



Reducing Creep Rate of polypropylene's by Soaking Solid solutions of CaCO_3

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ABSTRACT

The creep behavior of Polypropylene and Polypropylene/Calcium Carbonate were investigated by tested them at different concentration of Calcium carbonate filler (filler addition is done by soaked pp samples in CaCO_3 solution) at different temperatures. A dramatically changed in the FTIR was observed when pp soaked in CaCO_3 solution comparing with pristine one. It was found that the creep rate was lowered comparing to the pure Polypropylene. The Creep behavior of the polymer formed was observed to increase with increase in temperature and stress, Calcium carbonate enhanced creep rate and rapture time.

Keywords: Creep; Polypropylene; Calcium Carbonate; Creep rate

1. INTRODUCTION

Materials composite applications are strongly depend on their physical and mechanical properties such as elasticity, tensile strength, and resistance to high temperature. These properties are resultant of molecular structure, grain size, molecular weight, forces between molecules, and fillers (reinforcement materials). One method used to describe mechanical properties under steady loads for period long time is creep test.

Most materials especially plastics and polymers are sensitive to creep. Creep test is very important to predict the working life materials that machine component of them that subjected to steady load. Creep is time-dependent permanent deformation and is undesirable phenomena. This phenomenon is limited the life time of material. Polypropylene (PP) is thermoplastic polymers has good mechanical properties, sometimes its properties enhancement by filled it with fillers; inorganic fillers [1], or use organic fillers [2,3] Creep typically is presented by strain-time relation; creep consists of three regions: primary, secondary; and tertiary creep figure (1) illustrated creep regions.

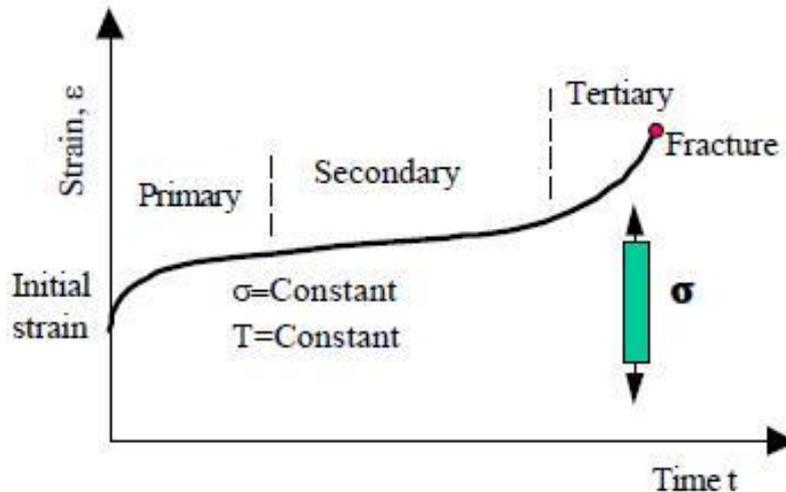


Figure 1. Creep typically behavior

To reduce the effect of grain boundaries cases creep phenomenon, addition of solid solutions to eliminate vacancies. Polymers exhibits both viscous liquid and elastic solid, that indicate polymers exhibits both behaviors together which make polymers to exhibit time-dependent strain [4]. The nature of molecular structure of polymers where formed with long and flexible chains, makes their response is highly dependent on the conditions of a test in which it is observed [5] and [6]. The elastic properties of a polymer (such as Young's modulus) are most predictable at low temperatures and rates of strain. The linear strain responses to stress that observed in these elastic conditions can changed to plastic by increasing the temperature or strain rate, the conditions at testing determine the mechanism through which the material will fracture [7] and the threshold limits of testing conditions is obtained from viscoelasticity. The polymer's transition in phase (viscoelasticity) may also be predictable in measurements of creep [8]. This project focuses on study the creep properties of polypropylene, and enhancement the material resistance to creep by soaking the specimen in CaCO_3 solution to form composite with good mechanical properties of creep.

Creep in materials may occurs in many mechanisms; they some of them depends on grain size of material like bulk diffusion creep (Narbarro-Herring) and grain boundary diffusion creep (coble creep). The second one is strongly depends on grain size then the first one [9]. The creep which is strongly depends on stress is dislocation climb creep, that is related to movement of dislocations [10]. While the creep mechanism that take place in polymers and viscoelastic materials is thermally activated gild mechanism [11]. When

polymeric material subjected to force, its response is explained using (Kelvin-Voigt) model. In this model material represented as a parallel component of spring and dashpot [12]. According to this model; a stiff material is creep and at a constant stress, the strain is tend to (δ/E) as time tends to infinity.

Methods to creep resisting

In material science many methods were adopted to resist creep deformation these method include [13]

1. Prevent ages of dislocation moving by using portieres distributed in matrix.
2. Materials that have bigger grain size is better resistance to creep than smaller grain size that is due to progress of grain bound arise at high temperature is become faster than in smaller grain size materials.
3. Generally materials that have higher meting temperature are more resist to creep.

Creep Recovery

UN like metals, polymers materials most of primary creep is vanished as load is removed, this is renowned as recovery. Recovery test is done polymer is showed creep, then record the strain initial creep Ishim medially recovered, but more time needs to recover the viscous-elastic of creep strain.

2. EXPERIMENTAL

2. 1. Materials and Preparation

The Polypropylene used was supplied by Baghdad Center for Orthotic. The CaCO_3 used in a composite. The specimens were used in this approach cut in recommended dimensions used in creep test, then immersed in a solution of CaCO_3 with concentrations (1gm/ml, and 2gm/ml), for five period times (1 to 5 weeks), and then completely dried at room temperature with air.

