously from the existing nuclei which is superposed to the fast crystallization mode.

It is to be noted that the nucleating agent does not change the Avrami exponent. However, it provides a much larger number of nuclei (proportional to G) than the number of already existing nuclei within the amorphous material (See table 1). Therefore, the crystallization for the sample with nucleating agent starts immediately at $t=0$ and shows a faster crystallization rate than the sample without nucleant.

For temperatures lower than $T_C=95^\circ\text{C}$ and higher than $T_C=100^\circ\text{C}$ only one slope with an Avrami exponent equal to $n=3$ is observed. This means that in these cases there exists a nucleation corresponding to a slow crystallization mode. At low temperatures ($T_C=90^\circ\text{C}$) the nuclei appear within the sample because the time required to crystallize is very large ($t_C=300$ min) and nuclei can be formed from the amorphous polymer. In this case the fast crystallization process is not observed because the crystallization temperature is too low. On the other hand, for temperatures larger than 100°C ($T_C=105^\circ\text{C}$) there appears also one single region of crystallization. (Figs. 3a and 7b). This is because the temperature of crystallization is very high and crystallization proceeds so rapidly that it seems reasonable to associate it to the fast mode. Finally, the Avrami constant, G , increases with T_C (table 1) indicating that the number of nuclei increases with rising crystallization temperature.

From the change of H , the half-time of crystallization, $\tau_{1/2}$, can be determined. This value represents the time required to obtain one half the maximum H -value. In Fig. 8 $\tau_{1/2}$ is represented as a function of T_c for all the samples investigated. As can be observed the nucleating agent reduces the half-time of crystallization considerably at a given T_c .

Influence of crystallization temperature on the limiting H -value after primary crystallization

In case of PET sample crystallized without nucleating agent crystallinity obtained at the end of the crystallization (table 2) is slightly larger than $\alpha=0.22$, in agreement with preceding results (11). This indicates that for these samples primary crystallization is completed ($\Phi=1$) leading to a constant microhardness value H_M for each crystallization temperature, i.e. the volume fraction of crystallized spherulites Φ is equal to unity ($\Phi=\alpha/\alpha_0$, α being the measured crystallinity after a given time t and α_0 the degree of crystallinity when primary crystallization is completed). From table 2 and Fig. 2a one also sees that the time, t_c , needed to reach the leveling off value H_M drastically decreases with increasing T_c . It is noteworthy that for these samples the final H_M -value is the same (100MPa) for all crystallization temperatures. This result is consistent with the value of $H \approx 220$ MPa obtained for the crystallized sample measured at room temperature (11). The latter H -value is equal to the sum of

$H_a=120\text{MPa}$ (hardness of the glassy material) and $H_M \sim 100\text{MPa}$ (hardness of crystallized PET measured at T_c).

For PET samples with nucleating agent (Fig.3) the crystallinity value at the end of the crystallization process depends on T_c . Here the value of α increases from $\alpha=0.179$ ($\Phi=0.81$) for the sample crystallized at $T_c=90^\circ\text{C}$ up to $\alpha=0.22$ ($\Phi=1$) for the sample crystallized at $T_c=105^\circ\text{C}$. For these samples, after primary crystallization $\Phi < 1$, i.e. in most cases the material is not fully occupied by spherulites. Consequently, the final H_M -value is a function of the volume fraction of spherulites.

Most striking is the fact that H_M is larger for samples with nucleating agent (Fig.3) (with $\Phi=1$ and $\alpha \sim 0.21-0.22$ ($T_c \approx 100-105^\circ\text{C}$)), than for the samples without nucleating agent (Fig.2). This result might be connected with a hardening effect of the material at high temperatures due to the influence of the nucleating agent. In a previous work the influence of the nucleating agent in reducing the level of lattice distortion^s in the spherulites was pointed out (17). This would explain why the samples with nucleating agent, having more nuclei yield a higher H-value than the samples without nucleating agent.

