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THE EFFECT OF POLYOLEFIN'S MOLECULE AND SUPERMOLECULE STRUCTURES ON SOME INDUSTRIAL PROCESSES

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SUMMARY: In this study, the raw materials and their structural properties were analyzed in synthetic polymer pipe production by the following events: 1) The effect of extruder processes to dynamic-mechanical properties of polyethylene (PE) and polypropylene (PP) pipes in pipe production; 2) The effect of the fiber direction on dynamic-mechanical properties and extruder materials; 3) The heat process on welding during the pipe production and the effect of polymer structure on welding duration; 4) Physical properties and structural changes of pigmented PE and PP raw materials. 5) The relationship between dynamic-mechanical properties of polymers with thermodynamic and kinetic concepts and effect of temperature. The results (that were) derived after several measurements are as follows: 1) The best stability properties were observed on the pipe samples which have same fibre direction. In samples with opposite and vertical fiber directions the stability properties are 30% lower. 2) The maximum dynamic-mechanical properties of the pipe samples were observed when the extruder temp. Is 463 k. These properties were lower in the pipe compared to the samples taken from the inner and outer part of the extruder. For the sample during this time the concentration of the oxygen groups are at the lowest and amorphous regions are at the highest level. These results prove that the temperature, the pressure and the cooling rate of the material taken from the extruder have too much effect on polymer structure. 3) Welding duration is investigated without changing the fibrillar structure. The best welding conditions have been obtained in case of deformation graphs with minimum areas. The results can be explained with the difference in polymer structures at different temperatures during pipe manufacturing process. 4) The σ, τ, γ values differ greatly in the samples taken from different companies (~ 50%). The analyses of IR spectra and microphotographs show that this difference depends on the differences of the polymer structures and the initial data.

INTRODUCTION

During the synthesis process of polymer; applied heat, radiation and pressure affect the raw materials that are produced. Polymer properties depending on synthesis process, are

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transferred to the product as mechanical-dynamical properties. Physical properties of polymer raw materials are dependent on molecule and molecular chains.

Selecting of extruder parameters (like temperature, pressure and rpm of screw) are important for transferring raw material properties. In addition to this, pigments and antioxidants added to raw materials also affect the end product [1]. There is a relationship between the fibre direction and dynamic-mechanic properties of pipes manufactured from PE and PP raw materials [2]. There is also a relationship between crystalline ratio, density and melt flow index [3]. These relationships play a big role in manufacturing process of pipes and etc. These properties characterise the raw materials' extrusion and injection capabilities, process factor and pipes' welding etc and other shaping processes (like welding). In the welding process, welding time, welding temperature and welding pressure depend on the materials structure and properties.

EXPERIMENTAL STUDY

PP (gray, green), PE100 (Blue), PE80 (yellow), PE63 (black) samples were used for the measurements. Colour pigments were added (max 2%) into the raw material before the extruding process, whereas antioxidants were added into the raw material's structure during the raw materials synthesis. PE63 raw material is a polyethylene, which includes 2% carbon. At this experiment, 6 different tests were used for the experimental study. Constant tension velocity at varying tensile stress, short term tensile strength, elongation at break, materials toughness, strain at yield, elongation at yield values have been determined at LLOYD LYROK equipment. Tensile samples have been prepared according to the ASTM 683M-89 and experiments have been done according to ISO R 527. According to the theory, design life and wearing time are thermokinetic process and polymers endurance (namely lifetime,τ) have been shown from the $\tau = \tau_o \exp((U_o - \gamma\sigma/kT))$ equation [4,5]. Here, U_o is the maximum bond breaking activation energy (kJ/mole) τ_o is (10^{-12}-10^{-13} for polymers) equal to the vibration frequency when the atoms have the equilibrium at their axis. γ is a parameter depends on the structure. According to this equation, design life is explained by U_o and τ_o values and polymers structures change is explained by γ values. Polymers life time and breakage strength can be explained by $\log\tau$ - $f(\sigma)$ curves. The relationship between polymer structures and variants are explained by breakage activation energy and τ which are found from $\log\tau$ - $f(10^3/T)$ curves. For this test, samples were prepared as a film at 15 Mpa pressure and 423 K for PE, 463 K for PP and experiments were repeated many times in room and up to 343 K