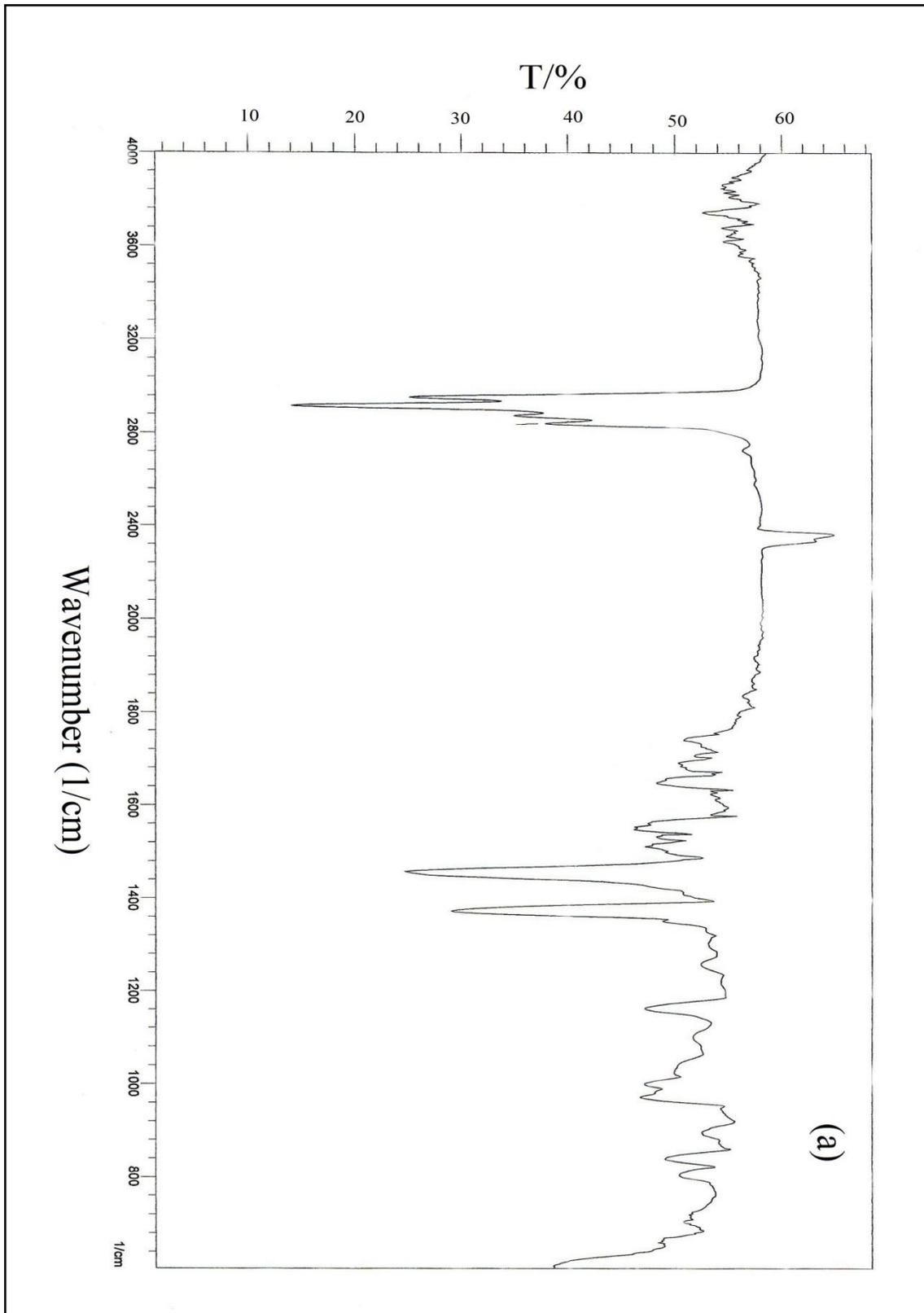
2. 2. Characterization

Fourier transform infra-red (FTIR) analysis were done for samples range of $4000-400 \text{ cm}^{-1}$ to gives out the indication of formation of the oxidation products by using Fourier-transform infrared (FTIR) spectroscopy (Thermo Nicolet, FT-IR Nexus). Pure polypropylene and, polypropylene with additive CaCO_3 were tested for creep properties: creep rate, primary elasticity, and fracture time (9life time) were measured at different conditions by using an Instron corporation machine.

