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The glass transition temperature investigation of polymers by molecular dynamic simulations

In this paper, the process of glass transition is studied, the theory of which is not fully developed. Computer modeling can be used to understand the theory of this phenomenon. The glass transition temperature is influenced by a large number of polymer parameters: cooling rate, pressure, presence of diluent, structural features, etc. We are considering a number of different polymers to test the ability of the pcff+ force field to determine the glass transition temperature. The effect of tactility, composition, pressure and the presence of a diluent on the glass transition temperature of polymers will be shown using molecular dynamics (MD) and pcff+ force-field modeling. The effect of tact was studied using the use of atactic, isotactic and syndiotactic poly(methyl methacrylate) and atactic, isotactic and syndiotactic polypropylene. The LAMMPS code integrated into the MedeA computing environment was used to simulate the molecular dynamics of polymers. The calculation of the glass transition temperature at different cooling rates is closely related to the balanced initial systems. Due to the inability of current atomistic simulations to achieve the required cooling rates, as in experiments, the gap was not sharp and quite obvious. The data obtained show that the pcf+ force field describes tactics quite effectively and gives differences in the glass transition temperature for different types of tact. For polymers diluted with CO_2, the glass transition temperature decreases almost linearly, which is in good agreement with the experiment. As expected, the pressure increases the glass transition temperature. However, at high pressure, the slope fracture disappears, and the determination of Tg becomes extremely difficult. The simulated annealing process will be applied to a set of polymers to obtain graphs of the specific volume versus temperature and determine the glass transition temperature.

Keywords: cooling rate, pressure, glass transition temperature, pcff+, molecular dynamics simulations.

Introduction

The glass transition temperature (T_g) is one of the most important parameters in amorphous polymer manufacturing [1]. Moreover, this parameter is essential in the selection of materials for various applications. In general, polymers with T_g below room temperature define elastomers, and polymers with T_g above room temperature define rigid, structural polymers [2].

Unfortunately, the glass transition phenomenon is not completely understood [3]. There is no theory which can fully explain observed behavior of polymers [4]. The computer simulations could help to show the link between the bulk properties and intermolecular forces [5] and bring us closer to understanding this phenomenon.

It is well known that T_g is affected by a wide range of polymer parameters. External variables include cooling rate, pressure, presence of diluent; structural features include molecular weight, composition, crystallinity, copolymerization, branching, cross-linking, stiffness, geometric factors etc.

In the present work we investigate a set of different polymers in order to test the ability of pcff+ force-field for the glass transition temperature determination. The tacticity effect was investigated using atactic, isotactic and syndiotactic poly(methyl methacrylate) (a-PMMA, i-PMMA and s-PMMA) and atactic, isotactic and syndiotactic polypropylene (a-PP, i-PP and s-PP). The pressure was applied for two polymer systems: polyvinyl chloride (PVC) and polystyrene (PS). In order to get the composition effect on T_g polyamide 6 and polyamide 66 (PA6 and PA66), poly(methyl methacrylate), poly(methyl acrylate) and poly(ethyl methacrylate) (PMMA, PMA and PEMA), poly(p-phenylene ox-ide) and polyethylene terephthalate (PPO and PET) have been investigated. The last one is the CO_2 effect on PPO's glass transition temperature.

Methods and materials

The LAMMPS code [6] integrated into MedeA computational environment [7] was used to simulate molecular dynamics of polymers. The major advantage of this software is the time spent for the calculation. At first a single repeat unit was built and relaxed. In order to construct polymer chain and amorphous cell the

Polymer Builder and Amorphous Materials Builder of MedeA environment respectively were used. Each polymer chain in this study was possessed by 100 repeat units. The head-tail orientation was used. The amorphous cell was represented by one polymer chain at 298.2 K. In Figure 1 a single repeat unit, polymer chain and amorphous cell of PPO as example are presented. For all simulations the pcff+ force-field was used, which is based on the pcff+ force-field [8]. The pcff+ force-field was constructed to work with wide range of polymers [5]. Ten randomly built amorphous cells were used to represent the phase space for each polymer.