temperature and so materials thermokinetic variations were found. Both tensile tests values were observed by computer. To determine the materials oxidation time and grade, samples were observed with IR spectrum and FTIR spectrometer whose measurement grade is 400-4000 cm^{-1} (λ= 2,5-25 μm) and structures' photos were taken from the Olympus polarization microscopes. To determine the materials' extrusion and injection capability, their DSC and Oxygen absorption time tests were done according to ASTM D 5028, so we have got many information about their melting point, melting and glassy transition temperature (T_g), crystallinity range and polymers stability and also according to ASTM D 2839, their melting flow index were measured to have the information about materials capability to use industrial application process. To establish the welding and to check the welding time, pipes' materials were tested and Pipes were welded with different temperature and different surface pressure and tensile tests were applied to welding sample. In different temperature pressure tests were done according to DIN 8074/8075 for PE, DIN 8077/8078 for PP.

RESULTS AND DISCUSSION

In Figure 1, the experimental results for the samples with pigmented and naturel are given. In Figure 2., the tensile experiment results for the samples which were produced from the different material and which have different fiber direction. In Figure1. and Figure 2. logτ - σ and service life τ - U curves have been shown.

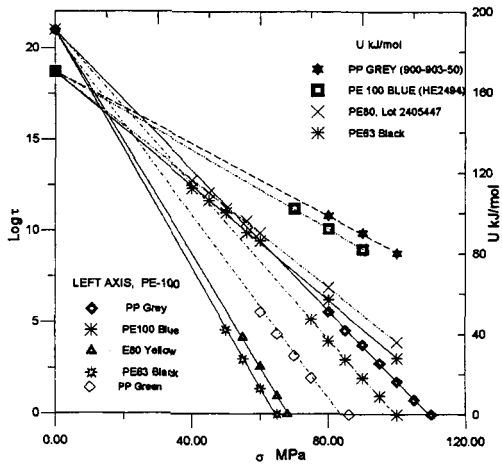

Fig. : 1. Service life(τ) – tensile stress (σ) and activation energy relationship for pigmented and non-pigmented samples.

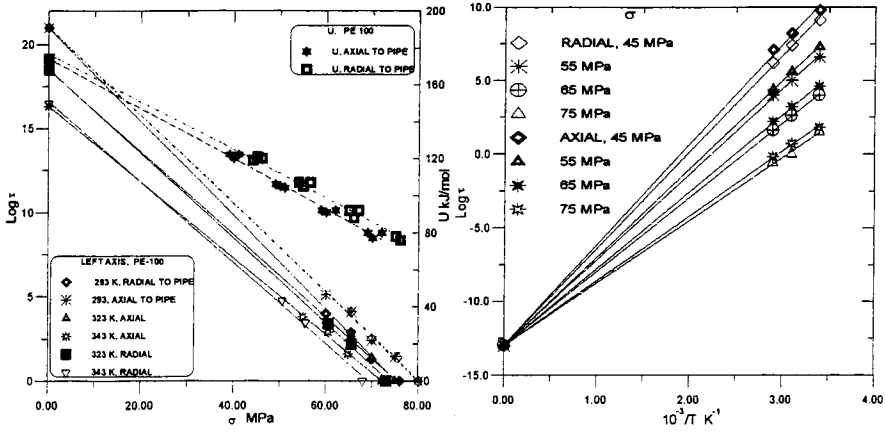

Fig. : 2. Service life(τ) – tensile stress (σ) and activation energy relationship for different fiber direction.