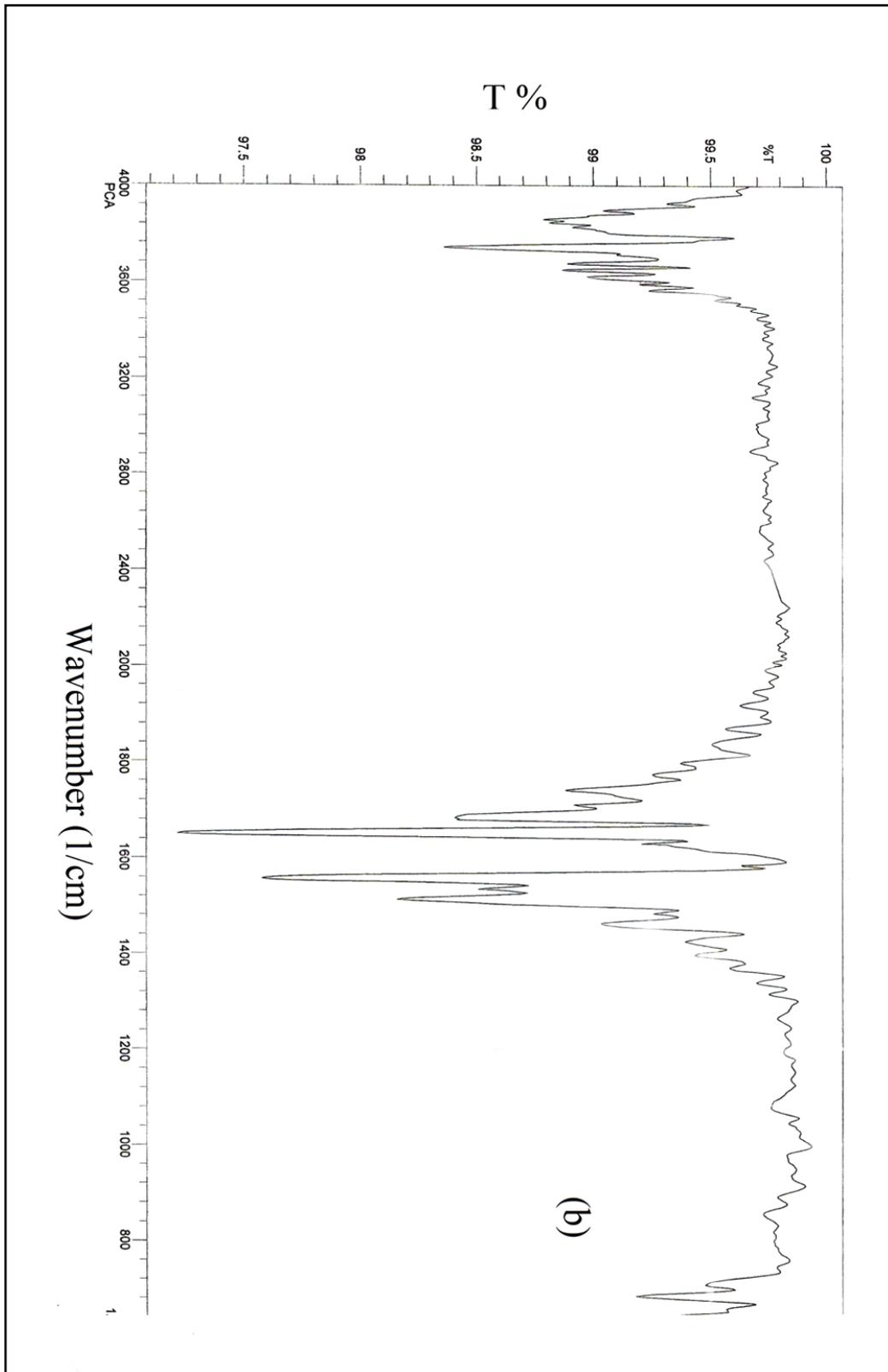
3. RESULTS AND DISCUSSION

3. 1. FTIR Spectra

The IR spectra of PP and PP- CaCO_3 were recorded as in figure 1-a. The spectra showed low intensity of vibration of the rocking of CH_3 and $-\text{CH}_2$ (at 115 cm^{-1}) and the stretching of $\text{CH}-\text{CH}_2$ (at 970 cm^{-1}) and $\text{CH}-\text{CH}_3$ (at 841 cm^{-1}) respectively [1].



(a)



(b)

Figure 2. FTIR spectra of: (a) PP, and (b) PP /CaCO₃

While middle intensity peaks were observed at 1460 cm^{-1} attribute to the asymmetry stretching vibration of CH_3 , and to the symmetry bending vibration of CH_3 at 1380 cm^{-1} . Sharpe spectrum appears in range $1560\text{-}1700\text{ cm}^{-1}$ where Vinyl group appears at 1635 cm^{-1} and carbonyl group appears at $1684\text{-}1725\text{ cm}^{-1}$. Weak peaks at $3400\text{-}3460\text{ cm}^{-1}$ attributed to hydroxyl group.

When comparing the FTIR spectra of PP with PP- CaCO_3 , in the case of PP- CaCO_3 , there are several shifting obtained for some beaks as exhibits in figure 1-b. Immerse pp in CaCO_3 solution produced a chemical reaction which result in the change of FTIR spectra and developed many new peaks in the carbonyl region came from extra carbon added to pp, and other new peaks in range $2835\text{-}2955\text{ cm}^{-1}$. In other hand several peaks vanished like that of hydroxyl group.

3. 2. Creep Properties

3. 2. 1. Polypropylene

Specimens of pure pp were tested at different temperature (18, 25, 50, and 80 °C) loaded with 2.0 MPa, and 3.5 MPa to investigate the creep properties. Figure (3) shows the general creep behavior of samples under constant load; increasing temperature reduced the intermediate range of curve (secondary creep).