The MD simulations were carried out firstly in the NVT ensemble at initial T=298 K and final T=300 K with a t=1 fs integration time step and in the Berendsen [9] thermostat. A relaxation annealing was carried out in the following way: the system was firstly heated to high temperature and then slowly cooled down. This process has been carried out using NPT ensemble with t=1 fs integration time step. Also, the Berendsen thermostat and barostat were considered to keep the system at prescribed temperatures and pressures. The non-bonded interactions have been computed using Ewald summation method [10] and nonbond cut-off equal to 9.5 Angstrom. The simulated dilatometry [11] was used with the heating rate equal to 3 10^{13} K/min, i.e., the system was firstly heated up by 50 K step with 100 ps duration time; and with the cooling rate equal to 7.5 10^{12} K/min, i.e., the system was cooled down then by 25 K step with 200 ps duration time. For each temperature the specific volume i.e., the inverse density, was reported. Then, averaging over all configurations was performed. The linear averaging was applied for beginning and the tail of obtained sequence (without the central part) and the break of the slope yielded the T_g. The linear fitting was performed using analysis of coefficient of determination (lines with minimum coefficient were taken). To compare the results for various polymers we used the same procedure for T_g extraction for all polymers.

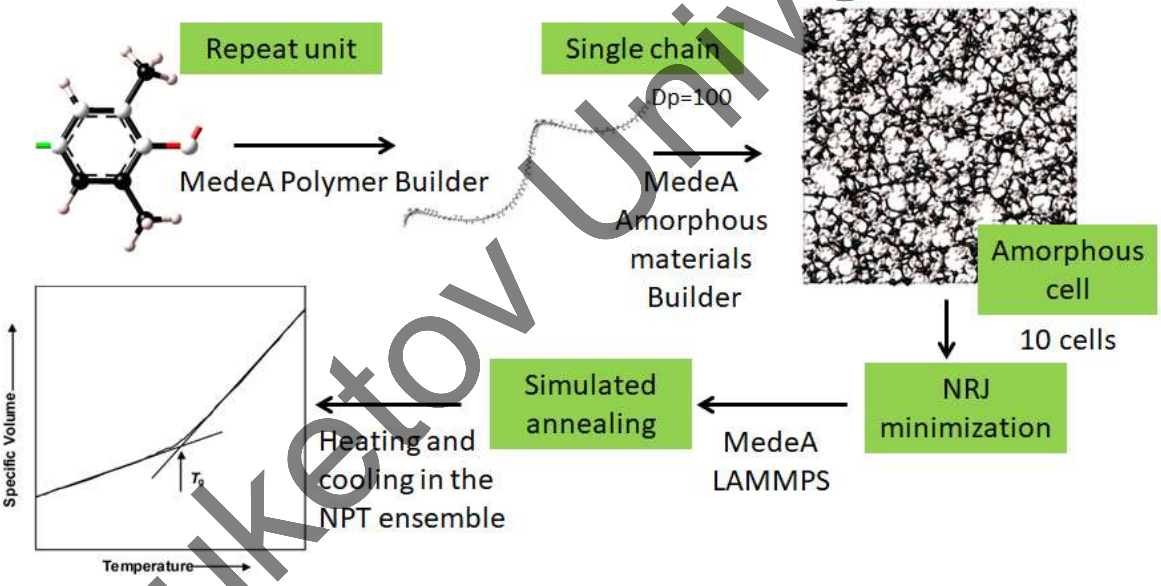

Figure 1. Stages of amorphous cell construction and T_g determination used in the present study.

Results and discussion

Tacticity effect

In the present work, three types of PMMA tacticities were considered: isotactic (i-PMMA), atactic (a-PMMA) and syndiotactic (s-PMMA). Results are presented in Figure 2. The specific volume versus temperature of PP in atactic, isotactic and syndiotacticities have been calculated as well. Results are presented in the Figure 2. The glass transition temperatures of all tacticities were obtained close to each other and a little bit higher than experimental temperatures extracted numbers are listed in Table 1. Pcff+ force-field describes tacticity quite well. However, T_g values determined for PMMA and PP are higher than the experimental values by 20-35% and 1-3%, respectively. That can be explained by the fact that LAMMPS program uses classical principles to simulate molecular dynamics. For some polymers this is important (as for PMMA), but for some it is not (as for PP).

Table 1

Experimental [12-14] and calculated using pcff+ force-field glass transition temperatures in Kelvin for atactic (a-PP), isotactic (i-PP) and syndiotactic (s-PP) polypropylene as well as isotactic, atactic and syndiotactic poly(methyl methacrylate) (i-PMMA, a-PMMA, s-PMMA).

