

## Rheological Behavior of Collagen Extracted From Different Animal Sources in Molten State Under the Influence Shear Stresses and Low Temperature

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**Abstract:** In this work, rheological properties of the vitalist polymer (collagen) extracted from the skins of sheep, cows and chickens were studied in the molten state. The experiments were carried out by a capillary rheometer.

The melt flow index (MFI), apparent shear rate ( $\dot{\gamma}_a$ ), apparent shear stress ( $\tau_a$ ), apparent viscosity ( $\eta_a$ ), non-Newtonian index (n) and apparent flow activation energy ( $E_a$ ) at constant shear stress for polymers studied were determined.

The results showed that the apparent viscosity for collagen extracted from skin of sheep was upper, and for collagen extracted from skin of chicken was lower.

This studied showed that the apparent viscosity decreases regularly with increasing temperature, also it was found that the melt flow index of polymers increases with increasing apparent viscosity.

**Key word:** Collagen, Rheological Properties, Molten State, Melt Flow Index.

### Introduction

Collagen is the most abundant animal protein polymer in animal tissues and constitutes approximately 30% of total animal protein, a fibrous protein, inextensible<sup>2-4</sup>. Molecular structure of collagen contains three polypeptide chains wound together in a tight triple helix. Each peptide subunit called  $\alpha$  chain is composed of about 1050 amino acid residues, which consist of approximately 33% glycine, 25% proline and 25% hydroxyproline, and a relative abundance of lysine<sup>1</sup>. The average length of each subunit is about of 300 nm and a diameter of 1.4nm<sup>5,6</sup>.

Collagen is an important biomaterial has a wide range of applications in leather and film industries, pharmaceutical applications including production of wound dressings, vitreous implants and as carriers for drug delivery, cosmetic because it has a good moisturizing property and biomedical materials, and food whereas heat denatured collagen called gelatin is important in food manufacturing<sup>1,2,4,5</sup>.

studied Samples were subjected to pressure and shear stress are low and suitable to their nature, according to the following equation<sup>7</sup>:

$$\tau_a = P_a.R / 2.L \quad (\text{dyne/cm}^2) \quad (1)$$

Where R (cm) is the capillary radius, L (cm) is the capillary length.

$P_a$  is the apparent pressure applied, it follows the influential mass in the piston that pushes the material through capillary, and is given by :

$$P_a = G / \pi.R^2 \quad (\text{dyne/cm}^2) \quad (2)$$

Where R (cm) piston radius, G (gram gravity) is mass pressing, whereas [1 gram gravity = 981 dyne].

The apparent shear rate ( $\gamma_a$ ) is given by<sup>8</sup> :

$$\gamma_a = 4Q / \pi R^3 \quad (\text{S}^{-1}) \quad (3)$$

R (cm) is the capillary radius, Q (g/sec) is the volumetric flow rate .

From knowing values of the apparent shear stress and apparent shear rate can be determination the apparent viscosity from equation<sup>10</sup>:

$$\eta_a = \tau_a / \gamma_a \quad (\text{Poise}) \quad (4)$$

The values of flow activation energy at a constant shear stress ( $E_a$ ) were determined by using equation:

$$E_a = R.(d \log \eta_a / d T^{-1}) \quad (\text{cal/mol.}^\circ\text{K}) \quad (5)$$

Where R is the gas constant (8.314J/mol. $^\circ\text{K}$ ), T is the temperature absolute ( $^\circ\text{K}$ ).

The values of melt flow index were determination by knowing mass of molten polymer that go out from certain aperture under effect the certain shear stresses and temperature, also depending on the type of polymer. Melt flow index is given by:

$$\text{MFI} = 600 . (G_m / t) \quad (\text{g/10min}) \quad (6)$$

Where  $G_m$  average weight of molten samples that flow from capillary, t is the time required for flow the molten sample<sup>10</sup>.

## Experimental

### Material and procedure

Collagen of skin sheep [density = 0.992 g/cm<sup>3</sup>], collagen of skin cows [density = 0.988 g/cm<sup>3</sup>], collagen of skin chicken [density = 0.979 g/cm<sup>3</sup>].