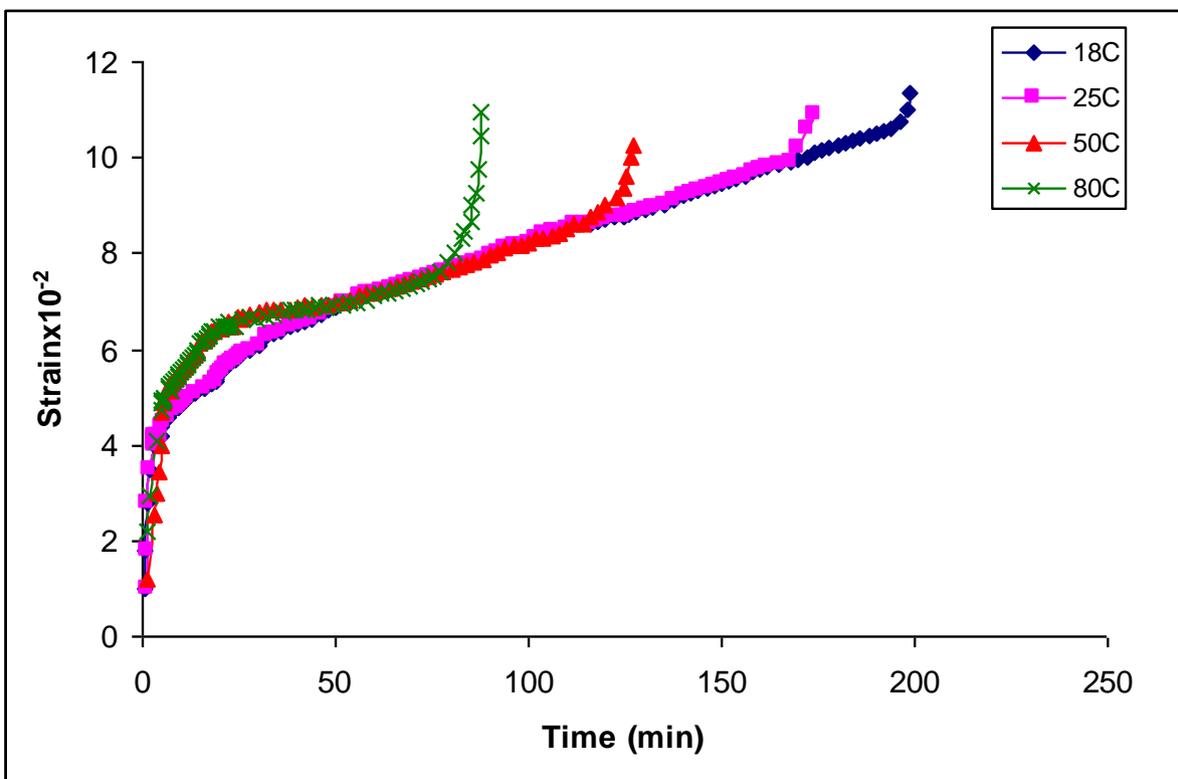


Figure 3. Creep comparative for pure pp at different temperature.

In the other side, higher temperature deforms pp samples which are reached the fracture point quickly; life time of material is strongly dependent on temperature as shown in Figure (4).

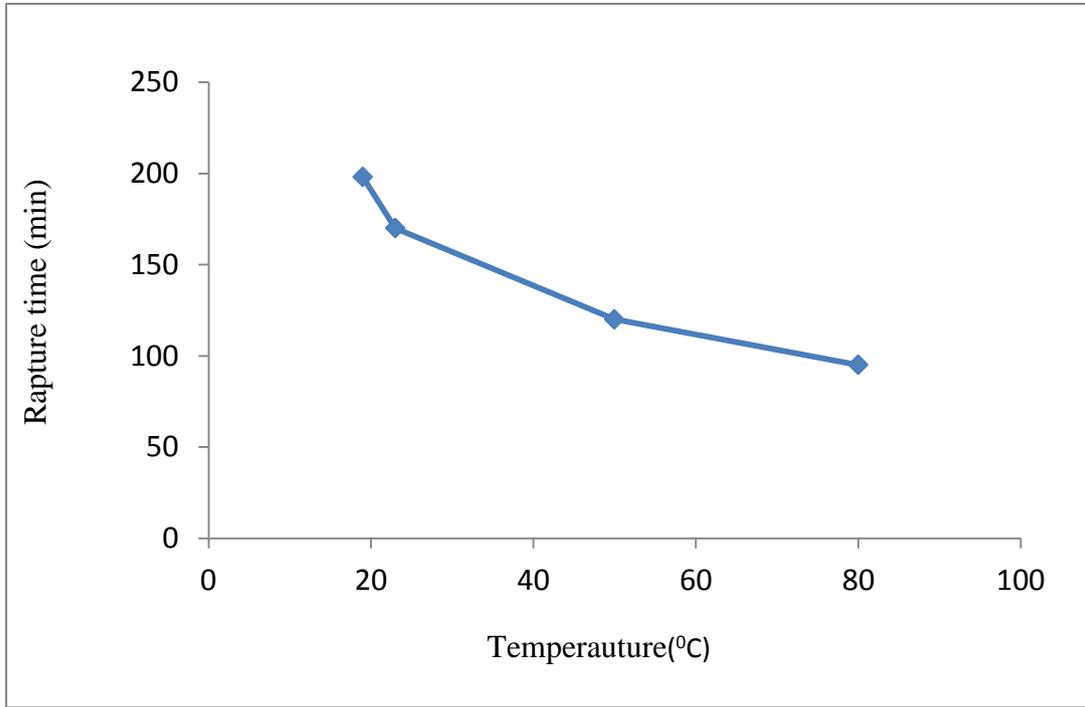


Figure 4. Rapture time as a function to temperature.

The sensitive parameter is the creeping rate ($\frac{\Delta \epsilon}{\Delta t}$) which acquire the time that material is being in used, and is determine from the slope in secondary range of creep, from curves in Figure (3), the creep rate is fast with evaluation temperature until to reach 50 °C.