	Calc, K	Exp, K
a-PP	275	260-266
i-PP	280	265-272
s-PP	275	266-268
i-PMMA	527	388
a-PMMA	470	378
s-PMMA	503	323

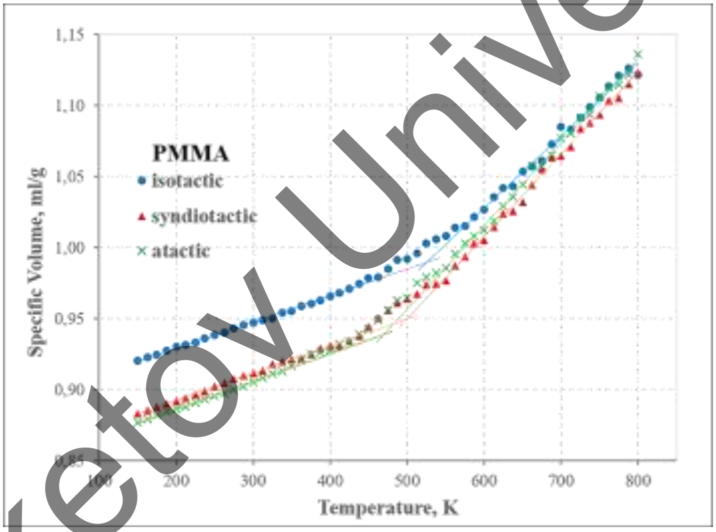

Figure 2. Calculated specific volume vs. temperature of PMMA in different tacticities

Composition effect

The thermal volumetric expansion coefficient indicates how the polymers volume will evolve when facing a change of temperature. For this study, coefficients were calculated for both glassy and liquid states of considered polymers using obtained specific volume versus temperature graphs and following formula:

$$\alpha = \frac{1}{V_{sp}}\left(\frac{\partial V_{5p}}{\partial T}\right)_{\rho} = \frac{1}{\rho},$$

where V_{sp} is a specific volume at given temperature, is a density of a polymer at a given temperature.

Simulated thermal expansion coefficients are reported versus experimental expansion coefficients for all considered polymers in Figure 3. Generally, the experimental coefficient of thermal expansion should be higher. One may notice that for PP there is better agreement than for the rest of the polymers. This can be explained by the fact that the PP has a simpler structure and, therefore, the calculations for it are more accurate.

Simulated T_g are reported versus experimental values for all considered polymers in Figure 4. It should be noted that PVC and PP have the best accordance with experimental values; PS, PPO and PMA have moderate agreement, and PET, PA6 and PA66 have the worse agreement. PVC and PP have the simplest and similar structure. PS and PPO have benzene ring and structure that is more complex. PET and both polyamides, have the most complex structure and long repeat units. Talking about polyamides in should be mentioned that PEMA has the biggest T_g among considered polyacrylates due to the longest sidechain. On the contrary, PMA has the smallest T_g. The PMMA polymer has the middle T_g. The big discrepancy from experimental value for the PEMA could be due to complex structure in comparison with PMMA and PMA.

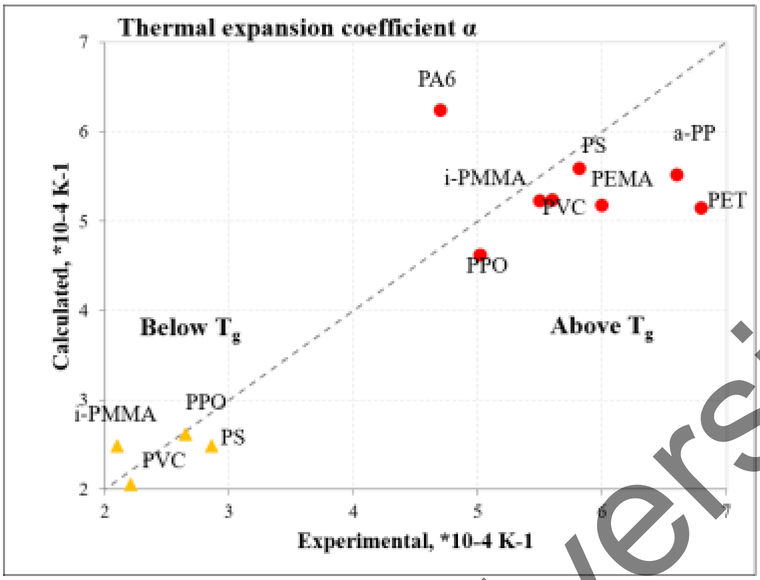

Figure 3. The simulated thermal expansion coefficients for liquid state at 300K versus experimental data from Ref. [15]. The experimental equivalence line is also displayed.