Collagen from all sources was preparation in laboratory biochemistry, department of chemistry, faculty of sciences, Damascus university.

Capillary rheometer, where used capillary his radius 0.5mm, and length 0.8cm. Studied samples were subjected to shear stresses following: (7994.447, 12359.35, 16543.83, 20313.18 dyne/cm<sup>2</sup>), at temperature (5, 10, 15  $^\circ\text{C}$ ).

## Results and discussion

### 1- Melt Flow Index (MFI)

The melt flow index determines flow qualities of molten polymers specific temperatures and under certain pressures, where the viscosity of molten represents the resistance to flow that you get molten polymer.

It is noted that there is an inverse relationship between the melt flow index and viscosity of the molten, and melt flow index function is account function industrial and commercial at the same time.

The table (1) shows values of melt flow index for collagen of skin sheep, collagen of skin cows and collagen of skin chicken, at different temperatures and under the influence of multiple shear stresses.

**Table 1. values of melt flow index (MFI g/10min) for collagen of skin sheep, collagen of skin cows and collagen of skin chicken**

15°C			10°C			5°C			temperature
chicken	cows	sheep	chicken	cows	sheep	chicken	cows	sheep	Source of collagen
MFI	MFI	MFI	MFI	MFI	MFI	MFI	MFI	MFI	mass pressing (dyne)
1.3	0.41	0.29	0.91	0.27	0.21	0.6	0.19	0.16	200820.5
2.3	0.75	0.49	1.6	0.5	0.39	1	0.34	0.28	310466.9
3.5	1.1	0.73	2.4	0.7	0.56	1.5	0.57	0.45	415581
4.4	1.5	0.99	3.2	0.95	0.78	2	0.79	0.59	510267.2

**2- Melt Flow curves**

Melt Flow curves represent transmutation apparent shear stresses versus apparent shear rate for each polymer of studied polymers at different temperatures. Benefit these curves in the appointment of non-Newtonian index (n), which is also useful to know the extent of deviation the flow from Newton's law. Non-Newtonian index (n) can be calculated from the equation of the following:

$$n = d \log \tau_a / d \log \gamma_a \tag{7}$$

The tables (2),(3),(4) shows the values of apparent shear stresses and apparent shear rate under the influence of multiple masses pressing and at different temperatures, also shows apparent viscosity at each temperature studied each of the collagen of skin sheep, collagen of skin cows and collagen of skin chicken, respectively.

**Table.2 apparent shear stress, apparent shear rate and apparent viscosity for collagen of skin sheep**

temp	<b>G (dyne)</b>	<b><math>\tau_a</math> (dyne/cm<sup>2</sup>)</b>	<b><math>\gamma_a</math> (s<sup>-1</sup>)</b>	<b><math>\Pi_a</math> (poise)</b>
5°C	200820.5	7994.447	2.717622	2941.707
	310466.9	12359.35	4.755839	2598.774
	415581	16543.83	7.643312	2164.485
	510267.2	20313.18	10.02123	2027.015
temp	<b>G (dyne)</b>	<b><math>\tau_a</math> (dyne/cm<sup>2</sup>)</b>	<b><math>\gamma_a</math> (s<sup>-1</sup>)</b>	<b><math>\Pi_a</math> (poise)</b>
10°C	200820.5	7994.447	3.566879	2241.3
	310466.9	12359.35	6.624204	1865.787
	415581	16543.83	9.511677	1739.318
	510267.2	20313.18	13.24841	1533.255
temp	<b>G (dyne)</b>	<b><math>\tau_a</math> (dyne/cm<sup>2</sup>)</b>	<b><math>\gamma_a</math> (s<sup>-1</sup>)</b>	<b><math>\Pi_a</math> (poise)</b>
15°C	200820.5	7994.447	4.92569	1623.011
	310466.9	12359.35	8.322718	1485.014
	415581	16543.83	12.39915	1334.271
	510267.2	20313.18	16.81529	1208.019