This is largely due to the fact that stress decreases the activation barrier for bond dissociation, thus allowing the molecular chains to move more easily; with increasing temperature, in fact when materials suffering stress they become hardening and resist the expansion produced by stress that is expressed as a work hardening.

The material hardening may described by the energy required to move the adjacent atoms far a distance each other which known (an activation energy, that decreases creep rate at 80 °C at which material become more resistance to creep as presented in Figure (5).

The primary range of creep starts after the material passes its elastic limits; the instantaneous creep (elastic region) is increasing with temperature; polypropylene returns to its original form as load removed, material become more ductility [13] Figure (6) shows that.

The applied load effect were investigated using two loads (2.0 MPa, and 3.5 MPa) at room temperature; higher load supplies higher stress on material which increase the speed of creep, in our case material behaves like nearly completely elastic manner under higher load that means material is out of its elastic range when loaded with 3.5 MPa, shown in Figure (7).

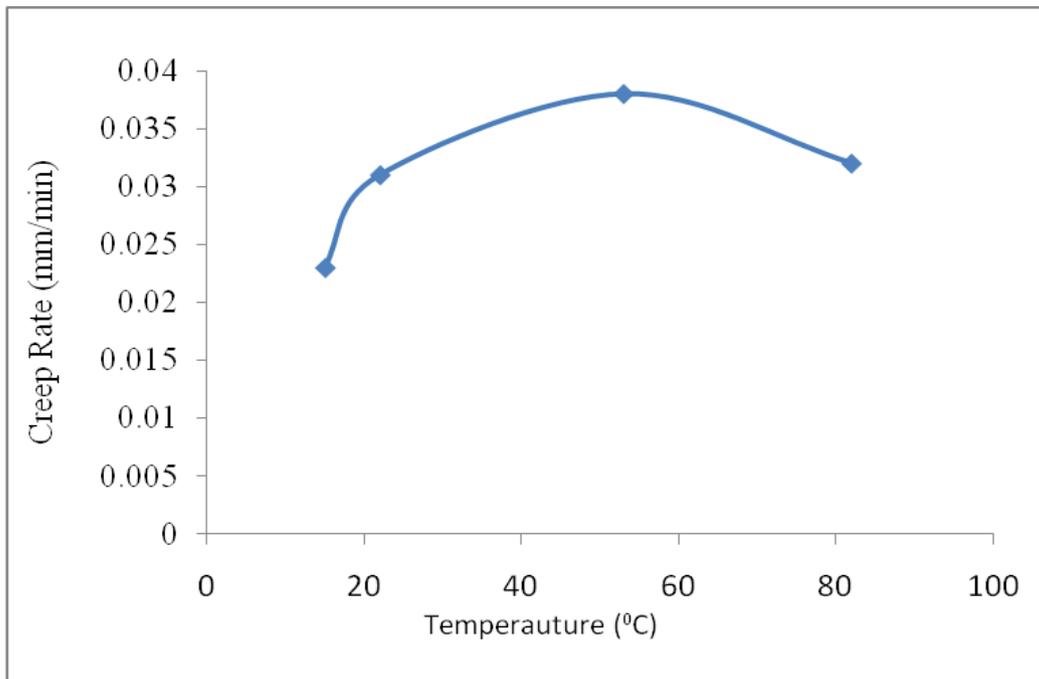


Figure 5. Creep rate as a function to temperature

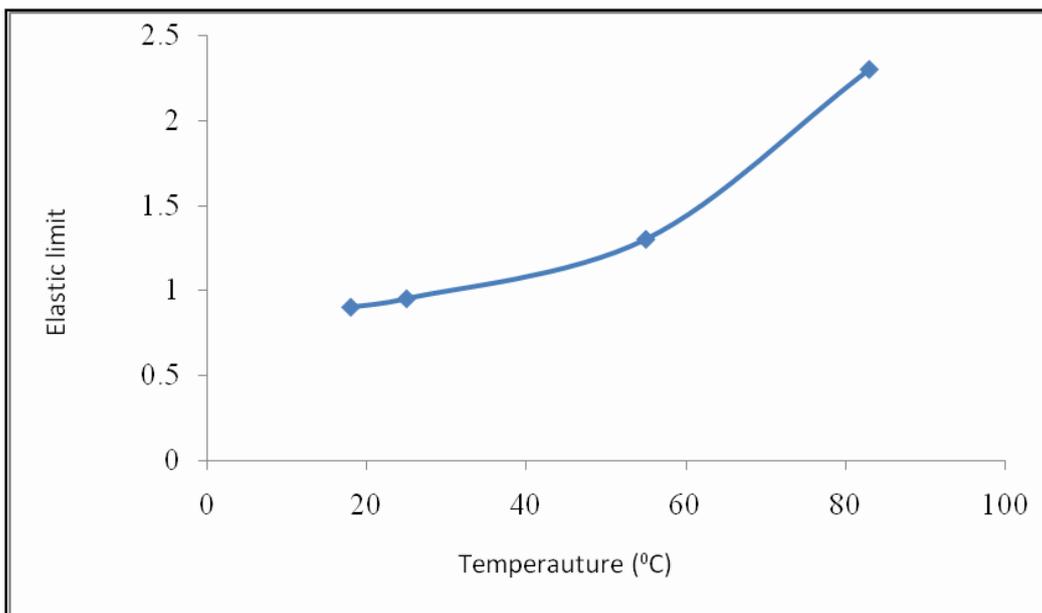


Figure 6. Elastic limit of material

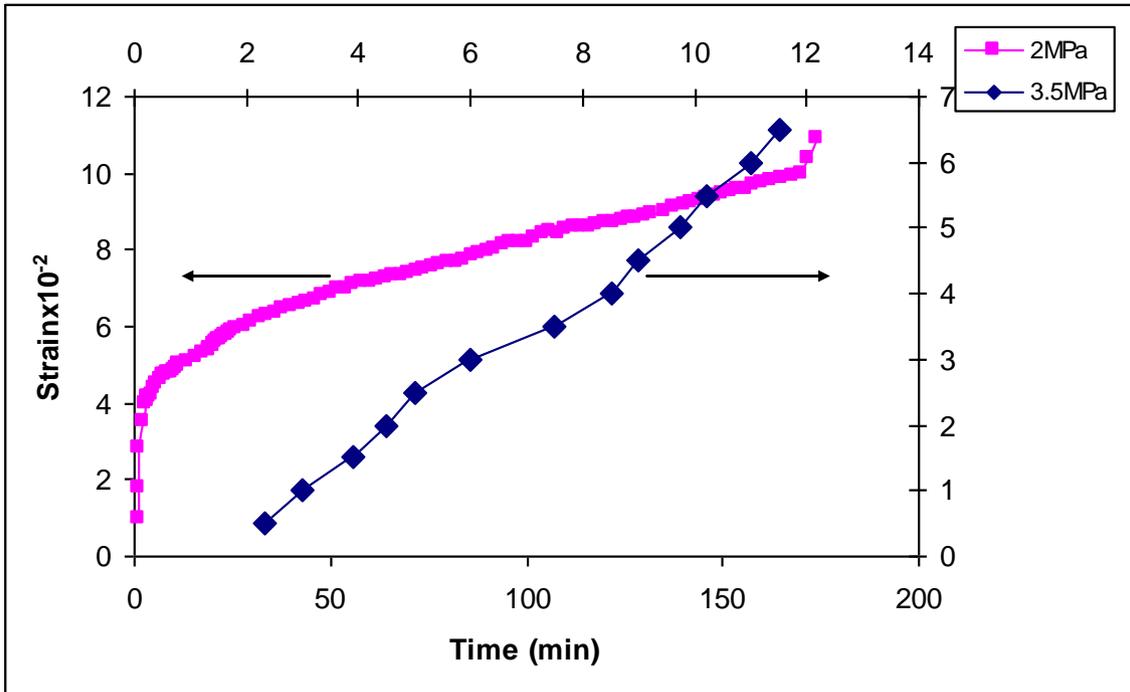


Figure 7. Load effect on creep

This may attribute to dislocation creep mechanism involving by gliding in a slip plane, a process requiring little thermal activation. This mechanism of creep tends to dominate at high stresses and relatively low temperatures.

3. 2. 2. Polypropylene/CaCO₃

Soaked samples acquire increment in weight proportional with soaking time as given in Table 1.

Table 1. Variation of weight ratio with soaking time.

Sample no.	Concentration (gm/ml)	Weight (gm)	Weight ratio (%)				
			1 week	2 weeks	3 weeks	4 weeks	5 weeks
1	1 gm/ml	1.7263	1.22	0.67	1.17	0.63	0.84
2		2.3039	0.19	0.44	0.96	0.27	0.19
3		2.5263	0.19	0.67	0.99	0.24	0.52
4	2 gm/ml	1.8898	0.01	0.27	0.84	0.42	1.02

Figures (8) and (9) shows the creep of sample with 0.84% and 1.02% weight ratio of CaCO_3 mentioned in Table 1 respectively; it is clear the enhancement in strain properties at room temperature for soaking method.

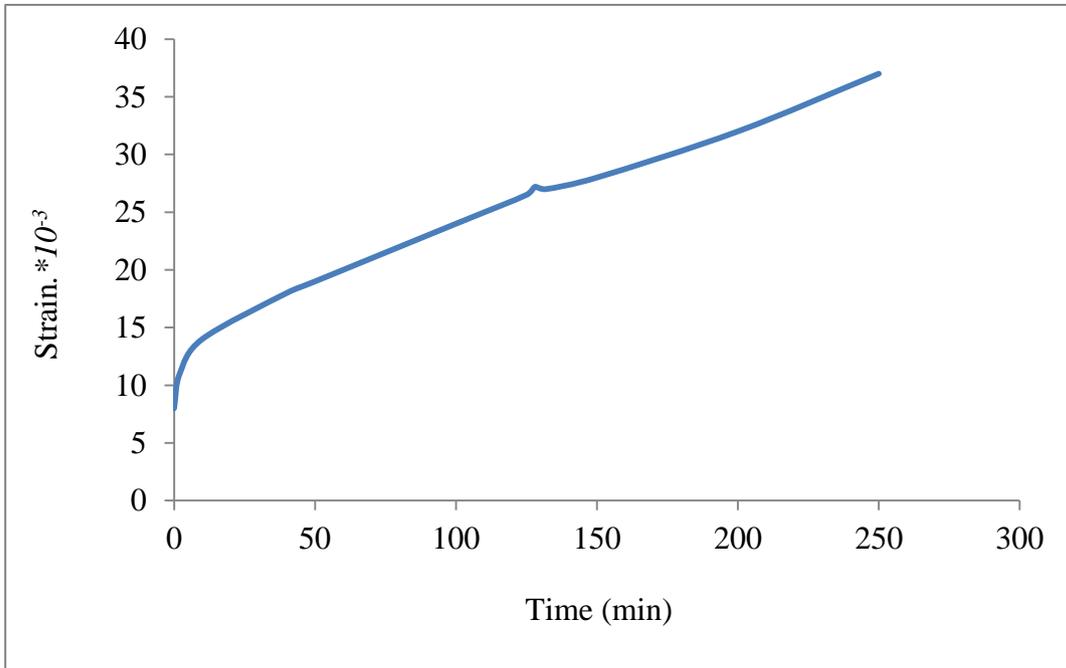


Figure 8. Creep of sample with 0.84% weight ratio of CaCO_3 .