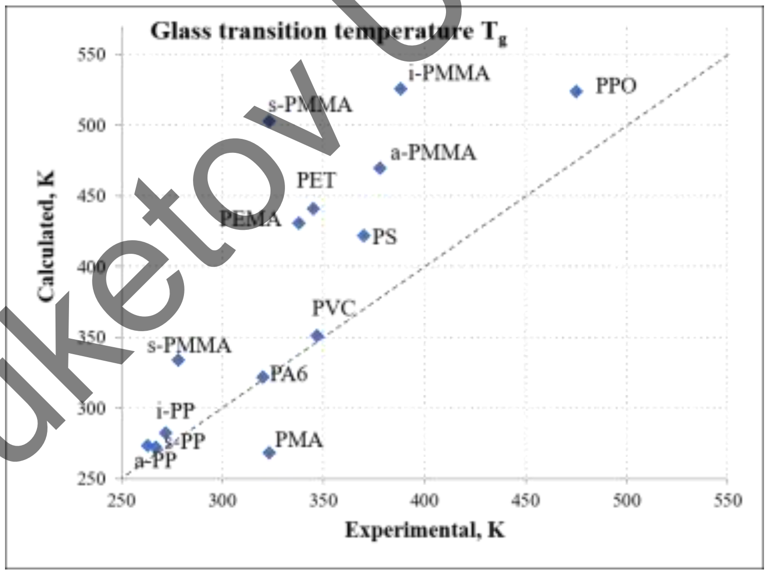

Figure 4. The simulated glass transition temperature versus experimental data from Ref. [15]. The experimental equivalence (dashed) line is also displayed.

Pressure effect

To investigate the pressure effect on T_g the calculations for PVC, PPO and PS were performed under 0, 60 and 100 MPa. Specific volume versus temperature graph for PVS is presented in Figure 5. Experimental values have been taken from [16, 17].

When the pressure goes up it becomes very difficult to determine T_g. With the high pressure, the curve corresponding to glassy state and experimental curve in the glassy state become closer. Extracted T_g at each pressure are presented in the Table 2 and linear relationship between experimental and simulated T_g can be identified. It could be assumed, that adding more configurations could improve the representation of curves and make determination of T_g more accurate.

Calculations under pressure were done for PS and PVC as well. Extracted values are collected in Table 2. As shown in the table the difference of T_g between 0-60 MPa and 60-100 MPa for both polymers are good predicted despite the low molecular dynamic duration time during calculations.

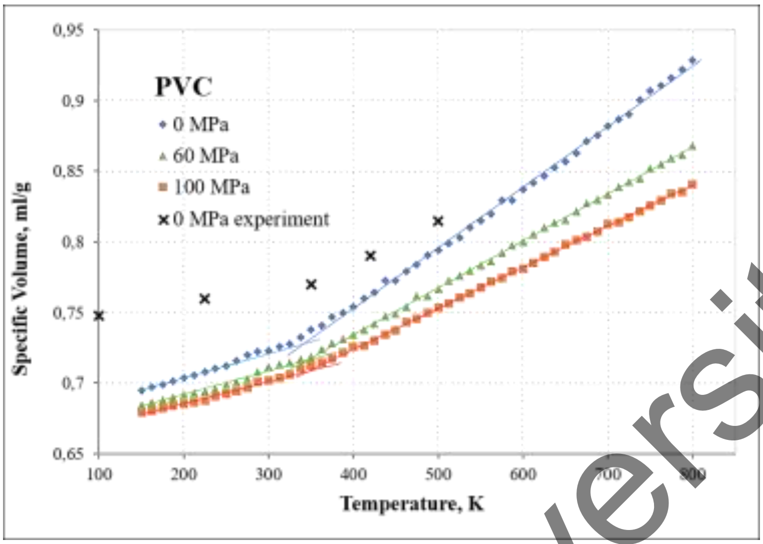

Figure 5. Calculated specific volume vs. temperature for PVC at the indicated pressures. Solid lines are linear fitting. Experimental data from [17].