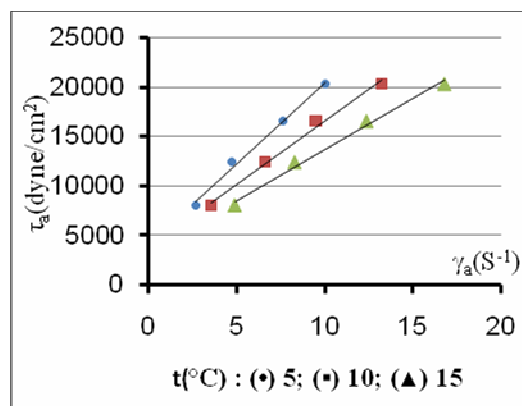
**Table.3** apparent shear stress, apparent shear rate and apparent viscosity for collagen of skin cows

temp	G (dyne)	$\tau_a$ (dyne/cm <sup>2</sup> )	$\gamma_a$ (s <sup>-1</sup> )	$\Pi_a$ (poise)
5°C	200820.5	7994.447	3.227176	2477.227
	310466.9	12359.35	5.774947	2140.167
	415581	16543.83	9.681529	1708.804
	510267.2	20313.18	13.41826	1513.846
temp	G (dyne)	$\tau_a$ (dyne/cm <sup>2</sup> )	$\gamma_a$ (s <sup>-1</sup> )	$\Pi_a$ (poise)
10°C	200820.5	7994.447	4.585987	1743.234
	310466.9	12359.35	8.492569	1455.314
	415581	16543.83	11.8896	1391.454
	510267.2	20313.18	16.13588	1258.883
temp	G (dyne)	$\tau_a$ (dyne/cm <sup>2</sup> )	$\gamma_a$ (s <sup>-1</sup> )	$\Pi_a$ (poise)
15°C	200820.5	7994.447	6.963907	1147.983
	310466.9	12359.35	12.73885	970.209
	415581	16543.83	18.68365	885.4709
	510267.2	20313.18	25.47771	797.2924

**Table.4** apparent shear stress, apparent shear rate and apparent viscosity for collagen of skin chicken

temp	G (dyne)	$\tau_a$ (dyne/cm <sup>2</sup> )	$\gamma_a$ (s <sup>-1</sup> )	$\Pi_a$ (poise)
5°C	200820.5	7994.447	10.19108	784.4551
	310466.9	12359.35	16.98514	727.6568
	415581	16543.83	25.47771	649.3454
	510267.2	20313.18	33.97028	597.9693
temp	G (dyne)	$\tau_a$ (dyne/cm <sup>2</sup> )	$\gamma_a$ (s <sup>-1</sup> )	$\Pi_a$ (poise)
10°C	200820.5	7994.447	15.45648	517.2232
	310466.9	12359.35	27.17622	454.7855
	415581	16543.83	40.76433	405.8408
	510267.2	20313.18	54.35244	373.7308
temp	G (dyne)	$\tau_a$ (dyne/cm <sup>2</sup> )	$\gamma_a$ (s <sup>-1</sup> )	$\Pi_a$ (poise)
15°C	200820.5	7994.447	22.08068	362.0562
	310466.9	12359.35	39.06582	316.3725
	415581	16543.83	59.44798	278.2909
	510267.2	20313.18	74.73461	271.8042

Also, chart curves in figures (1),(2),(3) shows transmutation apparent shear stresses versus apparent shear rate each of the collagen of skin sheep, collagen of skin cows and collagen of skin chicken, respectively.