On the left hand of graph, service life log τ - σ relations, on the right hand of graph, U design life - σ relations have been seen. In Figure 1,2., the relationship between temperature and service life has been given. As shown if figures, variations are linear, k is Boltzman constant, T is heating temperature and σ is a structural parameter and so $\tau = \tau_0$, exp $((U_o-\gamma\sigma)/kt)$ can be seen [4,5,6]. Here, τ_o is service life, when σ is 0, τ_o equals to τ and at the same time from $U = U_0 - \gamma\sigma$ equation. U_0 equals to U. When there is no strain, ($\tau_0=10^{-13}$), γ has been found from σ - U curves slope. γ is a structural parameter that is affected by external heating pressure, UV, O_2 absorption. And at the same time γ characterises non_homogeneous and supra-molecular stresses. The results are given in Figure 1. As shown, the lowest γ values are belong to PE100 and PPRC (gray) samples, the highest values belong to the PE63 (black) with added carbon black. Samples taken from the fiber direction have higher strength values then the samples taken from radial direction. And so service lifetime decreases in radial and PE63 samples. In the same way, log τ-γ curve's slope increases and this result shows that the resistance is decreases with time. As shown in Figure 2 and Table 1.

Table 1. Dynamic – Mechanic properties of pipe.

Samples	σ MPa τ=1,T=293K	U_o (Kj/mole)	τ_o (sec)	γ kj/mol.Mpa^{-1}	τ (sec) σ = 60MPa
PP Grey	110	175.8	10^{-13}	0.896	$3,5 .10^9$
PE100	100	175.8	10^{-13}	1.00	$3,2 .10^8$
PPGreen	83	175.8	10^{-13}	1.22	$,2 .10^5$
PE63Black	65	175.8	10^{-13}	1.44	$0,8 .10^2$
PE80	69	175.8	10^{-13}	1.384	700

Depend on σ, in pigmented polymers, bond breakage activation energy decreases suddenly and γ (slope of graph) structural parameters increases and service life of pigmented polymers

decreases because exponential coefficient in equation 1 decreases due to γ. Lowest σ and τ values were obtained for Carbon added PE63. For specimens having different fibre directions, higher values of σ were obtained from axial specimens (specimen parallel to pipe) than radial (specimen vertical to pipe) ones. As seen in Figure 1 and Figure 2, activation energies of pigmented polymers are decreased with increasing γ values, which lead to a decrease in service life. The results show that, wearing mechanism shows the same thermofluctuation characteristic [7] for all specimens and obeys thermokinetic theory (Equation 1). γ is dependent to its source, antioxidant, filler material and colour material. Curves that gathered from the tests with stable tensile speed and varying loads are given in Figure 4. Area under these curves shows the thoughness (absorbed energy). Thougness of pigmented and radial specimen is higher than the thoughness of pigmented and axial ones. Maximum load at break and flow rate of strain, which depends on molecular weight, is higher in specimens havinghigher σ and τ values. For further data, Reference [1,2] can be seen. For technical applications, PE63 black and same characteristic materials can be used in waste water pipes where there is no need for internal pressure and elasticity. Pipes manufactured by carbon added materials are resistive to UV and can be used under daylight. PE100 and PPRC pipes can be used where there is a need for high internal pressure, good ring stiffness ability, temperature resistivity and long service life. So additives have to be chosen

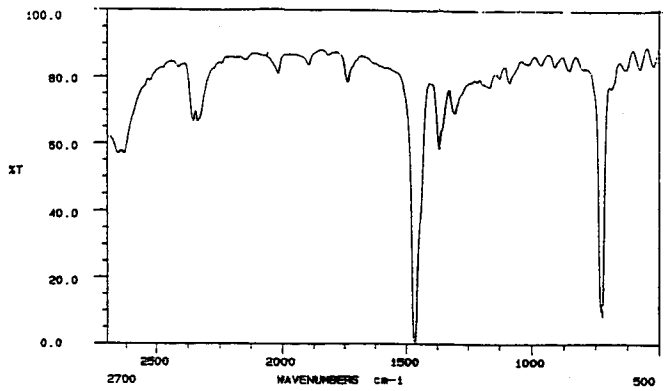

Fig.: 3. Typical IR Spectrums

according to technical field. Figure 3, Figure 4 show typical IR spectrums and microphotographs of fibres. In IR spectrums, its seen that optical densities of carbon oxygen peaks are smaller with lower σ values. As seen in Table 2. these materials have low oxygen

absorbing time. As much as the distance between fibres of Polymers are increases, the Van Der Valls forces between them are decreases and vice versa.