Table 2

Experimental [16, 17] and calculated using pcff+ forcefield glass transition temperatures in Kelvin for atactic PVC, PPO and PS for indiated pressures.

		0 MPa	60 MPa	100 MPa
PVC	Calc.	345	360	370
	Exp.	347	368	377
PPO	Calc.	525	550	570
	Exp.	475	505	525
PS	Calc.	370	395	415
	Exp.	420	440	460

Presence of diluent

For most polymers, the carbon dioxide (CO_2) can significantly change the mobility of the polymer melt and cause a reduction of T_g by tens of degrees [18, 19]. In the present study CO_2 molecules were added into the Poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) in different concentration.

Considering the fact that molecular weight of PPO with degree of polymerization of 100 equal to 1916.7 g/mole, the concentration of CO_2 was evaluated using formula:

$$\frac{N*M(CO_2)}{M(PPO)},$$

where N is number of CO_2 molecules in the amorphous cell of polymer, $M(CO_2)$ is molecular weight of CO_2, M(PPO) is molecular weight of PPO.

In Figure 6 the glass transition temperature has been plotted versus concentration of carbon dioxide. We can conclude that the glass transition temperature almost linearly decreases with the amount of carbon dioxide. From the qualitative point of view obtained results agree well with experimental data taken from

Ref. [20], from the qualitative point of view there is upward shift of calculated curve for around 80 K, which could be understood in terms of fast cooling during MD simulations.

		0 MPa	60 MPa	100 MPa
PVC	Calc.	345	360	370
	Exp.	347	368	377
PPO	Calc.	525	550	570
	Exp.	475	505	525
PS	Calc.	370	395	415
	Exp.	420	440	460

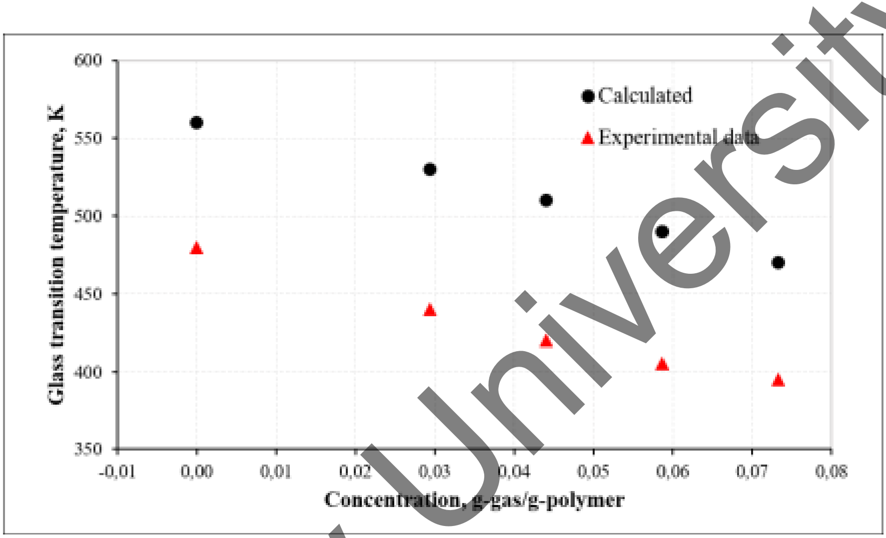

Figure 6. The calculated and experimental [20] glass transition temperature of PPO with CO_2 at various concentration

Conclusion

The computation of T_g at different cooling rates must be intimately associated with equilibrated initial systems. The break was not sharp and sufficiently obvious because of inability of present atomistic simulations achieve necessary cooling rates as in the experiments.

According to the data obtained, we can conclude that the pcff+ force-field describes tacticity quite effectively. We see differences in the glass transition temperature for different types of tacticities.

The atomic simulation was also successfully applied for polymers diluted by CO_2. In this case, adding CO_2 molecules into polymer system decreases the glass transition temperature almost linearly and this behavior agrees well with experiment. As was expected we have shown that the pressure increases T_g. However, when the pressure is high the break of the slope vanishes and determination of T_g becomes extremely difficult.