**Fig1.** transmutation apparent shear stresses versus apparent shear rate for collagen of skin sheep

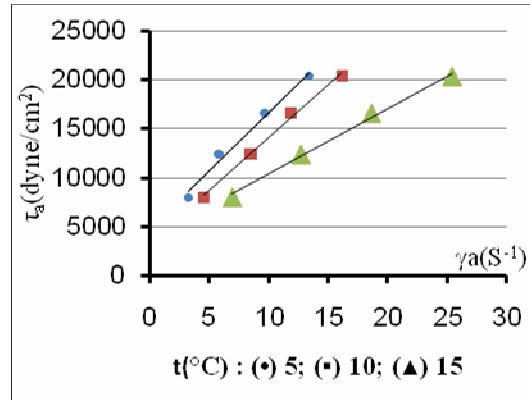


Fig2. transmutation apparent shear stresses versus apparent shear rate for collagen of skin cows

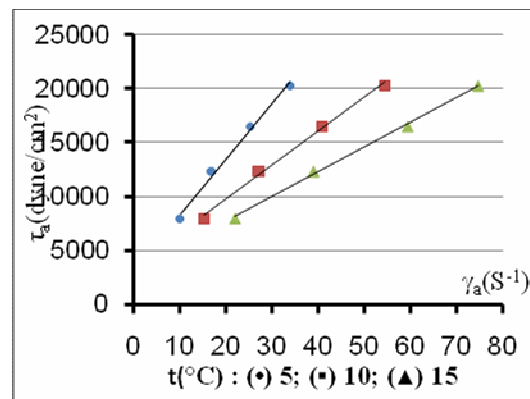


Fig3. transmutation apparent shear stresses versus apparent shear rate for collagen of skin chicken

Was appointed the Values of non-Newtonian index (n) according to melt flow curves. Table (5) shows the values of (n) each of the collagen of skin sheep, collagen of skin cows and collagen of skin chicken at each temperature studied.

Table.5 values of (n) for collagen of skin sheep, collagen of skin cows and collagen of skin chicken.

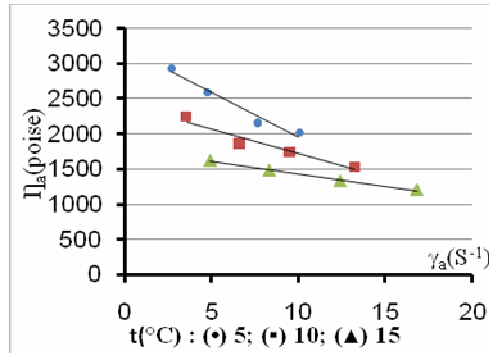
temperature	Collagen of skin sheep	Collagen of skin cows	Collagen of skin chicken
5°C	0.714	0.654	0.774
10°C	0.710	0.741	0.741
15°C	0.759	0.718	0.764

Notes from the values of (n) in the table(5), that all of them less than one therefore can say that the studied polymers belong in the their behavior to the fluid pseudo plastic within the studied range at studied temperatures and shear rates<sup>11</sup>.

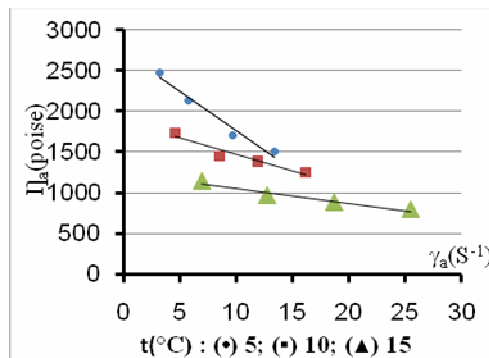
### 3- Apparent Viscosity Curves

Chart curves represent transmutation apparent viscosity versus apparent shear rate for each polymer of studied polymers at different temperatures.

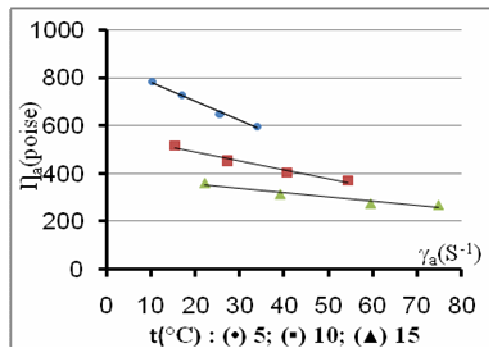
Describes the curves in Figures (4),(5),(6) transmutation apparent viscosity versus apparent shear rate for collagen of skin sheep, collagen of skin cows and collagen of skin chicken, respectively.