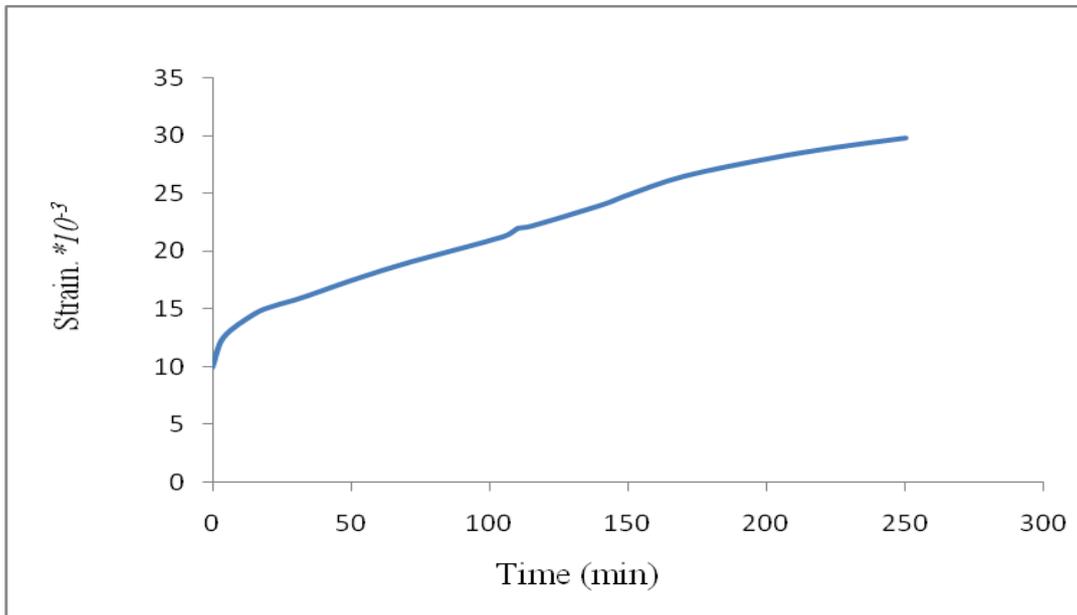


Figure 9. Creep of sample with 1.02% weight ratio of CaCO_3

The rupture time of concentrated of CaCO₃ solution is not appear in creep curve even at longer time test:, the material did not reach to its failed point after if doubled tested time, so its enough to show the test to (271 min) and (255 min) with respect to (1 gm/ml) and (2 gm/ml) respectively, Figure (8) illustrate that. The creep properties affected by filler's weight ratio at room temperature with (1 gm/ml) solution are presented in Table 2.

Table 2. Weight ratio effect on creep properties of pp. soaked in 1 gm/ml CaCO₃

Weight ratio (%)	Creep rate (mm/min)	Rapture time (min)	Limit of elastic
Pure	0.0235x10 ⁻²	198.5	0.94
0.52	0.07584x10 ⁻³	-	4.8
0.84	0.0103x10 ⁻³	-	10.3

At elevated temperature to (50 °C) and (80 °C) pp/CaCO₃ samples showed acceptable enhancement in strain as illustrated in Figure (10). Table 3 represents in briefly the creep properties at high temperature for pp soaked in (2 gm/ml) CaCO₃ for 4 weeks. These improvement to pp properties may attributed to repair pp structure which may involves cracks by filled them via CaCO₃ molecules that absorbed from solution, while mixed powder with polymer may caused defects in pp structure where CaCO₃ may site not exactly centered at cracks.