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Молекулалық-динамикалық модельдеу әдісімен полимерлердің шынылану температурасын зерттеу

Мақалада шынылау процесі зерттелген, себебі оның теориясы толық дамымаған. Берілген құбылыстың теориясын түсіну үшін компьютерлік модельдеуді қолдануға болады. Шыны температурасына полимерлердің көптеген параметрлері әсер етеді: салқындату жылдамдығы, қысым, еріткіштің болуы, құрылымдық ерекшеліктері және т.б. Біз pcff+ қуат өрісінің шыны температурасын анықтау қабілетін тексеру үшін бірқатар әртүрлі полимерлерді қарастырамыз. Полимерлердің шынылану температурасына тактильділік, құрамы, қысымы және еріткіштің болуының әсері молекулалық динамика (MD) және pcff+ force-field өрісінің модельдеулері арқылы көрсетілген. Тактикалық әсері атактикалық, изотактикалық және синдиотактикалық полиді(метилметакрилат), сонымен қатар атактикалық, изотактикалық және синдиотактикалық полипропиленді қолдану арқылы зерттелді. Полимерлердің молекулалық динамикасын модельдеу үшін MedeA есептеу ортасына біріктірілген LAMMPS коды қолданылды. Әртүрлі салқындату жылдамдығындағы шынының температурасын есептеу теңдестірілген бастапқы жүйелермен тығыз байланысты. Ағымдағы атомдық модельдеулердің эксперименттердегідей қажетті салқындату жылдамдығына қол жеткізуге қабілетсіздігіне байланысты үзіліс жеткілікті түрде өткір немесе айқын болмады. Алынған деректер pcff+ күш өрісі тактиканы жеткілікті тиімді сипаттайтынын және тактиканың әртүрлі түрлері үшін шыны ауысу температурасының айырмашылығын беретінін көрсетеді. CO2 сұйылтылған полимерлер үшін шыны ауысу температурасы дерлік сызықты түрде төмендейді, бұл тәжірибемен жақсы сәйкес келеді. Күтілгендей, қысым шыны ауысу температурасын арттырады. Бірақ жоғары қысымда көлбеу қисаюы жойылып, Tg анықтау өте қиынға соғады. Температураға қарсы нақты көлемнің сызбаларын алу және шыны ауысу температурасын анықтау үшін полимерлер жиынтығына имитациялық жасыту процесі қолданылады.

Кілт сөздер: салқындату жылдамдығы, қысым, шыны температурасы, pcff+, молекулалық динамикалық модельдеу.

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Исследование температуры стеклования полимеров методом молекулярно-динамического моделирования

В статье изучен процесс стеклования, теория которой не разработана полностью. Компьютерное моделирование можно использовать для понимания теории данного явления. На температуру стеклования оказывает влияние большое количество параметров полимеров: скорость охлаждения, давление, присутствие разбавителя, структурные особенности и т.д. Мы рассматриваем ряд различных полимеров для проверки способности силового поля *pcff+* по определению температуры стеклования. Влияние тактильности, состава, давления и присутствия разбавителя на температуру стеклования полимеров будет показано с помощью моделирования молекулярной динамики (MD) и *pcff+ force-field*. Эффект тактичности был изучен с помощью применения атактического, изотактического и синдиотактического поли(метилметакрилата) и атактического, изотактического и синдиотактического полипропилена. Для моделирования молекулярной динамики полимеров использовался код *LAMMPS*, интегрированный в вычислительную среду *MedeA*. Расчет температуры стеклования при различных скоростях охлаждения тесно связан с уравновешенными исходными системами. Из-за неспособности нынешних атомистических симуляций достичь необходимых скоростей охлаждения, как в экспериментах, разрыв не был резким и достаточно очевидным. Полученные данные показывают, что силовое поле *pcff+* достаточно эффективно описывает тактику и дает различия в температуре стеклования для разных типов тактичности. Для полимеров, разбавленных CO_2, температура стеклования снижается почти линейно, что хорошо согласуется с экспериментом. Как и ожидалось, давление увеличивает температуру стеклования. Однако при высоком давлении излом наклона исчезает, и определение Tg становится крайне затруднительным. Имитированный процесс отжига будет применен к набору полимеров, чтобы получить графики зависимости удельного объема от температуры и определить температуру стеклования.

Ключевые слова: скорость охлаждения, давление, температура стеклования, *pcff+*, молекулярно-динамическое моделирование.