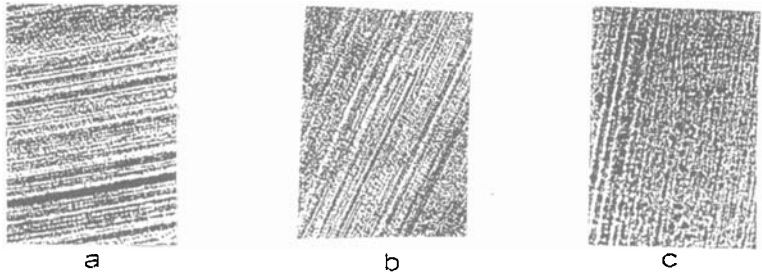

Fig. : 4. a. Axial direction, b. Spoiled fibre, c. Excessive pigmented fibre

This effects the dynamic properties of the pipe. Good fibre structure is formed with high crystal ratio [3]. For obtaining good fibre structure, optimum and valid pressure and temperature values are to be set during pipe manufacturing process. There is also a relationship between melting temperature, melt flow index density. If raw material is 100% crystal then the melting enthalpy is 65 cal/gr [9]. Table 2. Shows the melting enthalpy and melting temperature gathered form DSC. Test results of DSC are shown in Figure 5. We observed a high and narrow peak and no molecule unstability at the beginning and at the end of melt process. Materials are unimodal. Melt enthalpy of PE specimens are below these values. Melt flow must be between 0.3 – 0.5 gr/10 Min (5-kg weight) for pipe extrusion manufacturing. No pipe can be manufacture with flow index higher than 1 g/10 Min in extrusion pipe manufacturing. This value can be bigger in injection pipe manufacturing.

Table 2. The result of DSC and OIT tests of PP and PE samples.

Raw material	Onset Point	Peak Point	Enthalpy	Onset Melt.	Softening	Last Melt	O.I.T
		C	C	J/gr	C	C	Minute
PP Natural	26.7	125.76	146.85	30.2+12	87	162	
PPRC Natural	26.9	126.62	147.5	32.9+10	87	167	
PPH	4.54	160.42	174	381.5+167	132	190	>50
PE100	25.2	120.25	141.2	91.9+36	64	168	>30
PE100 Radiated	29	120.87	142.4	79.4+32.1	84	168	>70
PE100 Natural	25.7	118.68	140.5	87.7+36	62	165	>38
PE80	27.2	117.23	132	79.5+24.3	75	144	
PE80	29	119.76	130.3	76.4+27.6	76	145	
PE80	21.8	120.72	137.3	99+22.4	77.7	165	>34
PE80 Black	31.6	121.1	138	85.8+36.6	65	165	>48
PE80 Black	31.8	121	144	84.8+36	62	164	>48

Depending on additives, O.I.T times are decreasing receptively on PP, HDPE80, 100 and LDPE. Welding test at conditions of 155 – 230 C and 0 – 1.8 kg /cm^2 are performed to pipe specimens and all specimens were subjected to tensile tests.

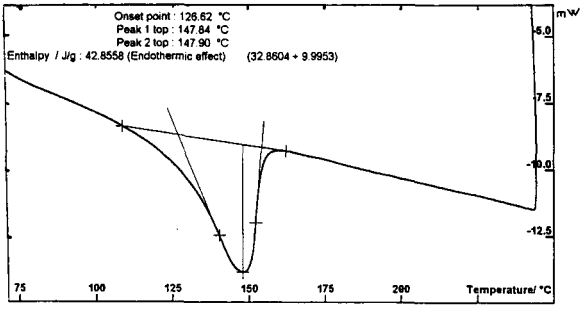

Fig. : 5. Typical DSC curves of PPRC Natural

The distribution of stress at yield is between 16 –35 Mpa and distribution of elongation at break is 250 % -500 %, this elongation value is lower than the original material elongation. The fibre structure of welding area was destroyed relatively to original (Figure 4). Its found out that welding conditions are good at 180-220 C and 0.8 – 1.8 kg/cm^2. Results were compared with DVS 68/4 and [10].

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