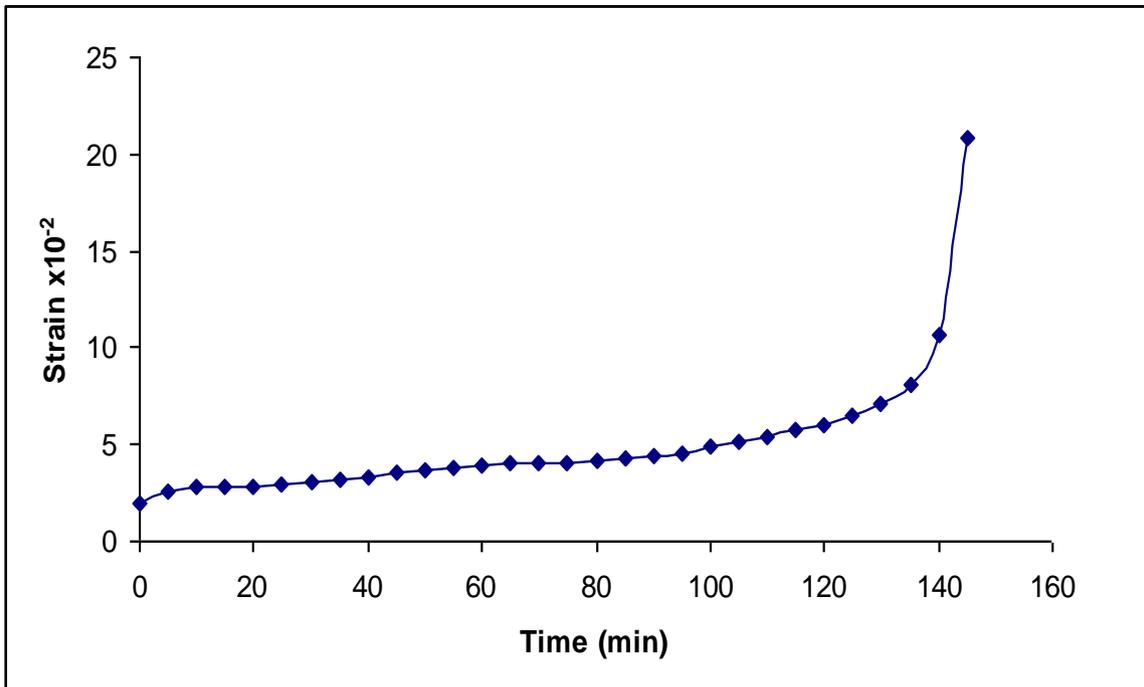


Figure 10. Creep at T = 50 °C

Table 3. Temperature effect on creep properties of pp soaked in 2 gm/ml CaCO₃

Temperature (°C)	Creep rate (mm/min)	Rapture time (min)	Limit of elastic
50	0.038x10 ⁻³	142	2.1
80	0.033x10 ⁻³	128	3.2

Figures (11) and (12) shows the effect of the additive CaCO₃ to improved the flexibility of the polymer properties.

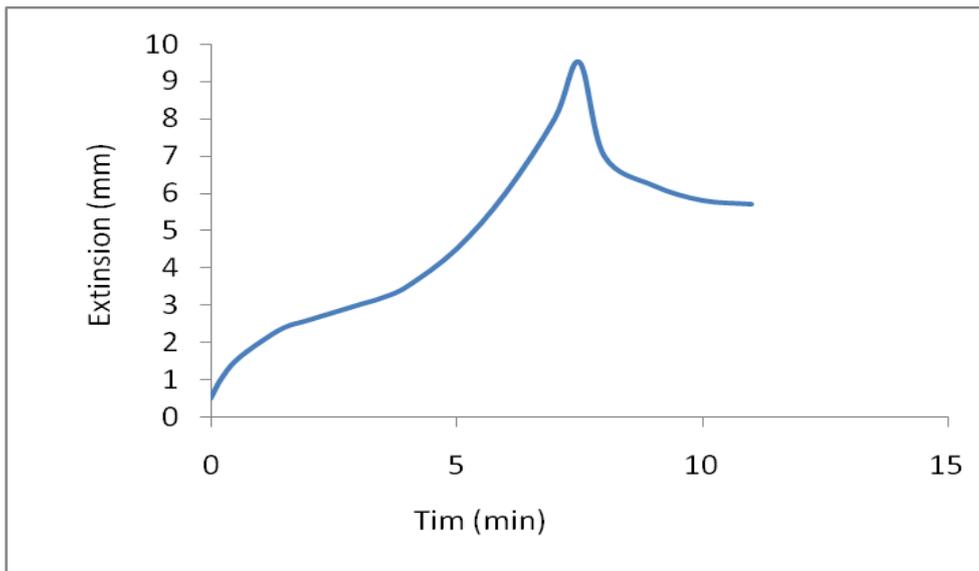


Figure 11. Recovery behavior of pp

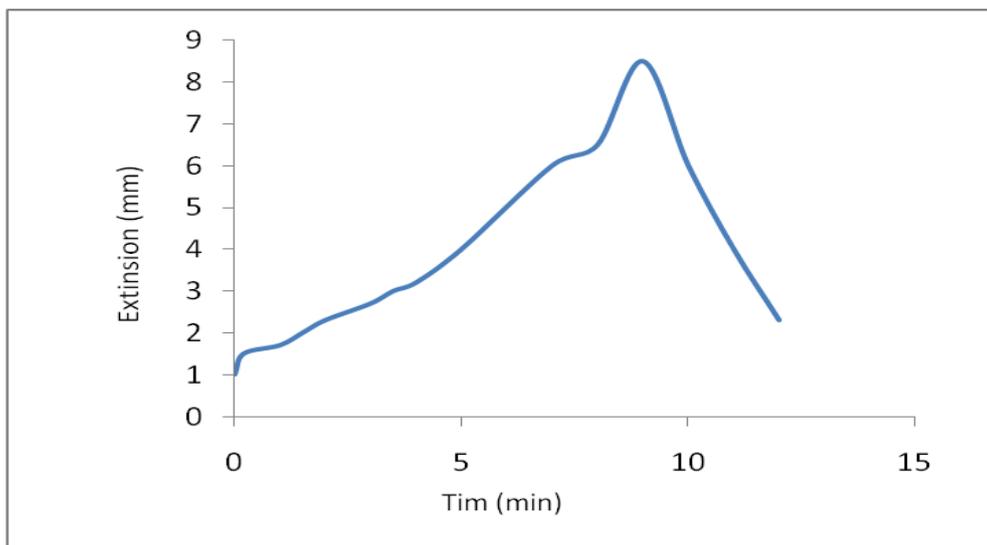


Figure 11. Recovery behavior of pp/CaCO₃

3. CONCLUSION

A simple method to increased material resistance of creep by soaking in CaCO₃ solid solution was adopted. This novel method provides capability to treat material with any engineering shape and even post polymerization. Finally soaking in solid solution did not need other treatment and it gives a very good results comparing with little amount of CaCO₃ which is about one order less than pristine pp.

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