Comparison of the H_M limiting values obtained at high temperatures ($H_M \sim 150\text{ MPa}$) in Fig. 3 -if one takes into account that $H_a=120\text{ MPa}$ for glassy PET (11)- with the value of PET crystal-

lized measured at room temperature suggests that the hardness of the spherulites (H_{sph}) is larger at high temperatures than at room temperature. From this result one might conclude that the microhardness of the spherulites suffers a decrease after solidification at room temperature. One may think that this decrease is partly due to a material relaxation during cooling which contributes to a softening of the spherulites at room temperature. On the other hand, the low H_a -values obtained for the aged polymer with nucleating agent (110 MPa) (Fig.5a), in contrast with $H_a \approx 120$ MPa for the polymer without nucleant (Fig.5b), might also contribute to explain the observed smaller values of H at room temperature for the samples with nucleant.

CONCLUSIONS

During primary crystallization of PET the following transitions can be distinguished using the microhardness technique:

- a) A pre-glass transition, also known as physical aging, which shows a hardening below T_g after long storage times. This transition involves local molecular ordering effects.
- b) A glass transition giving rise to a well defined softening behaviour involving long segmental motions.
- c) A transition observed in the aged material, before crystallization starts, which shows up as a time and temperature dependent hardening of the material. It is suggested that this phenomenon may involve a molecular ordering.

- d) Triclinic crystallization giving rise to a true final hardening of the material which can be: i) a fast process if crystallization starts from the nucleating agent or ii) a slow process if selfnucleation takes place.

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Table 1

Experimental values for the crystallization temperatures, T_c , Avrami exponent, n , and Avrami constant, G , for the different PET samples investigated.

Samples	T _C (°C)	n		G	

without n.a.	100	3.3		1.2x10 ⁻⁸	
	105	3.1		3.0x10 ⁻⁶	
	110	2.9		1.0x10 ⁻⁴	
	117	2.7		4.9x10 ⁻³	
with n.a.	90	2.8		4.9x10 ⁻⁸	
	95	3.0	3.3	5.5x10 ⁻⁵	2.3x10 ⁻⁸
	100	3.2	3.0	1.2x10 ⁻⁵	5.9x10 ⁻⁷
	105	3.3		2.4x10 ⁻⁴	

Table 2

Experimental values for the crystallization temperatures, T_C , crystallization time needed to reach the limiting H_M -value at the end of primary crystallization, t_C , density, ρ , crystallinity, α , and volume fraction of material occupied by spherulites.

Samples	$T_C(^{\circ}\text{C})$	$t_C(\text{min})$	$\rho(\text{g/cm}^3)$	α	Φ

without n.a.	100	240	1.369	0.22	1
	105	120	1.373	0.25	1
	110	60	1.374	0.26	1
	117	25	1.375	0.26	1
with n.a.	90	480	1.363	0.18	0.81
	95	180	1.366	0.19	0.89
	100	150	1.368	0.21	0.97
	105	15	1.369	0.22	1

LEGEND TO FIGURES

Figure 1. DSC scans for glassy PET without nucleating agent.
Top: physically aged material. Bottom: material immediately measured after quenching.

Figure 2. a) Variation of the microhardness for physically aged PET samples without nucleating agent as a function of crystallization time (t_c) for different crystallization temperatures (T_c). b) Microhardness variation as a function of time for the first steps of crystallization. Different symbols denote different crystallization temperatures.

Figure 3. a) Variation of the microhardness for physically aged PET samples with nucleating agent as a function of crystallization time (t_c) for different crystallization temperatures (T_c). b) Microhardness variation as a function of time for the first steps of crystallization.

Figure 4. Measured microhardness variation for fresh (not aged) PET samples with nucleating agent immediately measured after quenching as a function of crystallization time, t_c , for two different crystallization temperatures.

Figure 5. Variation of the microhardness, H , for glassy PET samples without (a) and with (b) nucleating agent as a function of temperature. Open symbols: physically aged (1 year storage) materials. Solids symbols: materials immediately measured after quenching in ice water.

Figure 6. Double logarithmic plot of the microhardness as a function of loading time for PET samples without (a) and with (b) nucleating agent. Open symbols: physically aged materials. Solid symbols: fresh materials measured after quenching.

Figure 7. Variation of $\log\{-\ln[1-(H-H_m)/(H_M-H_m)]\}$ as a function of $\log(t)$ for PET samples without (a) and with (b) nucleating agent for different crystallization temperatures.

Figure 8. Variation of the half-time of crystallization, $\tau_{1/2}$, as a function of crystallization temperature, T_c , for the investigated PET samples.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7