**Fig4. transmutation apparent viscosity versus apparent shear rate for collagen of skin sheep**



**Fig5. transmutation apparent viscosity versus apparent shear rate for collagen of skin cows**



**Fig6. transmutation apparent viscosity versus apparent shear rate for collagen of skin chicken**

Notes from the apparent viscosity curves that the viscosity decreases with increasing shear rate that within studied range at certain temperatures and shear rate. This behavior is characteristic of fluid pseudo plastic. When the shear rate increases the chains is organized toward the shear stress applied try to approach each other<sup>11</sup>.

#### 4- Flow Curves Energy

Viscosity transmutation versus inverted absolute temperature (1/T) were studied for each polymer of studied polymers at constant shear stresses (and therefore at constant loads).

Describes the curves in Figures (7),(8),(9) transmutation apparent viscosity versus inverted absolute temperature for collagen of skin sheep, collagen of skin cows and collagen of skin chicken, respectively.

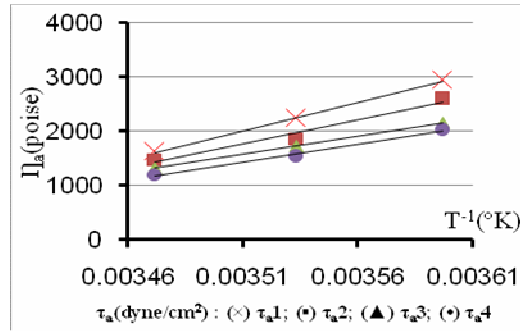


Fig7. transmutation apparent viscosity versus inverted absolute temperature for collagen of skin sheep

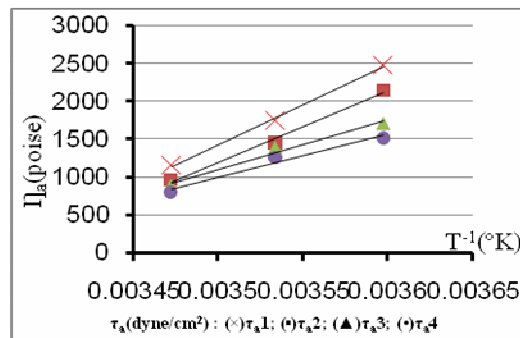


Fig8. transmutation apparent viscosity versus inverted absolute temperature for collagen of skin cows

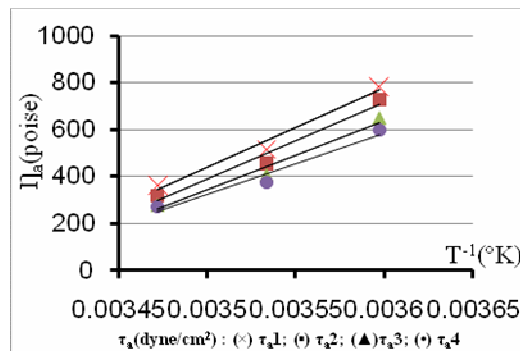


Fig9. transmutation apparent viscosity versus inverted absolute temperature for collagen of skin chicken

The table (6) shows the values of apparent flow activation energies for each polymer of studied polymers at certain shear stresses.

Table.6 values  $E_a$ (J/mol.°k) for collagen of skin sheep, collagen of skin cows and collagen of skin chicken

$\tau_a$ dyne/cm <sup>2</sup>	20313.18	16543.83	12.359.35	7994.447
$E_a$ (J/mol.°k) Coll-sheep	1.5675	1.73888	2.263888	2.438194
$E_a$ (J/mol.°k) Coll-cow	2.299	2.717	3.553	4.18
$E_a$ (J/mol.°k) Coll-chicken	3.643706	4.072574	4.287008	4.71504

Notes in general from the values of apparent flow activation energies of studied polymers that the activation energy increases with increasing shear stress, this is due to physical changes that occur to the viscosity when the values of shear stress is changed<sup>9</sup>.

## Conclusion

- 1- Melt flow index for collagen of skin cows less than Melt flow index for collagen of skin chicken, and higher than Melt flow index for collagen of skin sheep at certain temperature.
- 2- Melt flow index for each polymer of studied polymers increases with increasing temperature.
- 3- Apparent shear rate increases with increasing temperature, and applied shear stress on studied polymer.
- 4- Notes from the viscosity curves that the apparent viscosity decreases with increasing temperature and apparent shear rate.
- 5- Apparent flow activation energy for collagen of skin cows less than apparent flow activation energy for collagen of skin chicken, and higher than apparent flow activation energy for collagen of skin sheep.
- 6- Apparent flow activation energy for each polymer of studied polymers increases with increasing applied shear stress on studied polymer, thus increasing apparent shear rate.
- 7- Notes from melt flow curves that the relationship between apparent shear stress and apparent shear rate is linear relationship, and are subject to the low of energy (or Power Law)  $\tau = K.\dot{\gamma}^n$ , and non-Newtonian index (n) for studied polymers were less than one thus this polymers unsubject to Newton's law and classified that the fluid pseudo plastic.
- 8- The study gives the possibility to benefit of them in field of manufacturing and packaging.

## References

1. Senaratne,L.S.,Park,P.J.,Kim,S.L.,Isolation and characterization of collagen from brown backed toadfish (*Lagocephalus gloveri*) skin,2006,*Bioresource Technology*,97,191–197.
2. Bama,P.,Vijayalakshimi,M.,jayasimman,R.,Kalaichelvan,P.T.,Deccaraman,M.,Sankaranarayananana,S.,Extraction of collagen from catfish (*Tachysurus maculatus*) by pepsin digestion and preparation and characterization of collagen chitosan sheet,2010,*International Journal of Pharmacy and Pharmaceutical Sciences*,4,133-137.
3. Bolboaca,D.,Jäntschi,L.,Amino acids sequence analysis on collagen, 2007, Bulletin USAMV-CN,63-64.
4. Yan,M.,Li,B.,Zhao,X.,Ren,G.,Zhuang,Y.,Hou,H.,Zhang,X.,Chen,L.,Fan,Y.,Characterization of acid-soluble collagen from the skin of walleye Pollock (*Theragra chalcogramma*),2008,*Food Chemistry*,107,1581–1586.
5. Potaros,T.,Raksakulthai,N.,Rungrerdkreangkrai,J.,Worawattanamateekul,W.,Characteristics of Collagen from Nile Tilapia (*Oreochromis niloticus*) Skin Isolated by Two Different Methods,2009,*Kasetsart J.(Nat. Sci.)*,43,584–593.
6. O'Grady,J.E.,Bordon,D.M., Global regulatory registration requirements for collagen-based combination products: points to consider, 2003, *Advanced Drug Delivery Reviews*,55,1699–1721.
7. Hamad,K.,Deri,F.,Effect of Recycling on the Rheological and Mechanical properties of Poly (Lactic Acid)/Polystyrene Polymer Blend,2012,*Damascus University Journal for BASIC SCIENCES*,1,72-85.
8. Kaseem,M.,Hamad,K.,Deri,F.,Preparation and Studying Properties of Polybutene-1/Thermoplastic Starch Blends,2011,*Journal of Applied Polymer Science*,7,DOI 10.1002/app.35350
9. Kaseem,M.,Deri,F., Preparation and Characterization of Acrylonitrile – Butadiene-Styrene/Corn Starch Composites,2011,*Damascus University Journal for BASIC SCIENCES*,2,39-53.
10. Timothy,F.,James,L.,Flow Patters In The Reservoir of a Capillary Rheometer,1968,*Department of Chemical and Metallurgical Engineering*,203-209.
11. Hamad,K.,Deri,F.,Melt Rheology of Poly (Lactic Acid)/Low Density Polyethylene Polymer Blends,2011,*Advances in Chemical Engineering and Science*,1,169-176.

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